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Plenary Speakers
Professor Silke Christiansen is appointed full professor since 11/2013 at the Free University – Berlin, Physics department and running a research department for Nanoarchitectures for energy conversion at the Helmholtz Zentrum Berlin für Materialien und Energie, Germany. Moreover, she is running a research group in the department of Prof. G. Leuchs for Photonic Nanostructures at the Max-Planck Institute for the Science of Light in Erlangen, Germany. She received several awards including the MRS student award, a research fellowship award by the Bayerische Forschungsstiftung for a research stay at Columbia University, NY, USA and a Feodor Lynen Fellowship awarded by the Alexander von Humboldt Foundation to carry out research in silicon technology at TJ Watson Research Center of IBM, Yorktown Heights, NY, USA. Moreover, she is distinguished honorary professor at the Material Science Dept., Chungbuk University in Korea for 5 years (2014-2019). She has significant experience in the field of nano-materials for energy conversion, bio-medical sensing and opto-electronics. She advances materials based on correlated microscopies and spectroscopies for which she operates a lab@location with Carl Zeiss AG. She gained her scientific experience at various institutions in Germany and the USA, e.g. IBM’s T.J. Watson Research Center in Yorktown Heights, NY, USA, Columbia University, NY, USA, Max Planck Institute for Microstructure Physics and the Science of Light in Halle and Erlangen, Leibnitz Institute for Photonic Technology in Jena and the Friedrich-Alexander University Erlangen-Nürnberg. She has more than 350 peer-reviewed publications, more than 10 patents/- applications, more than 9900 citations and an h-index of 52.
THREE-DIMENSIONAL NANO-ARCHITECTURES IN ENERGY, BIO-MEDICAL, ELECTRONIC AND SENSING APPLICATIONS – OPTIMIZATION BASED ON CORRELATIVE MICROSCOPY AND SPECTROSCOPY AND MACHINE LEARNING

S.H. Christiansen

Complex nano-architectures of various material combinations (e.g. Si-nanostructures such as wires (NW) and cones (NC), GaN nanostructures, transparent conductive oxides e.g. Al doped ZnO, coinage metal nanoparticles e.g. wires, spheres, graphene and other 2D materials) integrated on Si wafer platforms will be presented for light absorption, light emission and sensing applications.

In this context we will show nano-material choices e.g. for surface enhanced Raman spectroscopy (SERS) and chemically functionalized SiNWs, SiNCs, GaN NWs with distinct resonances for optical sensing or distinct electrical performance in e.g. electronic nose devices based on resistors or field-effect transistors.

Materials and device optimization will rely on advanced correlated electron microscopy and spectroscopy (CORRMIC).

We will show how we utilize X-ray, electron- and ion microscopies and their analytics to acquire huge amounts of heterogeneous data with statistical significance to exploit deep learning strategies to further advance materials and device performance.
Prof. Sergei S. Sheiko
University of North Carolina at Chapel Hill, USA
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Professor Sergei Sheiko aims at the design of novel polymeric materials with unique properties for biomedical implants, soft robotics, and enhanced oil recovery. He is currently focused on time-programmable materials with architecturally encoded physical properties. Sergei is a George A. Bush, Jr. Distinguished Professor of Chemistry and Fellow of the American Physical Society.

Before joining the Chemistry Department at the University of North Carolina in 2001, Sergei has been working on his Habilitation in Polymer Chemistry at the University of Ulm in Germany and as Postdoctoral Fellow at the University of Twente in The Netherlands. He received a PhD degree in Polymer Physics from the Russian Academy of Sciences in 1991 and BS in Molecular and Chemical Physics from the Moscow Institute of Physics and Technology in 1986.
ENCODING TISSUE MECHANICS IN SILICONE

S.S. Sheiko

Machines of the Future will synergize biomimetic mechanics with artificial intelligence. An ideal actuator should mimic muscle by being passively elastic while also efficiently converting potential energy into mechanical strokes. An ideal body material should mimic skin by being simultaneously compliant and strong to accommodate actuator motion. One drawback of biological tissues, however, is that their softness requires water, which is an unreliable engineering material. To overcome this challenge, we have developed a materials design platform that predicts mechanical properties of elastomers by engineering brush-like polymer networks. Adaptable to any chemistry, the platform harnesses architectural parameters to encode tissue-mimetic softness, firmness, and extensibility within single-chemical-component systems. Applying this platform to archetypal poly(dimethylsiloxane) (PDMS), aka silicone, we have designed simultaneously supersoft and extremely strain-stiffening materials without using solvent as a material “softener”.
Dr. Konstantin Yu Amsharov studied chemistry at Saint Petersburg State University. In 2002 he received his Ph.D from the Institute of Macromolecular Compounds, Russian Academy of Science. From 2002 to 2004 he was a postdoctoral fellow in the group of Prof. Shamanin (Institute of Macromolecular Compounds, Russian Academy of Science). In 2005, he moved to Max-Planck Institute for Solid State Research, Stuttgart where he worked with Prof. Martin Jansen on several projects in the area of fullerene chemistry and synthesis of higher and non-IPR fullerenes. From 2009 to 2012 he received his habilitation in Organic chemistry in the subject “Direct synthesis of carbon based nanostructures: buckybowls, higher fullerenes and nanotubes” at the Institute of Organic Chemistry, University of Stuttgart, Germany. From 2005 to 2013 he was a Group Leader of the “Fullerene group” in the department of Prof. Martin Jansen (Max-Planck Institute for Solid State Research, Stuttgart). Since 2014 he is leading a junior research group (Heisenberg program) at FAU Erlangen-Nürnberg. His current research focuses on developing alternative synthetic approaches suitable for preparative production of various carbon allotrope in isomerically pure form based on using of organic substrates - polycyclic aromatic hydrocarbons. The characteristic feature of the approach is a zipper mechanism of cyclization (regiospecific condensation via Ar-Ar coupling in a domino fashion) by which the regiospecificity of each condensation step is unambiguously predefined by the specially “designed” precursor structure, which allows rational synthesis of sp2-carbon based nanostructures.
NANO-ZIPPING - A RATIONAL WAY TO ATOMICALLY PRECISE CARBON NANOSTRUCTURES

K. Amsharov

Carbon based nanostructures such as fullerenes, nanographenes, nanoribbons and nanotubes display outstanding electronic properties and are currently considered as leading materials for future electronics. Despite great success in the total synthesis of complex organic molecules, the rational synthesis of large carbon-based nanostructures still remains challenging. Our methodology is based on the synthesis of polycyclic aromatic hydrocarbons which are “programed” for the fabrication of desired nanostructures via domino-like intramolecular condensation (nano-zipping). Following this strategy various carbon-based nanostructures can be synthesized very effectively by regioselective “rolling-up” of the precursor molecules either by cyclodehydrogenation or by the tandem cyclodehydrofluorination. We have found that the C-F bond “activation” can be used for effective intramolecular cyclization. The process discovered is characterized by unprecedentedly high chemoselectivity and regioselectivity. This strategy opens the possibility for the facile synthesis of extended polycyclic aromatic hydrocarbons in macroscopic amounts with exceptionally high efficiency, including nanographenes,1 fullerenes,2 buckybowlss,3 isomer-pure nanotubes,4 Zig-zag nanographenes,5 and allows the fabrication of carbon-based nanostructures directly on insulating metal oxide surfaces.6

References
Alexander Novikov was born and raised in Moscow, Russia. He graduated from Moscow State Pedagogical University, Moscow, Russia, in 2010 (summa cum laude) and obtained his Ph.D. (summa cum laude) at the Saint Petersburg State University, Saint Petersburg, Russia, in 2013. He has held several Researcher, Postdoc, and Invited Lecturer positions in Russia, Portugal, Finland, Sweden, and Germany. He currently is a Senior Researcher at the Institute of Chemistry, Saint Petersburg State University, Saint Petersburg, Russia. He is an Expert of the Russian Science Foundation in fields of Quantum Chemistry, Computer Modeling, and Supramolecular Chemistry and co-author of more than 100 articles in reputable international scientific journals (Scopus ID: 50262902200). His research interests include theoretical studies in the following topics: cycloaddition and nucleophilic addition reactions, their mechanisms, driving forces, kinetics and thermodynamics; consideration of the catalysis of hydrocarbons oxidation processes and their conversion to alcohols, ethers, aldehydes, ketones and carboxylic acids; investigations of various unusual types of non-covalent interactions in organic, organometallic and coordination compounds.
THEORETICAL STUDIES IN ORGANOMETALLIC AND COORDINATION CHEMISTRY: REACTIVITY, CATALYSIS, AND NON-COVALENT INTERACTIONS

Novikov A.S.¹

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My presentation will address some issues about application of advanced quantum chemical methods (ab initio and DFT) as well as some special techniques (e.g., QTAIM, NBO, CDA, BSSE-correction, isodesmic reactions, HSAB principle theoretical model, Hirshfeld surface analysis) in studies of catalytic reactions and organic transformations assisted by metal complexes, e.g. oxidation of hydrocarbons, nucleophilic addition and cycloaddition processes (mechanisms, driving forces, kinetics and thermodynamics), as well as properties of coordination and organometallic compounds (e.g. conformational isomerism and rotational barriers, properties of chemical bonds, orbital and charge factors). Also we will discuss results of my investigations in field of supramolecular chemistry and theoretical studies of unusual non-covalent interactions (e.g., hydrogen, halogen and chalcogen bonding, π-stacking, anagostic and metallophilic interactions).

Acknowledgements. This work was supported by the Russian Science Foundation (project No. 19-73-00001).
Roberto Paolesse graduated cum laude in Chemistry at the University of Rome “La Sapienza” on 1983. He started his academic career at the Department of Chemical Science and Technologies of the University of Rome "Tor Vergata" in 1986 as Assistant Professor. From 2001 to 2012 he has been Associated Professor and from 2012 he is Full Professor of Chemistry at the same Department. In 1992-1993 he was Visiting Scholar at the University of California, Davis, collaborating with the group of Professor Kevin Smith.

He has been responsible of several National and European research projects, and he is now coordinator of the FET-OPEN project INITIO within the Horizon2020 EU program. Roberto Paolesse authored more than 400 articles on international journals, six patents and edited two books. His papers received 10079 citations with a H-index=53 (source SCOPUS, September 2019).

His research interests range from the synthesis and reactivity of metal complexes of porphyrins and related macrocycles to their application as sensing materials for the development of porphyrin based chemical sensors. Since 1993 he has been involved in the development and application of artificial sensorial systems (E-nose and E-tongue). He has been among the founders of the Sensors Group of the University of Rome Tor Vergata (http://sensorsgroup.uniroma2.it), where he is now co-director with Professor Corrado Di Natale.
PORPHYRINOID BASED CHEMICAL SENSORS

_Paolesse R._

Porphyrs and related macrocycles have been massively exploited as sensing materials in chemical sensors based on different transduction mechanisms. Practical applications are further allowed by using sensor arrays, where the cross-selectivity of sensing layers plays a key role for the analysis of complex matrices. The optimal design of sensor arrays greatly benefits from both the synthetic flexibility and molecular properties of porphyrinoids. Our group recently reported that sensors coated by corrole and porphyrin derivatives possess different sensing properties, proving to be a valuable team for gas and liquid phase sensor applications.
1 section

ADVANCED NANO CHEMISTRY AND NANOMATERIALS
SYNTHESIS OF THE (HYDROXYAPATITE)GOLD NANOCOMPOSITE WITH THE TUNABLE PARTICLE SIZE

Abakshonok A.V., Eryomin A.N., Agabekov V.E

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Nanocomposites, including nanoparticles (NPs) of noble metals, are of great interest because of their tunable absorption and scattering of light in the UV and visible regions. Hydroxyapatite (HA) can be the basis for the uniform placement of metal NPs on its surface. The purpose of this study was to develop the methods of the (HA)Au nanocomposite synthesis under ultrasound conditions with the ability to adjust the size of gold NPs being synthesized. While the synthesis of (HA)Au, a 50 mM glucose or 15% glycerol, 0-1.0 mM sodium citrate, 0-0.8 mM HAuCl₄, 0.5 mg/ml HA were used. In the absence of HA, the formation of gold NPs in a solution of 15% glycerin or 50 mM glucose is not very effective. HA significantly accelerates the process of NPs synthesis.

For the synthesis of gold NPs of large diameter on the surface of HA, glycerin or glycerin together with sodium citrate are suitable reducing agents. The size and amount of gold NPs associated with HA depend on the HAuCl₄ and glycerin concentrations and the presence of sodium citrate in the synthesis medium. In general, the diameter of gold NPs associated with HA increases with increasing concentration of HAuCl₄ in the synthesis medium (Fig. A, B). The use of glucose to obtain gold NPs with a diameter greater than ~30 nm leads to the agglomeration of gold NPs (Fig. C). The use of glycerin or glucose as a reducing agent together with sodium citrate in the synthesis medium in vitro leads to the formation of gold NPs of smaller diameter on HA grains, than using only glycerin or glucose alone.

Thus, the obtained nanocomposites can be used in the technique of resonant light scattering, based on the effect of the migration of plasmon resonance energy.
PHYSICOCHEMICAL PROPERTIES AND BIOLOGICAL ACTIVITY OF C\textsubscript{60} FULLERENE DERIVATIVE WITH L-ARGININE

Ageev S.V.\textsuperscript{1}, Sharoyko V.V.\textsuperscript{1}, Petrov A.V.\textsuperscript{1}, Semenov K.N.\textsuperscript{1,2}

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Water-soluble fullerene derivatives including adducts with amino acids can be considered as perspective compounds due to their antioxidant, antibacterial, antimicrobial and anticancer activity [1-3]. At the same time, it is important to carry out physicochemical investigation of these derivatives and to establish interconnection between their structure and behaviour in solid state, solutions, as well as biological activity.

This research is devoted to physicochemical and biological investigation of C\textsubscript{60}-Arg aqueous solutions. In the framework of our study, the measurements of density ($\rho$), viscosity ($\eta$), refraction index ($n_D$), nanoparticles’ size dimensions ($\delta$), zeta potential ($\zeta$), as well as experiments on binding with human serum albumin (HSA), antioxidant activity in the reaction with DPPH were conducted. Finally, the dynamic characteristics of two C\textsubscript{60}-Arg isomers (Fig. 1) in aqueous solutions with the use of molecular dynamics simulation were studied.

![Figure 1. C\textsubscript{60}-Arg isomers with uniform (left) and equatorial (right) distribution of L-arginine residues.](image)

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-015-00469).
SYNTHESIS AND CATALYTIC PROPERTIES OF GOLD NANOPARTICLES FORMED IN THE PRESENCE OF GUanosine MONOPHOSPHATE


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It has been recently shown that DNA can reduce HAuCl₄ affording particles with mean size of 2 nm [2]. Our aim was to investigate the ability of guanosine monophosphate (GmP) which is a structural unit of DNA to reduce Au(III) in the solution and to analyze catalytic properties of the formed Au NPs. The interaction of HAuCl₄ with GmP was studied at different ratios of GmP to Au in the solution. The GmP-Au complex was formed upon addition of HAuCl₄ to GmP solution, TEM analysis revealed the presence of nanoparticles only at the DNA/Au ratio below unity, after 48 hours (fig. 1). Reduction of 4-nitrophenol catalyzed by the obtained Au NPs was monitored by electronic absorption spectroscopy. No spectral changes were observed upon addition of 1000-fold excess of NaBH₄ to a solution of 4-nitrophenol and NaBH₄, evidencing that no reaction occurred in the absence of Au NPs. However, the addition of Au NPs induced rapid color change of the mixture. In summary, mixing GmP solutions with HAuCl₄ resulted in the Au-GmP complex and Au NPs formation, and the reduction of 4-nitrophenol to 4-aminophenol with sodium boron hydride was catalyzed by the Au nanoparticles obtained in the presence of GmP. The rate constant of 4-nitrophenol reduction catalyzed by Au NPs prepared in the presence of GmP 0.6 s⁻¹ was an order of magnitude higher in comparison with those formed in the presence of DNA or glucose 6.54 × 10⁻³ s⁻¹. The difference in the catalytic properties was likely due to the difference in the particles size.

References
Acknowledgements This study was financially supported by the Russian Foundation for Basic Research (project no. 17-08-01087).
SYNTHESIS AND PHASE FORMATION OF FLUORIDES IN MOLTEN NITRATE FLUX

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Inorganic fluorides gain a lot of attention due to their optical properties. These are applied as materials for photonics. Fluoride matrixes doped with rare-earth elements have biomedical applications. Metal fluorides can be prepared using a broad variety of techniques. However, almost all of them face the problem of hydrolysis, which leads to accumulation of oxygen impurities in samples.

In this work we report a molten-salt synthesis (MSS) of metal fluorides with NaNO₃ as a flux. Batsanova et al. [1] was the first who reported about preparation of metal fluorides from nitrate fluxes. The key idea of this method is to lower melt point of system by adding sodium nitrate as a flux. NaNO₃ have eutectic points with alkali-earth metal nitrates which were used as precursors. NaNO₃ acts as a medium to carry out the reaction. We have used sodium fluoride (NaF) as fluorinating agent. Typical chemical reaction can be described by following equation:

$$\text{M(NO}_3\text{)}_2 + 2\text{NaF} \rightarrow \text{MF}_2 \downarrow + 2\text{NaNO}_3$$

We have obtained individual calcium and strontium fluorides using MSS [2]. Scanning electron microscopy (SEM) images of prepared SrF₂ powder presents well-formed microcrystals with 0.8–10 μm diameter. CaF₂ microcrystals have same sizes without determined habit. Energy dispersive x-ray (EDX) analysis revealed that samples of individual metal fluorides have no major impurities and they are oxygen-free.

Up-conversion nanomaterial with fluorite matrix CaF₂:Er³⁺, Yb³⁺, Na⁺ was produced by MSS. Particles have spherical shape with 60–120 nm diameter. Sample has two emission lines in spectra 510–560 nm and 625–680 nm under 980 nm laser excitation. Obtained luminescent material does not require additional thermal treatment and have 1.2 % quantum yield.

References

Acknowledgements. Voronov V.V. Baranchikov A.E., Kuznetsov S.V., Yapryntsev A.D.
Modern scientific directions in the field of biosensors involve the modification of electrodes by nanomaterials instead of the use of enzymes as sensor-active elements. This facilitates charge transfer, prevents denaturation of molecules on the electrode surface, and increases the effective surface area of an electrode [1].

There are two most used synthetic methods for preparing microcomposite electrodes: in situ laser-induced deposition technique and direct laser sintering. The first one includes continuous laser irradiation of aqueous solutions, containing metal salt as an oxidizing agent and some reducing agent. Direct laser writing is pulsed laser irradiation of the previously spin-coated mixture of metal oxide/ salt, reducing agent and some polymer (PVP, for instance) as a linking agent.

In this work, we reported in situ laser-induced synthesis of sensor-active copper-silver microcomposite. This bimetallic microelectrode exhibits highly developed surface area and good electrical conductivity, and can be successfully used for glucose and alanine sensing demonstrating decent sensitivity (31,000 μA cm⁻² mM⁻¹ for D-glucose and 11,177 μA cm⁻² mM⁻¹ for L-alanine) and low limit of detection (2.8 μM for D-glucose and 0.83 μM for L-alanine).

References

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NEODYMIUM AND CERIUM CONTAINING APATITES WITH SLOW MAGNETIC RELAXATION

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Slow magnetic relaxation is a remarkable property of so called single-ion magnets (SIM): such compounds could retain a macroscopic magnetic moment during a certain time after removing magnetic field but this is an individual property of each magnetic ion. The majority of modern SIM represents magnetic ions surrounded by a volumetric organic ligands that provides a strongly anisotropic geometry. Interestingly that such conditions could be realized inside the inorganic solid state apatite matrix. Indeed we have recently found the slow magnetic relaxation of dysprosium [1] and terbium [2] that partially replaced alkaline earth cations in hydroxyapatite. Moreover the most impressive dysprosium containing sample is characterized by very high remagnetization energy barrier up to 1043 cm⁻¹. In this work we expand our research and have synthesized and studied calcium hydroxyapatites containing neodymium and cerium.

Nearly monophasic compound with nominal composition Ca₄.7₅Nd₀.2₅(PO₄)₃O₀.2₅(OH)₀.7₅ was synthesized by solid state synthesis. Structure refinement by the Rietveld method shows that neodymium is surrounded by 7 oxygens (6 from phosphates and one that is oxygen anion) but with one much shorter distance to the last one. Thereby neodymium forms “NdO⁺” cation with highly anisotropic geometry. This sample demonstrates the slow magnetic relaxation with narrow distribution of relaxation times and high compared with other Nd-based SIM remagnetization barrier of 93 cm⁻¹.

The synthesis of analogical cerium containing compound is less successful: the product is polyphasic but the main phase is characterized by apatite structure and contains cerium cations that partially substitute calcium. This phase also demonstrates slow magnetic relaxation with high remagnetization energy barrier of 163 cm⁻¹.

References

Acknowledgements. This work was supported by the Russian Foundation of Basic Research (project No 18-33-01285).
SYNTHESIS AND PROPERTIES OF N-METHYL-1-[4-CYTIZINOPHENYL]FULLERENE-C$_{60}$[1,9C]PIRROLIDINE

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The presence of C$_{60}$ and lipophilic properties membranotropic important for developing drugs against the pathogen of various infectious diseases [1]. However, at the present time is not yet established common biological effects and possible toxicity when used on live sites. In asking these questions is an interesting study of the fullerene derivative known in medicine drug. In line with this trend we conduct a study of synthesis and properties of the fullerene derivative – N-methyl-1-[4-cytizinophenyl]fullerene-C$_{60}$[1,9]pirrolidine (1).

Reacting C$_{60}$ with N-methylglycine (sarcosine) and 4-cytizinilbenzaldehyde (Prato reaction [2]) in refluxing toluene under argon for 20 hours resulted in the formation of N-methyl-1-[4-cytizinophenyl]fullereneC$_{60}$[1,9]pirrolidine (1). Unreacted starting materials and product (1) after the reaction were separated by column chromatography on SiO$_2$, eluting with hexane and then with hexane-toluene (1:1) (yield 38%).

The structure of the synthesized compound (1) is proved by IR, $^1$H- and $^{13}$C-NMR spectroscopy.

References
α-Amino acids are among the most important biologically active substances, which in living organisms are the structural elements of proteins and endogenous compounds. Amino acids and their mixtures are widely used as additives in food production, active components of pharmaceutical preparations for parenteral and sports nutrition, treatment and prevention of diseases. The content of amino acids in foods and medicines is strictly regulated, since the therapeutic effect is achieved at a certain concentration of the biologically active substance. Arginine (Arg) is a semi-essential amino acid, an important part of the diet of animals and humans, and plays a significant role in the urea cycle and energy metabolism. Arginine promotes wound healing and stimulates the release of various hormones and enzymes. Therefore, the development of a sensitive method for quantifying Arg in biological fluids has a profound effect on the diagnosis of diseases. A promising approach for the determination of arginine is spectrophotometric registration of the change in the color of silver nanoparticles (NPs) as a result of their aggregation in the presence of arginine. The purpose of this work was to assess the possibility of using silver nanoparticles for the spectrophotometric determination of arginine. Silver nanoparticles were synthesized by borohydride and citrate methods and their size and optical properties were investigated. Spectrophotometric determination of arginine by its own absorption in the visible region is impossible. However, silver NPs can act as a spectrophotometric reagent for the determination of arginine in connection with their possible aggregation and the associated displacement of the surface plasmon resonance band (SPR). It was shown that in the case of silver nanoparticles synthesized by the citrate method, no changes were observed in the absorption spectra of NPs in the presence of arginine, which is probably due to the too large size of silver NPs. In the case of silver NPs synthesized by the borohydride method, a shoulder in the region of 500 nm is formed on the absorption spectra in the presence of arginine. In this case, there is a linear dependence of the optical density at \( \lambda = 500 \text{ nm} \) versus arginine concentration in the range of \( 5 \cdot 10^{-4} - 8 \cdot 10^{-3} \text{ M} \), the square of the approximation coefficient was 0.98.
Multicomponent water-salt systems are ubiquitous in nature, and also are extremely useful for industrial applications, so their study is of particular scientific interest. Water-based systems are environmentally beneficial alternative to many of the currently available technologies. There is no problem of utilization for such systems, since their components are part of natural soils, also multicomponent water-based electrolyte solutions are refrigeration agents and exhibit properties similar to inorganic non-toxic ionic liquids [1]. The thermodynamic description of water-salt mixtures containing ions of alkali and alkaline-earth metals contributes to their spread use [2]. In this study, a multicomponent water-salt system including magnesium and cesium chlorides MgCl2-CsCl-H2O was studied at a molar ratio of Cs/Mg=1/1.63. The dissolution enthalpy of double magnesium-cesium chloride MgCl2∙CsCl∙6H2O was determined by the calorimetry method. The thermal effects of dilution were determined by the method of differential dilution calorimetry. Based on the experimental results obtained and the water activities [3], activity coefficients and chemical potentials of water were calculated. Relative partial molal enthalpies of dilution and entropy were also calculated. These dependencies were presented in the form of composition-property diagrams and analyzed for the coincidence of inflection points with the position of the eutectic region for these systems.

References:

Acknowledgements: Scientific measurements were performed in the Research Park of the Saint Petersburg State University “Thermogravimetric and Calorimetric Research Centre”
PHOTOSENSITIZERS BASED ON CYCLOMETALATED COMPLEXES OF D6-METALS FOR DYE-SENSITIZED SOLAR CELLS


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The most important component in Grätzel solar cells (DSSC) is the sensitizing dye responsible for absorbing light and participating in the charge separation process. The improvement of the photosensitizer is based on knowing how specifically the variation of ligands or metal affects the target optical and electrochemical characteristics of the complex, as well as its stability. Herein, we present the results of our study aimed at creation of a model of the dye, which establishes the main factors affecting the properties of the photosensitizer and their (factors) connection with the structure and electronic properties of ligands and metal.

Figure 1. Complexes in this study.

More than 40 new coordination compounds of iridium (III) and rhodium (III) were synthesized and comprehensively studied. The influence of both types of ligands (antenna and anchoring) on stability, as well as optical and electrochemical properties of the complexes, have been established, which made it possible to significantly improve the very primitive dye model that was previously available. Based on this model, an integrated approach has been developed, consisting in the rational selection of metal and ligands, and aimed at obtaining stable and effective photosensitizers for solar cells. The use of this strategy allowed us to synthesize a number of dyes, which demonstrated good stability and efficiency when performing in DSSC.

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INFLUENCE OF MORPHOLOGY ON THE CAPACITANCE PROPERTIES OF CeO₂ NANOPARTICLES

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CeO₂ nanostructures of different morphology were synthesized under hydrothermal conditions. The structure, elemental composition, shape and size of the obtained nanoobjects were analyzed using the X-ray diffraction, energy-dispersive X-ray spectroscopy and transmission electron microscopy. It was shown that hydrothermal treatment of cerium nitrate at 180°C, 15 MPa in strongly alkaline solutions for 24 hour leads to the formation of cubic CeO₂ nanoparticles with a wide size distribution. In case of carrying out the synthesis at lower temperatures and simultaneously increasing the alkali content in the composition of the hydrothermal medium, CeO₂ crystallizes in the form of rods with a diameter of 10 nm and a length of 200 nm.

Electrochemical properties of prepared oxides were tested in standard 3-electrode cell. The working electrodes were prepared by dispersing of oxide in the DMF solution containing carbon black, PVDF. The glass carbon electrode with working area 1.3 cm² was covered with 0.3 ml of prepared dispersion and dried at 60 °C. Cyclic voltammetry and galvanostatic charge discharge experiments were performed with the CeO₂ with different morphology in the potential range -0.2V – +0.5V vs Ag/AgCl reference electrode. The results demonstrate that CeO₂ in the form of cubes has significantly higher specific capacitance in comparison with CeO₂ rods. This can be attributed to the difference in the specific surface area of these oxides.

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A NEW WATER-SOLUBLE FULLERENE DERIVATIVES WITH FOLIC ACID

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It is known that the number of expression or activity of folate receptors on most tumor cells is significantly higher than the corresponding values for normal cells [1]. In this regard, derivatives of fullerenes and endohedral metallofullerenes with folic acid can be promising agents for targeted cancer therapy using photodynamic therapy, chemotherapy, radiofrequency thermal therapy, radiotherapy [2, 3].

In this work, new water-soluble fullerene derivatives with folic acid have been obtained. The structure of the obtained derivatives was investigated by using UV-VIS, FT-IR and elemental analysis. The aggregation properties of the derivatives were characterized by DLS.

Figure 1. UV-VIS spectra of folic acid (1) and fullerene derivatives with folic acid (2): a — in NaOH 0.1M, b — in water

References
We present a microscopic Müller matrix technique \cite{1,2} to optically characterize a unique carbon-metal hybrid material fabricated by laser induced deposition \cite{3}. These carbon flakes exhibit an orthorhombic carbon matrix intercalated with bi-metal nanoparticles. Due to the small lateral dimensions of the flakes (microns), standard optical measurement techniques cannot be applied. We use a custom-made system to perform a detailed polarization analysis of individual carbon flakes using two liquid crystals variable retarders \cite{4}. The experimentally measured Müller matrix reveals the optical properties of the material such as attenuation and birefringence \cite{5}. The investigated structure shows wavelength-dependent attenuation and strong optical birefringence on the order of 0.1, which is constant across the visible spectral range \cite{2}.

References


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HALOGEN BONDING OF BROMOFLUOROBENZENES WITH BROMIDE DIMETHYLICYANAMIDE PLATINUM (II) COMPLEX

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Halogen bonding (XB) is widely applied in different areas such as supramolecular chemistry, crystal engineering, catalysis, etc. Although the vast majority of XB research does not include organometallic compounds, the application of these substances as XB participants is very useful for the design of new materials.

Iodoperfluorobenzenes are XB classic donors for both organics and metal complexes. Meanwhile their bromo- analogs were poorly investigated in co-crystallization with metal complexes.

In this work, we studied the co-crystallization of 1,2-bromotetrafluorobenzene, 1,4-dibromotetrafluorobenzene, and bromopentafluorobenzene with trans-[PtBr₂(NCMe₂)], since this complex was investigated by us as an interesting XB acceptor [1]. In all structures of the adducts of the complex with bromoperfluorobenzenes, the C–Br⋯Br–Pt XB were detected by single-crystal XRD experiments. In the cases of dibromotetrafluorobenzenes, this halogen bonds provide the construction of infinite supramolecular chains.

![Figure 1. Objects of research.](image)

Figure 1. Objects of research.

References
SYNTHESIS, CHARACTERIZATION AND FUNCTIONAL PROPERTIES OF COMPOSITE NANOPARTICLES BASED ON Fe₃O₄ AND ACYCLIC DIAMINOCARBENE COMPLEXES OF Pt(II) AND Ir(III)

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Organo-inorganic hybrid nanoparticles (NPs) are complex systems consisting of an oxide core, a NP, a spacer, and a metal complex. As the core of the NPs can act as iron oxide NPs that can exhibit magnetic properties; in the role of a spacer, various organic substances are used that contain functional groups, namely, polymers and biologically active compounds and organic complexes of transition metals with ligands of various nature act as a metal complex. The constituent components of hybrid particles are able to exhibit different physicochemical properties, but at the moment there are no studies of the mutual influence of the parts of the system on each other.

The aim of our work is to develop and optimize the approach to the synthesis of hybrid organic-inorganic NPs of a given functionality due to the combination of the nature of the core, the spacer and the metal complex. NPs of iron oxide, polyethylene glycol of various molecular weights and isoanide iridium complexes were chosen as objects of study.

The first step includes the preparation of magnetite NPs by a typical co-precipitation procedure. In the next step, the magnetite surface was coated a SnO₂ layer with a thickness of 2 nm using SnCl₄ and NH₄OH. Then, polyethylene glycol (PEG-300 and 3000) was grafted to as-prepared NPs by activating the surface OH- group using chloride ions. The terminal PEG hydroxyl groups were modified by APTES. This allowed us to introduce amino group for the subsequent addition of the metal complex. All stages of the synthesis were characterized by a complex of physicochemical methods such as FTIR spectroscopy, elemental analysis, TGA-DSC. Magnetic and optical properties of as-prepared samples with complex structure are also under discussion.

Acknowledgements. This work is financially supported by RFBR grant 18-03-01066. Scientific research was performed at the Research Park of St. Petersburg State University Educational Resource Center of Chemistry: Centre for X-ray Diffraction Studies, Center for Optical and Laser Materials Research, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.
NEW CHROMOPHORES CONTAINING 2,5-DI(THIOPHEN-2-YL) 1H-PYRROL-1-YL FRAGMENT: SYNTHESES AND INVESTIGATION OF OPTICAL AND ELECTROCHEMICAL PROPERTIES

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The synthesis and investigation of a new set of N-substituted 2,5-di(thiophen-2-yl)-9H-pyrroles are presented. Spectral and electrochemical characteristics as well as the frontier orbital energies and HOMO/LUMO gaps of the compounds synthesized have been evaluated and described [1-2].

References

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PEROVSKITES AS NEW CATALYSTS AND ANTIBACTERIAL MATERIALS

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Complex oxides with perovskite structure have long been in the focus of researchers' attention and have already found their application in the chemical, electronic industry, energy, catalysis and other fields. Despite of the extensive study of perovskites in many areas of science, the study of their antibacterial activity has only begun to develop.

At present, due to the reduction of oil resources and the increase in their cost, interest in alternative sources of light hydrocarbons is increasing. Fischer-Tropsch synthesis is the most promising way to obtain them, as it allows from the simplest substances, carbon monoxide and hydrogen, to obtain the most valuable organic compounds, among which the target or most valuable components are light olefins.

In this paper, we evaluated the catalytic and antibacterial activities of complex oxides with the perovskite structure GdCo$_{1-x}$Fe$_x$O$_3$, GdMn$_{1-x}$Fe$_x$O$_3$ and GdCo$_{1-x}$Mn$_x$O$_3$ ($x=0; 0.2, 0.5, 0.8; 1$).

Studies on the catalytic activity in the Fischer-Tropsch process were carried out in a flow-through catalytic unit at different component ratios (CO:H2) at atmospheric pressure in the temperature range of 523-708 K. It was found that perovskites exhibit resistance to carburization in the Fischer – Tropsch process, and stability after high-temperature processes.

Antibacterial activity was investigated using gram-negative bacteria - Eschrichia coli by two methods diffusion method for agar and Shake-Flask method. MBC were determined.

As a result, it was shown that complex oxides GdCoO$_3$, GdFeO$_3$ and GdMnO$_3$ exhibit better antibacterial activity when replacing part of the transition metal atoms on other transition metal atoms.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant № 18-33-01209.
IMPACT OF THE ACTIVATING ABILITY OF NANOSTRUCTURED CARBON ON THE WORK OF THE NEGATIVE ELECTRODE OF A NEW-GENERATION SEALED LEAD-ACID BATTERY

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Lead-acid batteries are the most demanded ones in the world market, covering various areas of technology such as nuclear and thermal energy, military equipment and many others. One of the main problems of lead-acid batteries is the process of sulfation of the negative active plate under conditions of high-speed partial charge, which limits the battery life. The solution of this problem is the addition of carbon components to the negative active mass of the plates.

The purpose of this work was the structural and electrochemical properties studying of the negative electrode with various carbon additives for the SKA.

Carbon technical extended Art Nano GT (TU VU 691460594.004-2017) (Perspective Research and Technology, Minsk), Art Nano GT (treated with ozone), Art-nano GT (processed by DMF), (LLC Advanced Research and Technology, Minsk), carbon nanostructured technical activated Art Nano, brand NSU S (TU BU 690654933.001.-2011), Art Nano NSU “C” (ozone treatment), “Art-nano” of the NSU “S” brand (DMF treatment) (Promising Research IAOD and technology, Minsk) were used as a carbon additives in the negative mass of the lead electrode. The content of the carbon additives was 0.5, 1 and 1.5 wt.%. It was found that with the addition of carbon components, the discharge capacity and the utilization rate increase compared with electrodes without carbon additives, regardless of the concentration of carbon. And the addition of such components make pores increasing in with a radius of less than 0.1 μm, regardless of the amount of introduced carbon.

The morphology of the surface of negative electrodes with carbon additives with 1 wt.% concentration at the 6th charged cycle was investigated. It showed that samples with carbon additives have rounded crystals with smaller sizes, the structure is more branched, which is related with the addition of carbon particles into the volume of the active mass. Carbon particles are electrically conductive, and the electrochemical reaction of lead ion reduction can occur on their surface. The newly formed lead surrounds carbon grains and includes in the volume of the negative active mass.

The addition of carbon particles in the amount of 1 wt.% showed the best electrochemical properties.
Cationic metal-organic frameworks are of distinct interest due to abilities for incorporation of anions for catalytic, photochemical, selective sorption and separation applications. Using neutral ligands is the method to synthesize cationic MOFs specifically. For example, di-N-oxide bridges are promising building blocks due to unusual topologies of coordination networks forming, as well as easy coordination to the wide range of oxophilic metal centers. [1] Coordination polymers based on N-oxides are quite rare. In particular, just a few examples of 1,4-diazabicyclo[2.2.2]octane di-N-oxide (odabco) - based MOFs are reported in the literature. But, odabco containing coordination polymers and organic adducts were shown to have ferroelectricity and thermally induced phase transitions [2-3] (e.g. breathing) which are related to the axial rotation of odabco bridge fragments. So, we purposed to investigate odabco as a ligand in a wide range of solvothermal systems (different solvents, temperatures, transition metal salts, reagent ratios etc.) and obtained a series of M$^{2+}$ and M$^{3+}$- based compounds. The impact of different synthetic conditions on the forming structures is discussed in detail.

References

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Currently, the use of semiconductor films as multisensory systems for analytical chemistry is being actively studied [1]. One of the main problems is obtaining reproducible, selective and highly sensitive detectors. This is impossible without a basic research of the relationship between the chemical composition of films, their morphology and functional properties. This report presents the results of the study of nanoscale films of different composition based on tin dioxide used as a detector for capillary gas chromatography. The studies were carried out using scanning electron microscopy, X-ray fluorescence and gas chromatography-mass spectrometry [2]. The effectiveness of the films is illustrated by the examples of the analysis of test systems (fig. 1). An algorithm for calculating the identification features of various classes of organic compounds is also proposed.

References
PHASE TRANSITIONS AND ELECTRICAL PROPERTIES OF Ag$_2$Se THIN FILMS FORMED BY LASER ABLATION

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Silver selenide in alpha modification has a wide range of interesting properties, first of all, high ionic conductivity. The alpha modification of Ag$_2$Se, stabilized at room temperature, is a perspective material for the creation of electronic elements, such as batteries and chemical current sources. The electrical properties, phase transitions, and crystallization features of thin silver selenide films obtained by laser ablation were studied. In a multilayer sample consisting of alternating layers of Ag$_2$Se and oxide glass silver selenide in alpha modification was detected at room temperature.

This work was supported by the Russian Foundation for Basic Research (project No 17-03-00121) All studies were carried out in the Researchpark of St. Petersburg State University.
TRANSMITTING METAL-OXIDE INTERACTION BY SOLITARY CHEMICAL WAVES: H₂ OXIDATION ON ZrO₂ SUPPORTED RHODIUM

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Catalytic hydrogen oxidation has been studied since the times of Faraday (1834) [1]. The increasing experimental and theoretical efforts in recent years, caused by the growing importance of hydrogen based energy generation in fuel cells, have resolved the intermediate reaction steps and shed light on the accompanying spatiotemporal effects from the nm- to the µm-scale [2]. Nevertheless, the formation of water by oxidation of hydrogen on noble and other transition metals remains a complex reaction with many interesting and unexplored features. For example, the interaction of catalytically active metal nanoparticles with the supporting oxide surfaces is still a research challenge. Particularly, the exact role of metal-support boundary effects, caused by the active sites along the metal-oxide interface, is not entirely clear. Recently, a long-range effect of metal-oxide boundaries in CO oxidation on oxide supported Pd was detected here we demonstrate a similar effect in a Rh/ZrO₂ model system on the reactivity of Rh in H₂ oxidation. The atomically narrow (<1 nm) interface between a Rh particle and ZrO₂ causes a remarkable shift in the kinetic behavior of the entire µm-sized particle, i.e. affecting metal sites thousands of nanometers away from the interface. The effect was directly observed by photoemission electron microscopy (PEEM) using the kinetics by imaging approach [4], which allows the evaluation of reaction kinetics for individual supported particles within the resolution limit of PEEM. The observed effect is attributed to the critical role of the perimeter sites for the initiation of activation and deactivation fronts (chemical waves) during H₂ oxidation, which transmit the metal-oxide interface effect over the entire Rh particle.

References

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SYNTHESIS AND AGGREGATION PROPERTIES OF MONOSUBSTITUTED PILLAR[5]ARENES CONTAINING N-ALKYLAMIDE AND N-(AMINOALKYL)AMIDE FRAGMENTS

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In recent decades, the attention of researchers is attracted to supramolecular polymers, due to their interesting chemical properties. Architectural and dynamic parameters which determine polymer properties, such as degree of polymerization and molecular weight, are a function of the strength of the noncovalent interaction, which can reversibly be adjusted. A unique macrocyclic platform for the synthesis of supramolecular polymers is pillar[n]arenes discovered in 2008. The introduction of various substituents into the structure of pillararenes allows the creation of new macrocyclic receptors with unique properties. The synthesis of pillar[5]arenes containing primary and secondary amino groups is a complex problem, solution of which leads to new compounds with practically useful properties. The functionalization of pillar[5]arene platform by the amide fragments, which can form hydrogen bonds, results in pre-organization of the macrocycle structure and provides coordination centers as a control element for self-organization. In the course of the study, we synthesized monosubstituted pillar[5]arenes containing N-alkylamide and N-(aminoalkyl)amide fragments [1]. The structure of the obtained macrocycles was confirmed by a complex of physical methods of NMR $^1$H, $^{13}$C and IR spectroscopy.

References

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Layered double hydroxides (LDH) are compounds consisting of brucite-like layers, in which part of divalent cations are isomorphically substituted by trivalent ones. Arising positive charge is compensated by anions, which are located in interlayer space. LDHs can be represented by the following formula:

\[ \left[ \text{M(II)}_{1-x} \text{M(III)}_x \left( \text{OH} \right)_2 \right]^{x+} \left[ \text{A}^{n-} \right]^{x-} \left[ \text{yH}_2\text{O} \right]^{x-}, \]

where \( \text{M(II)} \) and \( \text{M(III)} \) are divalent and trivalent cations respectively, and \( \text{A}^{n-} \) is \( n \)-valent anion. Incorporation of rare earth elements may allow to obtain materials possessing specific optical, electronic and magnetic properties [1, 2]. Co/Al-Ce layered double hydroxide was synthesized by coprecipitation method followed by hydrothermal treatment. The technique and synthesis conditions were chosen based on our previous work [3], in which nickel-aluminum-cerium LDH was successfully synthesized. Sample was prepared with an atomic ratio \( \text{M(II)}/\text{M(III)} = 3 \) and \( \text{Ce}^{3+}/(\text{Al}^{3+} + \text{Ce}^{3+}) = 0.05 \). The obtained compound was explored by powder X-ray diffraction, energy-dispersive X-ray spectroscopy, transmission electron microscopy, thermogravimetric analysis and differential scanning calorimetry.

Analysis results show that the synthesized material is layered double hydroxide with rather high crystallinity and it doesn’t contain any phase impurities. EDX indicates the presence of cerium, so we can admit an incorporation of rare earth element into the layered structure. Crystal lattice parameters were calculated using PDXL program: \( a = 3.01 \) Å, \( c = 22.811 \) Å.

References

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INVESTIGATION OF THE ELECTRONIC STRUCTURE OF METAL OR CHALCOGEN SUBSTITUTED MoS$_2$ BY HIGH-ENERGY SPECTROSCOPY METHODS

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MoS$_2$ is one of the most studied transition metal dichalcogenides, and is considered to be a promising in electrocatalysis, photocatalysis, as a cathode material, and in other areas. Modifying MoS$_2$ by doping we can produce materials with the necessary electronic properties. Solid solutions based on MoS$_2$ doped with non-isovalent metal atoms (electron-rich Re and electron-deficient Nb compared to Mo) and chalcogen atoms are investigated within this work using X-ray photoelectron (XPS) and X-ray emission spectroscopy (XES).

X-ray photoelectron spectra and X-ray emission spectra of the core and valence levels of compounds with composition Mo$_{1-x}$M$_x$S$_2$ (M=Re, Nb, x = 0.05, 0.1, 0.15), MoS$_2$-$x$Q$_x$, (Q=Se, Te, x = 0.1, 0.15, 0.2, 0.25), which give information about the charge state of atoms included in the structure and their contribution to the chemical bond, were analyzed. The results of XPS Mo3d and S2p spectra analysis of Mo$_{1-x}$RexS$_2$ are consistent with hypothesis that Re atoms replace Mo atoms; in this case, electron density is delocalized from Re atoms to nearby Mo and S atoms. XPS Re4f spectra of the Mo$_{1-x}$RexS$_2$ samples show that the formation of Re dimers occur in a whole range of Re concentrations. When the Re concentration reaches 15% large island-like clusters are formed.

The change in partial Mo3d and S3p DOS after doping can be studied using Mo Lβ2.15 and S Kβ XES. Contributions to deeper energy range of Mo4d DOS upon doping with both metal and chalcogen are increase significantly. On the contrary, contributions of S3p to DOS after doping with metal atoms changes insignificantly and redistributes with the replacement of chalcogen. It is associated with an increase in the ionic radius of the dopant, because the difference of ionic radii leads to a significant distortion of the crystal lattice and therefore the electronic structure of MoS$_2$. 

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Lead-acid batteries (LAB) are the undisputed leaders in the field of automotive, stationary and traction batteries. However, when used in hybrid electric vehicle (HEV), irreversible sulfation of negative active mass (NAM) occurs in high-rate partial-state-of-charge (HRPSoC) conditions, which significantly limits the battery life. The actual direction of solving this problem is the introduction of additives of various types of carbon.

The purpose of this work was to study the structural and electrochemical properties of the negative electrode with the addition of carbon for the LAB. As carbon additives in the NAM of the lead electrode, multi-walled carbon nanotubes (“Art-nano” NSU “S” (TU BU 690654933.001.-2011)) and multilayer graphene (“Art-nano GT” (TU BU 691460594.004-2017)) were used (manufactured by «Advanced Research & Technologies» LLC). It was obtained that the introduction of carbon additives in the amount of 1 mass. % increases discharge capacity, NAM utilization ratio and number of cycles when tested under HRPSoC conditions.

The methods of impedance spectroscopy were used to study the processes occurring at the negative electrode. An equivalent electrical circuit was proposed, which included the ohmic resistance of the electrolyte R1, the C1-R2 block associated with a thin tightly packed film of lead sulfate, and the parallel-connected CPE1-R3 block associated with the porous structure of the electrodes. The calculation of the elements of the proposed equivalent circuit showed the change in resistance values R3 associated with the porous structure of the electrodes. The study of the structural characteristics of the electrodes showed that in the presence of carbon additives, the formation of pores with radii of less than 0.05 microns, an increase in the total porosity and specific surface of the electrodes occurs. A mechanism is proposed for the effect of carbon additives on the process of sulfation of negative LBA electrodes.
Supercapacitors have become one of the most promising energy storage systems, since they are characterized by high power density, fast charge-discharge, and long-term cyclic stability. However, the initially low energy density is inherent in traditional supercapacitors, which limits their widespread use, prompting researchers to develop new types of supercapacitors with improved characteristics. Asymmetric supercapacitors assembled using two dissimilar electrode materials have a clear advantage due to the wider voltage window, which allows a significant increase in energy density.

The purpose of this work was to study the electrochemical properties of carbon-based electrodes based on nanostructured NSU “S” (TU BU 690654933.001.-2011) and carbon of the technical advanced “Art-nano GT” (TU VU 691460594.004-2017) (manufactured by Advanced Research and Technology LLC ) and establish the possibility of its use in an asymmetric supercapacitor in an aqueous electrolyte.

Electrochemical properties were studied by the methods of cyclic voltammetry and galvanostatic.

It was found that carbon Art-nano GT is not suitable as a material for the electrodes of an asymmetric supercapacitor in an aqueous electrolyte. The electrodes prepared from this carbon grade had satisfactory mechanical properties, only after the active mass was treated with ultrasound before being applied to the tantalum substrate. The resulting electrodes had a very low specific capacitance of 2-6 F·g⁻¹.

Electrodes prepared on the basis of the carbon of the NSU "C" brand, both with and without the use of ultrasound, had satisfactory mechanical properties. The specific capacity of these electrodes was 27-57 F·g⁻¹. The resulting electrodes can be used in an asymmetric supercapacitor in an aqueous electrolyte.
NOVEL NO\textsubscript{x}-DONOR FOR BIOMEDICAL APPLICATIONS BASED ON THE KEPLERATE Mo\textsubscript{72}Fe\textsubscript{30}

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We report on the novel inorganic complex [Mo\textsubscript{72}Fe\textsubscript{30}-(NO\textsubscript{2})\textsubscript{6}](NO\textsubscript{2})\textsubscript{x}, where x=14±3, synthesized by the exposition of giant nanocluster polyoxometalate (POM) crystals in the dry-NO\textsubscript{2} and NO stream. The vibrational spectroscopy showed the saving of Keplerate Mo\textsubscript{72}Fe\textsubscript{30} structure and formation of nitrate ions: sharp intensive signal at 1385 cm\textsuperscript{-1} and weak signal at 1287 cm\textsuperscript{-1} in IR and Raman spectra, respectively. That coordination of NO\textsubscript{2} molecules in POM crystals occurs by the two ways – inside (in-plane, Fig.1) or above (out-of-plane) of the hexagonal POM pores as it was observed from XPS spectra. In-plane coordinated NO\textsubscript{2} molecules belong to the constitutional ligands that is opposite to out-of-plane coordinated ones, which are delocalized at 298 K. However, below 200 K, a new EPR-signal with g-factor of 4.3 appears that corresponds to localisation of all nitrate ions leading to distortion of FeO\textsubscript{6} octahedra towards the tetrahedral symmetry. Thus, in POM crystal, there are two types of NO\textsubscript{3} ions – constitutional strong-bonded and weak-bonded, which can be released from the crystal during the thermal destruction (above the 493 K) or the dissolution in aqueous media at neutral pH (near 7.2-7.4) and room temperature. The later is interesting for biomedical applications where such complex could play the role of NO\textsubscript{x}-delivery system for \textit{in vivo} production of nitrogen monoxide, which is a very important signalling molecule.

Figure 1. Model of NO\textsubscript{2} coordination in hexagonal pores of POM showing the NO\textsubscript{3} \textsuperscript{-} ion formation and octahedral-to-tetrahedral transition of FeO\textsubscript{6} polyhedra at the cryogenic temperature observed on EPR spectra. The purple and yellow colours correspond to the Mo and Fe oxygen polyhedra, respectively.
Group 13 element trihalides are strong Lewis acids which form stable donor-acceptor (DA) complexes with bifunctional N-donors. Resultant 13-15 DA complexes are adducts or group 13 metal-organic frameworks (13-MOF) of different kinds. Most of 13-MOFs described are built using poly-carboxylate linkers [1], and there are only a few examples of using N-donors. Thereby synthesis and characterization of new 13-15 complexes built up with bifunctional N-donors are important tasks.

Recently we first established crystal structures of MX₃ (M=Al, Ga; X=Cl, Br) complexes with 1,2-bis(4-pyridyl)ethylene (bpe). Complexes obtained exhibit a broad set of architectures: adducts, coordination polymers (CPs) (1D, 2D, mixed 1D-2D CPs), binuclear ionic complex. Due to the remarkable diversity of the possible reaction products, the target synthesis of the complex desired generally results in the hardly-splittable mixture formation irrespective of the synthetic conditions. This work, in turn, focuses on the complexes of MX₃ (M=Al, Ga; X=Cl, Br) with 1,2-bis(4-pyridyl)ethane (bpa). All complexes were synthesized by direct interaction of MX₃ (M=Al, Ga; X=Cl, Br) with bpa without the use of organic solvents. Because of the moisture and air sensitivity of group 13 element halides and of the reaction products, all synthetic operations were carried out in whole glass apparatuses under vacuum. Either equimolar amounts of components were used or two-fold excess of one reagent was employed. Solid state structures of adducts (e.g. (MCl₃)₂·bpa) as well as coordination polymers (e.g. ½[MCl₂(bpa)₂]⁺[MCl₄⁻]) were established by single crystal X-ray analysis.

References

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GREEN CHEMISTRY APPROACH TO THE SYNTHESIS OF BRIGHT BLUE EMITTING Cd-Zn-S QUANTUM DOTS

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Over the last decade, chalcogenide quantum dots (QDs) with bright and stable photoluminescence have gained much attention because of the variety applications they afford [1]. Due to the quantum size effect, it is possible to tune the band structures and thereby the optical properties of semiconductor QDs by simply controlling their sizes and shapes.

In this work, we present a study of the temperature influence on the structure, morphology, and optical properties of Cd$_{0.15}$Zn$_{0.75}$S QDs using a new sulfur source. In our recent investigations [2] we have successfully replaced harmful and expensive phosphine sulfides (such as trioctylphosphine and tributylphosphine sulfides) on eco-friendly and commercially available N,N'-disubstituted and N,N',N'-trisubstituted thioureas. All syntheses were conducted in an organic dispersion medium with a non-coordinating solvent 1-octadecene (ODE) by hot-injection and one-pot synthetic methods in the temperature range 220 – 300 °C. The structural and compositional characterization of QDs was performed by X-Ray diffraction and Energy Dispersive X-Ray Spectroscopy (EDS). It was found that nanoparticles have different particle shape with face-centered cubic structure and the average size of 3-4 nm. The crystal growth and optical features were analyzed by UV-VIS and photoluminescence (PL) spectroscopy. The obtained Cd$_{0.15}$Zn$_{0.75}$S QDs exhibit favorable narrow emission peaks and photoluminescence quantum yields (PLQY) up to 67 %.

References

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The study of the surface of α polymorph of 9,10-diphenylanthracene crystals by the THz-Raman spectroscopy method allowed us to detect zones with a modified metastable structure. Under the action of laser radiation at a wavelength of 785 nm, monotonous changes in the crystal structure in the direction of the formation of more stable α polymorphs can be observed in the detected zones. The found metastable structure of 9,10-diphenylanthracene may be associated with the appearance of surface oxygen vacancies.

Figure 1. Raman spectra of the 9,10- diphenylanthracene polymorphs.

References
ELECTROCHEMICAL PERFORMANCE OF REDUCED GRAPHITE OXIDE IN VARIOUS ELECTROLYTES

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Significant reduction of the sizes of portable devices and at the same time an increasing of clock frequency and processor power makes the development of effective energy storage devices such as supercapacitors (SC) and Li-ion batteries relevant (LIB’s). The promising materials for these applications are carbon nanomaterials, electrically conductive polymers and transition metal oxides. The selection of the most effective electrolyte is an important moment as well. In this work, the thermally treated reduced graphite oxide was synthesized as electrode materials for electrochemical devices. RGO is a graphene-like nanomaterial functionalized by oxygen-containing functional groups (OCFG). The RGO thermal treatment allows controlling the OCFG content in the material. It makes possible to control such important material characteristics as electro conductivity, wettability and specific surface area.

In this work, we synthesized a graphite oxide by modified Hummers method as a precursor for RGO synthesis. The RGO was synthesized by acid treating graphite oxide. Further, the RGO was thermally expanded at 250°C (RGOTE) and thermally annealed at 500°C (RGO-500), 600°C (RGO-600), 700°C (RGO-700). The change in OCFG content with the temperature increasing was investigated by XPS, IR and Raman spectroscopy methods. It was shown that thermal expansion allows obtain the materials with developed surface (Fig. 1). The samples specific surface areas were obtained by BET method. It was shown that the specific surface area reaches ~300 m²/g. The electrochemical performance in various electrolytes (1M H₂SO₄, 1M KOH, 1M NaCl for SC and 1M LiPF₆ in PC/EC for LIB’s) was obtained by cyclic voltammetry and charge-discharge cycling methods.

Figure 1. SEM images of: (a) RGOTE, (b) RGO-500, (c) RGO-600, (d) RGO-700.

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SYNTHESIS AND STUDY OF THE ELECTROCHEMICAL PROPERTIES OF PEDOT-BASED COMPOSITES WITH TRANSITION METAL OXIDES

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Low-cost transitional-metal oxides – tungsten trioxide (WO₃) and molybdenum trioxide (MoO₃) have attracted considerable interest as promising supercapacitive materials due to their non-toxicity, high electrochemical activity and environmentally friendliness. As these compounds have low conductivity, their electrochemical performance (specific capacitance and cycling stability) can be enhanced by making their composites with conducting polymers. Poly-3,4-ethylenedioxythiophene (PEDOT) is often used in supercapacitors, both as a conducting matrix and to maintain the microstructure of metal oxide deposits during charge-discharge process.

WO₃ was electrochemically deposited from a metastable acidic solution of isopolytungstate on glassy carbon (GC) electrodes coated by PEDOT films [1]. The morphology of WO₃ deposits was studied using SEM, TEM and EDX analysis. MoO₃ was synthesized by hydrothermal method from (NH₄)₆Mo₇O₂₄·4H₂O according to the procedure described in [2]. The PEDOT:PSS/MoO₃ composite was prepared by mixing MoO₃ with PEDOT:PSS aqueous dispersion and Nafion® as a binder and drop-cast onto GC electrode.

Electrochemical behavior of PEDOT/WO₃ and PEDOT:PSS/MoO₃ composites was investigated in 0.5M H₂SO₄ by cyclic voltammetry and galvanostatic charge-discharge methods. The average values of specific capacitances obtained from CV data were 67 mF/cm² (324 F/g) for PEDOT/WO₃ and 93 mF/cm² for PEDOT:PSS/MoO₃.

The obtained results indicate that PEDOT/WO₃ and PEDOT:PSS/MoO₃ composites can be promising electrode materials for supercapacitors.

References

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HYDROTHERMAL SYNTHESIS OF POWDERS AND EPITAXIAL FILMS IN VO₂ - TiO₂ SYSTEM

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The VO₂ – TiO₂ system is unique in terms of the functional properties of its components. Vanadium dioxide shows a semiconductor-metal transition at approximately 68°C with a sharp change in the resistivity. Titanium dioxide is a wide-gap dielectric, a well-known photocatalyst, and is often used as transparent coatings for VO₂ films. Similarity of crystalline structures between TiO₂ and VO₂ allows the epitaxial growth of their layers in core-shell nanoparticles [1] and film heterostructures [2]. Such composites will provide the combination of the functional properties of vanadium and titanium dioxides and expand the area of their practical application.

The synthesis of these structures is a complicated process due to influence of many factors such as the phase composition and microstructure of the films, adhesion, and localized deformation at the film-substrate interface on materials properties. In turn, the main method of nanopowders VO₂ and TiO₂ obtaining is hydrothermal synthesis allowing change time, temperature, concentration, filling percentage of the autoclave, precursor dependence, reducing agents, with the aim to control structure, morphology and phase composition of produced particles [3]. The aim of this work is the hydrothermal synthesis of nanopowders with an interesting particles morphology and oriented films on single-crystal substrates in the TiO₂ – VO₂ system.

Hydrothermal synthesis was carried out in autoclaves with Teflon reactors with a volume of up to 60 ml at temperatures of 190 – 230°C for 1 – 24 hours using water-soluble complexes of titanium and vanadium as precursors. The powders and films on R-sapphire substrates were studied by XRD, SEM, EDX and XPS methods. To obtain crystalline coatings, the samples were annealed in a vacuum quartz-tube furnace under specific oxygen pressure. The electrical and optical (IR, THz range) properties of the materials were studied.

References

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PREPARATION AND STABILIZATION OF NANOEMULSIONS WITH LINSEED AND PUMPKIN OILS

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Recently, interest in the controlled delivery of drugs and biologically active substances has increased significantly. Targeted drug delivery has a number of significant advantages over conventional therapy, for example, they improve the pharmacokinetics with a lower content of the dosage form [1]. Nanoemulsions are promising candidates for use in targeted drug delivery. The main advantage of nanoemulsions is the ability to encapsulate hydrophobic drug compounds [2, 3], as well as the ability to protect drug compounds from destruction in the environment of the body.

The purpose of this work was to obtain O/W nanoemulsions containing pumpkin or linseed oil. For the preparation of nanoemulsions, the method of temperature phase inversion was used. The concentration of the oil phase in nanoemulsions was 25 vol.%. Various mixtures of nonionic surfactants were used as nanoemulsion stabilizers.

Increasing surfactant concentrations led to decreasing the sizes of oil droplets in nanoemulsions with pumpkin or linseed oil. The minimum average diameter of oil droplets was about 16 nm. Stability of nanoemulsions toward flocculation and creaming was improved by using of cross-linked acrylic polymer. The effect of the gelling agent on the stability of nanoemulsions was studied. The stability of nanoemulsions increased with increasing concentration of gelling agent. The concentration of the gelling agent of 0.2 mass.% was enough to obtain nanoemulsions stable for a long time.

References
SIZE EFFECT OF Au NANOPARTICLES SYNTHESIZED IN THE PRESENCE OF DNA IN CATALYTIC REACTIONS

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Gold nanoparticles (AuNPs) are efficient catalysts of various reactions [1]. Since a catalyst efficiency is determined by its particles size, it is important to prepare AuNPs with tunable size and investigate their catalytic properties.

We obtained AuNPs via HAuCl₄ reduction with NaBH₄ in the presence of DNA, an attractive matrix to obtain stable AuNPs [2]. Catalytic activity of the AuNPs was studied using the reaction of p-nitrophenol reduction with NaBH₄.

The size of the AuNPs could be tuned by changing the molar ratio between DNA and Au in the mixture (1:1, 5:1, or 20:1) and the time of NaBH₄ addition (immediately after mixing DNA and HAuCl₄ solutions, 2 h, or 7 days). The catalytic reaction rate constants $k$ determined for the obtained AuNPs were systematically varied between 0.73 and 2.1 min⁻¹ depending on the synthesis conditions. The lowest $k$ value was observed for immediate reduction of the 1:1 DNA:HAuCl₄ mixture (affording relatively large AuNPs, cf. Fig. 1a), while the highest $k$ value was found for reduction of the 20:1 DNA:HAuCl₄ mixture after its keeping during 7 days, which gave smaller AuNPs (Fig. 1b).

In summary, we demonstrated that ultrasmall AuNPs exhibiting high catalytic activity can be obtained in the presence of DNA matrix.

Figure 1. TEM images and absorption spectra of AuNPs prepared under different conditions (see text for details)

References

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SOLUTIONS OF BIFUNCTIONAL AMINES AND SILVER SALTS.
FORMATION OF NANOPARTICLES

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Nowadays there are many works describes synthesis and properties of argentum nanoparticles. In many of them methods of reduction silver from solutions with polymer structures are proposed [1]. The aim of this research was to study the mechanism of the reaction and the product of oxidation.

Selected amines contains two amino groups therefore these compounds could be used as model structures in studying processes of formation argentum nanoparticles in solutions, contains polymers and silver salts.

To study formation of AgNPs through serial time intervals after mixing the solutions of amines and silver salt, absorption spectra was measured. Particle formation was observed due to an increase in the absorption intensity at the wavelength corresponding to the plasmon resonance of silver nanoparticles ($\lambda = 450$ nm, Fig. 1)

References

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An effective way of solar energy conversion is based on using a photosensitizer in solar cells (DSSC). The development of stable and efficient devices requires understanding the mechanisms of the basic processes occurring in the cell, in particular, electron transfer. Herein, we demonstrate that polyiodide chains play an important role in charge transfer in DSSC. An X-ray study of co-crystals of cationic Cyclometalated iridium(III) complexes with polyiodides gives insight into the dye-mediator interactions and thus into the electron transfer process. Depending on the initial iodine concentration various polyiodide architectures can be obtained in the resulting co-crystals, from insular triiodides to infinite polyiodide chains. UV-light exposure leads to structural changes in co-crystals with infinite chains whereas the discrete iodides remain unchanged. We suppose that after UV-irradiation the excited dye molecules are deactivated by charge transfer to the polyiodide chains (but not to insular anions) that is accompanied with partial oxidation of the iridium ion confirmed by electron spin resonance spectroscopy.

Figure 1. Fragment of co-crystal structure containing both insular and chain polyiodides.

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NdCoO₃ NANOCRYSTALS FORMATION MECHANISM AND KINETICS FROM POWDERS OBTAINED IN GLYCINE-NITRATE COMBUSTION CONDITIONS

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Formation kinetics and mechanism research of perovskite-like nanocrystals is a promising direction, since it allows optimizing the conditions for obtaining crystallites with a narrow particle size distribution. This work describes the peculiarities of the phase formation processes in NdO₁.₅-CoOₓ system from precursors obtained in conditions under glycine-nitrate combustion as well as the nucleation kinetics of NdCoO₃ nanocrystals at temperature treatment. Samples corresponding to NdCoO₃ stoichiometry were obtained under the conditions of G/N = 0.35; 0.55; 0.75 ratio according to the synthesis method described in details in works¹,². The obtained samples were annealed in air at T = 500–800 °C for 2-120 min. The kinetics research was performed in the annealing – quenching mode with subsequent X-ray phase analysis.

It is shown that NdCoO₃ nanocrystals yield with narrow particles distribution at heat treatment of X-ray amorphous precursor formed in the oxidizer conditions goes quickly enough, reaching extent of transformation equal 0.8 already in 1 h isothermal endurance at 600 °C. NdCoO₃ nanocrystals formation at heat treatment of the products representing crystal phases of various structure, formed in the conditions of stoichiometric glycine - nitrate ratio and excess of reducer, is complicated. It is connected with need of expenses of time for CoO oxidation (G/N = 0.55) and Co (G/N = 0.75) to Co₃O₄ at the further heat treatment, and with absence, apparently, of structural predecessors. The dependence of NdCoO₃ fractional conversion on time at various processing temperatures is satisfactorily described by the Avrami-Erofeev nucleation model equation. The calculated parameters of the model allow suggesting the probable mechanism of NdCoO₃ nanocrystals formation and estimate their apparent activation energy, the value of which is 338±32 kJ/mol.

References

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SYNTHESIS OF MACROCYCLIC POLOXOVANADATES WITH RARE EARTH METAL CATIONS

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Polyoxometalates are anionic clusters composed of early transition metals and oxygen atoms. They attract much attention in broad fields such as catalyst chemistry, magnetochemistry, photochemistry, and pharmaceutical chemistry. VO₄-based polyoxometalates construct a ring structure by corner-sharing of VO₄ tetrahedra. Tetravanadate [V₄O₁₂]⁻, which dominates in acetonitrile, is too small to capture metal cations inside the ring. However, it coordinates to various transition-metal cations. When the size of the ring is expanded to more than six VO₄ units, it can become large enough to accommodate various metal cations at the center, thus acting as a crown ether type ligand. In this presentation, we focus on the combination of rare-earth metal cations and VO₄-based polyoxovanadates. By the reaction of [Et₄N]₄[V₄O₁₂] and rare-earth metal sources in acetonitrile, three types of rare-earth metal containing polyoxovanadates was synthesized (Figure 1). The ionic radius of lanthanide is gradually decreased with increasing atomic number. The macrocyclic structures was controlled by the ionic radius of the center metal cations[1-3].

![Figure 1. The molecular structures of the series of rare-earth metal containing polyoxovanadates.](image)

References
HOW CAN WE STABILIZE AN OXIDO- OR HYDROXIDO-UNIT FROM AQUEOUS SOLUTION?

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Metal oxides have attracted much attention in various applications. To mimic the structures and the properties of metal oxides, many oxido-bridged metal complexes have been reported. In this study, we are researching intermediate oligomer species between the bulk solids and the small coordination compounds.

To stabilize such oligomer species, we are proposing protecting groups to terminate further hydrolysis. Previously, we stabilized [{Co(tacn)}<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>] (1) by using an electrophilic protecting group of {Co(tacn)}<sup>3+</sup> (tacn, 1,4,7-triazacyclononane). Interestingly, cluster 1 plays an important role of a starting material leading to a key intermediate species of {Co(tacn)}<sub>2</sub>Mo<sub>3</sub>O<sub>13</sub> unit for the formation of [{Co(tacn)}<sub>4</sub>H<sub>2</sub>Mo<sub>7</sub>O<sub>27</sub>]<sup>2+</sup> (2) and [{Co(tacn)}<sub>4</sub>H<sub>3</sub>Mo<sub>4</sub>O<sub>17</sub>]<sup>5+</sup> (3) (Figure 1) [1].

Recently, we discovered that the {Co(tacn)}<sub>2</sub>Mo<sub>3</sub>O<sub>13</sub> intermediate works as a nucleophilic protecting group (i.e., ligand) to stabilize 3d-transition metal complexes. Through this study, we emphasize that the utilization of suitable electrophilic or nucleophilic protecting groups allows us to stabilize metal oxido- or hydroxido-clusters without exception on periodic table.

Figure 1. Structures of clusters 1, 2, and 3. Pink, blue, red, light blue, black, and white balls show Mo, Co, O, N, C, and H atoms.

References
This work describes the synthesis, structural and spectroscopic characterization of a new niacin hexamolybdocobaltate \([\text{C}_6\text{H}_6\text{NO}_2]_2[\text{H}_3\text{O}]_2[\text{CoMo}_6(\text{OH})_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}\) (I), which is an efficient building block in a design of more complex supramolecular assemblies promising as catalysts or single-molecule magnets [1]. It has been prepared and studied by means of chemical analysis, single-crystal X-ray diffraction, NMR and IR spectroscopy. The crystal system is triclinic, space group P-1, unit cell parameters \(a=9.2303(19)\) Å, \(b=10.700(2)\) Å, \(c=10.850(2)\) Å, \(\alpha=95.95(3)^\circ\), \(\beta=110.01(3)^\circ\), \(\gamma=105.11(3)^\circ\), \(V=949.9(4)\) Å\(^3\) [2]. It is known the complex of nicotinic acid with dodecatungstum phosphate, in which heteropolyanions in polyhedra form cavities filled with molecules of nicotinic acid [3].

The structure of \([\text{C}_6\text{H}_6\text{NO}_2]_2[\text{H}_3\text{O}]_2[\text{CoMo}_6(\text{OH})_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}\) includes an isolated heteropoly anion \([\text{CoMo}_6(\text{OH})_6\text{O}_{18}]^{4-}\) that can be classified as the Perloff’s-type anion, four outer-sphere cations includes two protonated molecules of nicotinic acid \((\text{C}_6\text{H}_6\text{NO}_2)^+\) and two hydronium cations \(\text{H}_3\text{O}^+\), and six hydration water molecules.

References
AN ALIGNED OCTAHEDRAL CORE IN A NANOCAGE: SYNTHESIS AND PLASMONIC PROPERTIES

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Plasmonic metal nanostructures with complex morphologies provide an important route to tunable optical responses and local electric field enhancement at the nanoscale for a variety of applications including sensing, imaging, and catalysis. Here we report a high-concentration synthesis of gold core-cage nanoparticles with a tethered and structurally aligned octahedral core and examine their plasmonic and catalytic properties. The obtained nanostructures exhibit a double band extinction in the visible-near infrared range and a large area electric field enhancement due to the unique structural features. In addition, the obtained structures had a photoelectrochemical response useful for catalyzing the CO\textsubscript{2} electroreduction reaction. Our work demonstrates the next generation of complex plasmonic nanostructures attainable via bottom-up synthesis and offers a variety of potential applications ranging from sensing to catalysis.

![Figure 1. Dark field TEM (a) and SEM (b) images of the structure](image)

Figure 1. Dark field TEM (a) and SEM (b) images of the structure

Acknowledgements. This work was supported by the Council on grants of the President of the Russian Federation MK-6153.2018.3.
CREATION OF DRUG DELIVERY SYSTEMS WITH TRIGGERED RELEASE: pH- AND ENZYME-SENSITIVE LINKERS

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Today the number of severe diseases could be effectively treated with an application of biomacromolecular drugs, as they have high specificity of action and can interact with multiple targets [1]. However, their wide application is limited by their fast rate of inactivation into the organism, as well as by their immunogenicity [2]. These problems could be mounted via the creation of special encapsulated dosage form, which allows control over biomacromolecular drug delivery and releases at the site of action. Therefore, the development of effective systems, which are capable of safely delivering a drug to the required site of action, protect the drug from degradation in the body’s environment and systemic distribution before the target cells penetrate into the intracellular space is in the list of the most important tasks for modern chemical science.

This work is devoted to obtaining and investigation of pH and enzymatically sensitive linkers to create the systems capable for inducible drug delivery based on the difference in pH and enzymatic composition of extracellular and intracellular media. Cross-linked polymer particles were chosen as such systems, in which cross-links are formed by special bifunctional molecules that are stable in the extracellular medium but degrading inside the cells, namely at acidic pH or in the presence of specific enzymes.

References

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The work is devoted to the study of the structural phase transformations of nanotubular nickel hydrosilicates Ni_3Si_2O_5(OH)_4 in air [1] and nickel-magnesium hydrosilicates of composition (Mg_{1-x}Ni_x)_3Si_2O_5(OH)_4 (x = 1 and 0.67) in reducing media in the temperature range 25 – 1000 °C.

Nickel and nickel-magnesium hydrosilicates were obtained by a hydrothermal method at a temperature of 350 °C, a pressure of 20 MPa, and a 10-hour exposure to 0.1 M NaOH solution. The obtained nickel hydrosilicates were processed in air at temperatures of 400, 600 and 1000 °C. At 400 °C, the crystal structure did not change significantly, at 600 °C a nickel hydrosilicate phase transition occurred with formation of sepiolite-like Ni_4Si_6O_{15}(OH)_2. At 1000 °C, a highly crystallized phase of nickel orthosilicate Ni_2SiO_4 was formed.

Nickel-magnesium hydrosilicates were kept in a flow of argon-hydrogen mixture for 1 hour in the temperature range of 400-900 °C. Depending on the temperature, complete or partial reduction of nickel cations in the form of metal nanoparticles was observed. By using transmission electron microscopy, it was found that the size of nickel metal particles depends on the percentage of nickel in the original sample and on the temperature of the experiment. Thus, the particles formed during the reduction of hydrosilicate with a nickel content of 67% were larger, and their size distribution was wider than in the case of particles formed during the reduction of pure nickel hydrosilicate.

References

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We present a procedure to grow thin films of lead-containing materials such as lead sulfide (PbS) with ‘solution Atomic Layer Deposition’ (sALD) [1], a technique which transfers the principles of ALD from the gas-phase (gALD) to liquid processing. Pure and crystalline thin films are successfully deposited on planar and three-dimensional substrates at room temperature with a procedure that exhibits the unique ALD characteristics of self-limiting surface chemistry and linear growth. Conversion of PbS to the hybrid perovskite methylammonium iodoplumbate (methylammonium lead iodide, MAPI, CH3NH3PbI3) leads to a material which can serve as the light absorber in a photovoltaic device.

Figure 1. (a) Principle of sALD, (b) conversion of PbS to MAPI.

References

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SYNTHESIS AND PROPERTIES OF QUADRUPLE-DECKER SANDWICH COMPLEXES OF LANTHANIDES(III)

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Today phthalocyanines (Pcs) are applied in many areas, including electrochromic components in information display media and molecular magnets. Lanthanide sandwich type Pcs are among the most promising compounds in these areas.

![Synthesis of lanthanide quadruple-deckers and NIR spectra in CCl4.](image)

Figure 1. Synthesis of lanthanide quadruple-deckers and NIR spectra in CCl4.

In the course of this study, a series of quadruple-decker lanthanide(III) sandwich complexes was synthesized (Fig. 1) with high yields up to 90% [1]. The compounds were characterized by a range of physicochemical methods: 1H NMR, MALDI TOF/TOF, UV-Vis-NIR, TG-MS, and electrochemistry. The UV-Vis-NIR spectra indicate that an increase in the ionic radius bathochromically shifts the main absorption bands; in the NIR region the maxima shift from 1262 to 1618 nm for Ln = Lu and Eu, respectively (Fig. 1).

The completed studies allow us to offer these compounds as electrochromic components in information display media, molecular magnets, and IR labels.

References

Acknowledgement. This work was supported by the Russian Scientific Fund (project No 17-13-01197).
At the present time, the mixed (Janus) nanotubes have not yet been synthesized. Nevertheless, the rapid progress in the synthesis of nanosystems allows us to hope that such an opportunity will appear in the nearest future. Theoretical modeling of these systems will undoubtedly contribute to the achievement of this goal. To date, several computational works have been published on the study of Janus nanotubes based on MSSe (M = Mo, W). Among them, more attention was paid to the calculations of electronic structure and stability of Janus molybdenum dichalcogenide nanotubes, and relatively fewer works were devoted to similar tungsten dichalcogenide nanotubes.

In our previous work [1] we have used the hybrid density functional theory (DFT) to compare the structural and electronic properties, stability, vibrational frequencies, and thermodynamic functions of MoS$_2$ and WS$_2$-based single-wall nanotubes using for both the same calculation scheme approach implemented in the CRYSTAL17 computer code [2].

In this study we take a similar approach to obtain and compare the stability, geometry and electronic properties of MSSe (M = Mo, W) Janus nanotubes at different wall compositions, chiralities and diameters. Different types of nanotubes are considered – with S or Se atoms on the outer (inner) shell of the nanotube. It was found that nanotubes Se(out)MS(in) (M = Mo, W) with average diameter ($D_{avr}$) greater than $\approx$40 Å have the negative strain energy. Our calculations show that the band gap is direct for zigzag MS$_2$ and S(out)MSe(in) nanotubes but it becomes indirect in armchair nanotubes. For the MSe$_2$ and Se(out)MS(in) nanotubes of both chiralities, the band gap is mostly direct, except the armchair tubes with $D_{avr}$<18 Å and zigzag tubes with $D_{avr}$ in interval from 18 to 26 Å where it is indirect.

References

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Transformation of ligands in transition metal complexes are of paramount importance in metal complex catalysis and metal-mediated synthesis, in this report we will consider 1,3-bipolar cycle addition of acyclic nitrone \( p\text{-tolC(H)=N(O)CH}_3 \) to the nitrile ligands in complex \( [\text{PtCl}_2(\text{NCC}_6\text{H}_4\text{COH})_2] \). The interaction of the nitron with the nitrile \( \text{NCC}_6\text{H}_4\text{COH} \) without the metal center is not possible even in harsh conditions (90 °C, 240 h). However coordination of nitrile to Pt(II) center leads to activation of the nitrile functionality of the interaction of the nitron with the nitrile ligands in the complex \( [\text{PtCl}_2(\text{NCC}_6\text{H}_4\text{COH})_2] \) via \([2+3]\)-cycle addition becomes possible.

The obtained complex was separated and characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR and infrared spectroscopies high resolution masses spectrometry (electrospray ionization), and also elemental analyses (C,H,N)

References

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THREE-DIMENSIONAL SCAFFOLDS BASED ON POLYMERIC MICRO- AND NANOPARTICLES FOR TISSUE ENGINEERING

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Critical-sized bone defects created due to infection, tumor resection, or traumatic fractures need external interventions in order to regenerate bone, maintain or improve its function. Although autografts are considered as the gold standard treatment [1], it remains challenging for the clinicians to select between autografts, allografts or engineered tissues [2]. This has led to the extensive research of biomaterials for tissue engineering in the last several decades [3]. Nevertheless, there is a lacks of studies, which deal with generation of scaffolds with spatiotemporal distribution of osteogenic factors and controlled micro/nanotopology. The development of such scaffolds is essential, because the combination/distribution of various materials could resemble the complexity of natural bone tissue, and allow controlled precise reconstruction of all its components.

The ideal strategy for regenerative bone therapies is to use a “smart” biomaterial scaffold that can modulate the process of healing while providing mechanical support. Particles of different nature and size, possessing various rigidity and surface area can be joined together in different combinations to tune the mechanical properties and surface topology of the pores. Moreover, the useful peculiarities of the particles are the possibilities of their surface modification and different substances entrapment into their inner volume, which allow the spatial distribution of osteogenic or angiogenic factors and their temporally controlled release.

This research is devoted to the creation of biofunctional three-dimensional matrices based on polymeric micro- and nanoparticles. The polyester, polysaccharide and gelatin-based particles were obtained. The particles were characterized using the dynamic light scattering method and their morphology was studied by transmission electron microscope. In addition, the cytotoxicity of the obtained particles as well as their printability were studied.

References


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NEW ALKOXY DERIVATIVES OF LAYERED PEROVSKITE-LIKE TITANATES HLnTiO₄ AND H₂Ln₂Ti₃O₁₀ (Ln = La, Nd)

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Protonated layered perovskite-like oxides are solid crystalline substances in which two-dimensional perovskite slabs alternate with interlayer spaces containing protons. Being solid acids, they are able to react with some organic compounds giving inorganic-organic hybrids, i.e. substances consisting of chemically bonded inorganic and organic parts in which the inorganic part serves as a spatial frame [1]. Their formation may occur in two ways: either as intercalation of organic bases following an acid-base mechanism, or as grafting, that is a process similar to well-known esterification in organic chemistry. The second way, as a rule, takes place in the case of reactions with alcohols and leads to covalent alkoxy hybrids. Such derivatives are of high interest as promising heterogeneous photocatalysts, materials for electronics and precursors in producing surface modified nanolayers which may become a basis for new semiconductor films and nanoparticle superlattices [2].

The present work is devoted to synthesis and investigation of covalent inorganic-organic derivatives of protonated titanates HLnTiO₄ and H₂Ln₂Ti₃O₁₀ (Ln = La, Nd) with saturated alcohols as organic components. Possibility of the hybrids synthesis is studied in a wide range of conditions including solvothermal and solvothermal-microwave ones. Characterization of the products is performed using modern physicochemical methods (X-ray diffraction, Raman and nuclear magnetic resonance spectroscopy, thermogravimetry, elemental C,H,N-analysis, scanning electronic microscopy) with an emphasis on hybrids structure, composition, thermal stability and morphology.

References

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THE EFFECT OF THE ACTIVE COMPONENT CONTENT ON THE CATALYTIC ACTIVITY OF NICKEL SULFIDE CATALYSTS IN DEOXYGENATION OF STEARIC ACID

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Despite the rapidly changing oil prices, interest in renewable resources persists. Triglycerides of fatty acids are one of the promising types of such feedstock. The deoxygenation of such products yield paraffins of fuel composition or higher olefins, which are important products serving as a feedstock for the preparation of detergents, synthetic oils, additives, etc. Metals such as Pd, Pt, Ni or metal sulfides, generally on supports ($\gamma$-Al$_2$O$_3$), are used as catalysts [1]. Recently, it has been shown that nickel sulfide Ni$_3$S$_2$ powder can selective catalyzed decarbonylation of fatty acid to higher olefins. These catalysts as distinct from known Ni and Ni sulfide containing ones appeared to have relatively low side activities. The aim of this work was to study the effect of the active component content in the catalyst on the catalyst efficiency in decarbonylation of stearic acid to high olefins [2].

We studied nickel sulfide catalysts supported on alumina or silica by hydrogen reduction of Ni sulfate as the precursor. The amount of loaded metal ranged from 1.5% to 9%, the reduction temperature was 400°C under a hydrogen pressure of 10 atm for 3 h. The experiments were carried out in an autoclave at a hydrogen pressure of 15 atm and a temperature of 350°C.

The results of the research showed, that in the presence of the of the alumina- and silica gel-supported catalysts, the olefin selectivity exhibits a tendency to increasing from 30 to 55% with an increase in the nickel content in the catalyst from 1.5 to 9% respectively. For the two supports the increase in the conversion is not monotonous: initially, upon switching from the 1.5%Ni catalyst to the samples containing 3-6 wt % Ni, the conversion quite rapidly increases; afterwards, the increase ceases. The catalysts were studied by TEM combined with Xray microdiffraction, the results of the analysis showed the presence Ni, NiO, NiS and Ni$_3$S$_2$ phases on catalysts. In addition to the phase composition, the particle size of the active component can be responsible for the activity of the catalysts; the average particle size for the alumina and silica gel supports, is 3.1 ± 1.0 and 5.2 ± 1.2 nm, respectively.

References
ELECTROKINETIC CHARACTERISTICS OF POROUS GLASSES IN SOLUTIONS CONTAINING MULTIPLY CHARGED IONS (La$^{3+}$, Fe$^{3+}$)

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Porous glasses (PGs) (silica content >95%) - products of thorough chemical processing of two-phase alkali-borosilicate glasses of a certain composition - including nanoporous ones, and nanostructured systems prepared on their basis are modern functional materials distinguished by a very wide spectrum of possible fields of application, from highly active sorbents to matrices for producing composite quartzoid glasses. The analysis of the literature data shows that most of the research devoted to the study of the electrosurface properties of silicon oxide was carried out in 1:1-charge electrolyte solutions. Therefore, it was of interest to study the specific features of the behavior (efficiency ratio $\alpha$, transport numbers $n_+$ and $\zeta$-potential) of micro- (MIP) and macroporous (MAP) glasses in solutions containing specifically adsorbing multivalent iron (III)[1] and lanthanum ions in a wide range of pH values and (10$^{-1}$ – 10$^{-5}$ M) electrolyte concentrations.

When comparing the results of the study of various three-charged ions, it was shown that the low-nitratated La$^{3+}$ ion shows practically no specificity for the silica surface and is similar in behavior to the indifferent sodium ion. Whereas Fe$^{3+}$ ion exhibits distinct specificity to it. It was shown that the $\alpha$ (equal to the ratio of the specific electrical conductivities of pore and free solutions) decrease with increasing LaCl$_3$ concentration in accordance with the decrease in the contribution of ions of double electric layer (DEL) to the electrical conductivity of the pore solution. Whereas a different dependence was observed from the classical one for FeCl$_3$ solutions. It was observed that the values of $\alpha$<1, that is, the appearance of concentration regions of the equilibrium solution, in which the electrical conductivity of the pore solution becomes less than the free one. It was also found that $\zeta$-potential is negative in almost the entire LaCl$_3$ concentration range, while $\zeta$-potential becomes positive already at low FeCl$_3$ concentrations (~6.5×10$^{-4}$ M).

References


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Deflocculants in refractory concrete are defined as chemical agents who in small and miniscule amounts counteract an aggregation (flocculation) of fine and ultrafine particles in high-concentrated refractory mixes [1]. The most common deflocculants in practice are PCE-based deflocculants, hydroxycarboxylic acids and sodium tripolyphosphate (STPP). Behavior and efficacy of a particular deflocculating agent depend on composition and properties of refractory mix such as pH, binder type and content of aggregates and matrix. Often in cement-free compositions based on colloidal silica widely used commercial deflocculants are rendered ineffective and decrease the stability of colloidal binder. From this perspective it’s important to look for new dispersing and plasticizing agents that could show stable behavior irrespective of composition refractory concrete based on colloidal binder.

This work was study the deflocculation properties of different agent on refractory compositions consist of matrix components (corundum filler <0.063 mm, reactive alumina, silica fume) and aggregates (mullite or corundum 0-3 mm). The binder was a commercially available NH4+ stabilized colloidal SiO2 which was introduced in mixture in non-diluted or diluted with water form. A plasticizing effect was observed when introduced as few as wt. 0.005 % of pyrocatechol and its impact on flowability was proportional to amount of pyrocatechol in the mix. Meanwhile plasticizing ability of citric acid, STPP or PCE vary influenced by changes in concentration of colloidal SiO2. Matrix of all the samples in a dried state and after heat treating at 1400 °C was studied by means of XRD and SEM. The resulting matrix after sintering comprised of mullite and corundum and looked the same for all samples. All SiO2 from colloidal binder and microsilica fully reacted into mullite.

References
INFLUENCE STRUCTURE OF CARBON NANOTUBES ON THEIR ELECTROCHEMICAL PROPERTIES

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Carbon nanotubes (CNT) have unique properties, such as large specific surface, high electrical conductivity, chemical stability and etc. These properties give advantage of CNTs for application as electrode materials for supercapacitors, lithium-ion batteries, solar cells. Therefore, the structure of CNTs determines the parameters and characteristics of materials made on their basis.

The main methods of CNT production are catalytic chemical vapor deposition (CCVD) synthesis. The parameters of synthesis of CNTs, such as flow gases, ratio gases, time of synthesis, temperature and etc., are optimized for obtain of CNTs with desired properties [1].

In the research, we use of supported polyoxomolybdate cluster $\text{Mo}_{12}\text{O}_{28}(\mu_2-\text{OH})_{12}\{\text{Co}(\text{H}_2\text{O})_3\}_4$ as a catalysts precursor for the CCVD synthesis of CNTs. The advantages of these catalysts are that there have molecular clusters structure for the formation of discrete catalyst particles with a controlled size [2]. The alloy nanoparticles mixed with MgO substrate, which has a highly developed specific surface. The oxide magnesium MgO substrate was eliminated from the product using diluted HCl treatment.

In the present work was studied influence of temperature profile of CCVD process, catalyst composition and flow rates of CH$_4$/H$_2$ on structure and properties of CNT. The obtained were tested as electrode materials for a supercapacitor performance. The deformation leads to significant changes in electrical conductivity: with an increasing deformation of CNT, its conductivity decreases.

References

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SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION METHOD FOR THE DEPOSITION OF NICKEL FERROCYANIDES, AS A NEW METHOD OF CONTROLLED SELF-ASSEMBLY OF CATHODIC MATERIALS

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Transition metal ferrocyanides are promising cathode materials for magnesium-ion aqueous batteries. Firstly, properties of the cathode material based on these compounds can be set by changing the composition, morphology and size of particles [1]. Secondly, by their nature, transition metal ferrocyanides are similar to zeolites and they can intercalate cations of alkali and alkaline-earth elements in an aqueous solution without destroying the crystal structure [2, 3].

The successive ionic layer adsorption and reaction method allows obtaining thin films of transition metal ferrocyanides possessing meso- and macropores. The presence of mesopores can favourably affect the diffusion of magnesium ions in an aqueous solution, which will ensure good cyclability of the cathode material.

In the present work nickel ferrocyanide films were obtained, containing and not containing potassium ions, on a conductive substrate of tin oxide doped with fluorine (FTO). The obtained nickel ferrocyanide films were studied by XRD, SEM, EDX, ATR-FTIR, XPS methods. The presence of mesopores in films was confirmed by the method of small-angle X-ray scattering (SAXS).

Electrochemical studies in solutions of potassium chloride and magnesium chloride made it possible to establish the mechanism of magnesium ion intercalation and to reveal the negative effect of potassium ions on the process of intercalation of multiply charged ions.

References

Acknowledgements. The studies were conducted using the equipment and resource centers Science Park Saint Petersburg State University RC Geomodel, RC Innovative Technologies of Composite Nanomaterials, RC X-ray Diffraction Studies.
Acetone and methyl ethyl ketone (MEK) have the greatest practical importance among ketones. Acetone is produced through a large-tonnage cumene process. The imbalance of the phenol and acetone market creates conditions for the overproduction of the latter. Development of the technology for producing MEK from acetone would allow the excess of acetone to be removed from the market and make MEK more accessible.

The first studies of the gas-phase condensation of acetone with methanol to MEK were carried out at the turn of the 1960s-1970s. The Cu/TiO$_2$ system was used as a catalyst [1]. But the study has not received further development due to low activity and rapid deactivation of the catalyst. In recent years, more active and selective catalysts based on SiO$_2$ and Al$_2$O$_3$ have been discovered [2, 3]. However, Cu/SiO$_2$ catalysts have low stability. Cu/Al$_2$O$_3$ catalysts are stable but have a low selectivity of the methanol conversion to MEK, which is caused by the side reaction of dimethyl ether formation due to the acidity of Al$_2$O$_3$. The goal of our work is to develop a catalyst based on Al$_2$O$_3$, which has a low acidity due to its modification with Mg. It can be expected that a decrease in acidity will lead to an increase in the selectivity of methanol conversion to MEK.

The Cu/Mg-Al$_2$O$_3$ system was chosen as the object of research. The effect of magnesium modification of the support on the catalyst performance was investigated. The properties of the Cu/Mg-Al$_2$O$_3$ catalyst are compared with the known catalysts based on SiO$_2$ and Al$_2$O$_3$. It is shown that the modification of alumina with magnesium allows preparing a more active and selective catalyst.

References

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PHOTOCATALYTIC ACTIVITY OF THE AMINE-INTERCALATED LAYERED TITANATE $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ IN THE REACTION OF HYDROGEN PRODUCTION

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Layered perovskite-like oxides are complex oxides that consist of alternating perovskite blocks and blocks of different structure. Layered perovskites containing alkali metal cations in the interlayer space have been widely studied as ionic conductors, ferroelectric materials and photocatalysts. Layered oxides represent a unique class of photocatalysts, which have the ability to intercalate substrate molecules into the interlayer space, to exchange cations for different structural units. These properties already allowed creating highly efficient photocatalytic systems (e.g. for hydrogen production, organics decomposition) and open wide possibilities in the future [1]. The present research considers photocatalytic activity of the triple-layered perovskite-like titanate $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$, its protonated ($\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$) and butylamine intercalated form ($\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}\cdot\text{nBuNH}_2$) in the reaction of hydrogen production from aqueous methanol, ethanol or butanol solutions. Effects of alcohol concentration, catalyst amount and platinum loading on the photocatalytic efficiency were investigated. The butylamine-intercalated titanate modified with platinum showed the highest quantum efficiency which was determined by ferrioxalate actinometry.

Fig. 1. Efficiency of $\text{H}_2$ evolution form alcohol solutions under UV-light

References

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Counterfeit products or reusing of decommissioned equipment carry a safety hazard. The search for the marking methods leads the scientists and engineers to the field of nanotechnology, which found a useful application in almost every technological and industrial area. Detection of the nanoobjects is only possible with the identification of their properties, which makes it possible to hide the mark inserted in the object from the eyes. Luminescence is one of the most promising properties because it has a high detection sensitivity, moreover the dependence of the luminescence properties on the structural and concentration parameters allows the creation of a unique spectral code.

Our group has developed a spectral coding system that allows creating unique fluorescent nanomarkers based on metal oxides doped with rare-earth ions. These objects are well suited for solving the problem of marking of metal products with severe operating conditions. The work is devoted to the study of the process of introducing particles into the metal surface and luminescent properties analysis of the implanted nanoparticles before and after the interaction with the laser radiation under the condition of their contact with metal alloy surface.

Metal oxides are the most promising compounds for solution of the problem. Their chemical inertness and the stability of the physical and chemical properties over a wide temperature range are the major parameters for the successful implantation of the luminescent nanoparticles in the surface layer of metal products. The implantation of the particles into the surface layer was performed with the powerful laser irradiation. The laser illumination of the metals leads to local heating followed by melting and, partially, evaporation of the surface. After the laser treatment a well-defined mark can be observed in the area of the laser spot. Translation of the laser beam on the sample surface can be used to create a visible image or a symbol. Nanoparticles can be implanted in the melting area under certain conditions. In such a way the laser-induced incorporation of luminescent nanoparticles into the metal surface allows both visible marking of the object and simultaneous spectral coding.
IMPACT OF VO₂ NANOPARTICLES MORPHOLOGY ON ITS ELECTROCHEMICAL BEHAVIOR

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VO₂ (B), layered metastable phase of VO₂ has demonstrated promising properties as cathode material for Li-ion batteries. Great number of publications is devoted to investigation of such battery properties but there is a lack of information on impact of VO₂ morphology on electrochemical behavior. In our work, using hydrothermal synthesis, we obtained VO₂ nanoparticles from V₂O₅ and H₂C₂O₄. Stoichiometric ratio of the initial reagents was determined spectrophotometrically (1:4).

The temperature regime of the synthesis was selected to obtain pure VO₂ (B), conforming to our previous research. To change the morphology of nanoparticles we used capping agents: etidronic (ETDR), salicylic (SAL), succinic acids (SUC), 1,10-phenanthroline (PHEN) and pyrocatechin violet (PYR). UV-Vis spectra proved that capping agents did not form complexes with VO²⁺.

Obtained nanoparticles were characterized with XRD, SEM, FTIR and Raman spectroscopy. Also zeta potential of the samples was measured. According to XRD results, all specimens represented VO₂ (B). However, Raman spectra showed that samples without capping agents and with phenanthroline had an impurity of VO₂ (A). SEM images demonstrated that all of the samples represent spherical nanoparticles consisting of different structural components.

For the specimens with the highest surface area and lowest zeta potential charge-discharge curves were investigated. The obtained data demonstrated that VO₂@ETDR sample possessed the highest capacity 206 mAh/g and its stability remained unchangeable after 50 cycles. To investigate the occurring processes during the charge and discharge the cyclic voltammetry was used. The samples with any capping agent and VO₂@ETDR showed two anodic and two cathodic peaks, apparently, related to insertion/deinsertion of Li ions into the volume and the surface of the materials.

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SYNTHESIS AND LUMINESCENCE PROPERTIES OF YVO₄
NANOCRYSTALLINE POWDERS DOPED WITH A GROUP OF RARE
EARTH IONS

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This work is devoted to the synthesis and study of the nanocrystalline particles containing the rare earth ions. Metal oxides are the most promising compounds for rare earth doping due to their chemical inertness and the stability of the physical and chemical properties over a wide temperature range. These facts allow us to use of the such materials for medical purposes (due to their biocompatibility), in the field of machine building and instrument making (thermal stability and hardness), etc. The luminescence properties of the rare earth ions can be controlled by changing the crystalline lattice, synthesis conditions, the type of the ions, and their concentration. Each rare earth ion, inserted into a specific matrix, demonstrates a set of luminescence bands with appropriate spectral positions and relative intensities. A material doped with group of rare earth ions is a unique system. The research of this system is of particular interest because of fundamental purposes and wide range of possible applications. For the synthesis of nanocrystalline particles was used the modified Pechini method. In this method the amorphous powder is prepared by the standard Pechini method and then calcined in the molten salt at high temperature. This method results in the formation of the uniformly doped weakly agglomerated oxide particles with well-organized crystalline structure. The structure ensures the high luminescence yield, while the small size of the particles affords to prepare stable colloid solutions and suspensions. The unique electron configuration of the rare earth ions, the luminescence bands position slightly depends on the particles size and the environment. The luminescence spectrum demonstrates the possibility of simultaneous excitation of the rare earth ion group by pumping through a host. In the measured spectrum, one can distinguish emission lines originated from each introduced ion (for example, for Nd³⁺- 1065 nm, for Er³⁺- 554 nm, and for Tm³⁺ - 476 nm). The luminescence properties of YVO₄ nanocrystalline powders doped with different types and concentrations of the rare earth ions (Nd, Tm, Er) were studied. The results of the phase composition (XRD), crystal unit cell parameters, morphology (SEM) and particle size distribution were also obtained (DLS).
CRYSTAL SOLVATES AS PRECURSORS FOR SYNTHESIS OF INORGANIC MATERIALS


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At present, crystal solvates of inorganic salts with various organic solvents attract the attention of researchers due to their catalytic activity [1], the possibility of their use for the synthesis of perovskite-like structures [2], etc. However, the processes leading to the formation of solvates of a certain composition and structure are little studied. One of the most common methods for the synthesis of these compounds is their salting out of binary solutions with an indifferent solvent (acetone, ethyl alcohol, diethyl ether). This method allows to obtain only monoligand complexes. At the same time, the use of mixed ligand solvates as precursors may allow for a more subtle variation in the direction of synthesis and to obtain higher yields in the reactions.

In this work, we consider the ternary systems containing copper (II) chloride and bromide and a binary organic solvent by analogy with previously studied systems. Crystal solvates in these systems are presented in equilibrium with saturated solution and formed spontaneously. Their composition and structure directly depend on the properties of the solution. It was found that solvates containing more donor solvent molecules have a large crystallization region on the solubility isotherm in the ternary system. The evolution of the composition and structure of the equilibrium crystal solvates in the ternary system is also shown, depending on the composition of the mixed solvent. The reasons for the formation of solvates of a certain structure are analyzed from the point of view of the Lewis theory and the HSAB-theory.

References

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Owing to synergistic combination of hybrid organic-inorganic nature and chemically active porous structure, metal-organic frameworks emerged as a new class of functional materials - soft porous crystals. The current trend in chemical industry is utilizing such crystals as hosting flexible elements for diverse applications as gas and energy storage, filtration, catalysis and sensing. From the physical point of view, metal-organic frameworks are considered as molecular crystals with hierarchical structure providing the structure-related physical properties crucial for the future of energy transfer, data processing and storage, high-energy physics, and light manipulation [1].

I will represent the metal-organic frameworks as a new family of functional materials in modern physics: from porous metals and superconductors, topological insulators, classical and quantum memory elements, to optical superstructures, materials for particle physics and even molecular scale mechanical metamaterials. Based on complementary properties as crystallinity, softness, organic-inorganic nature and complex hierarchy I will describe how such artificial materials extend their impact on applied physics and become the mainstream in material science.

References

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SYNTHESIS OF ORGANIC-INORGANIC HYBRIDS BASED ON LAYERED PEROVSKITE-LIKE BISMUTH TITANATE

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Hybrid organic-inorganic compounds based on layered perovskite-like oxides is a new promising class of materials which properties could be tailored by targeted modification of both organic and inorganic parts. Preparation of such materials is recently focused on a stepwise approaches including subsequent hydrothermal and microwave-assisted hydrothermal intercalation and grafting reactions that lead to the formation of bulk hybrid compounds followed by their exfoliation into 2D organically modified nanosheets. [1] Such hybrid compounds and nanosheets are considered as perspective materials exhibiting photocatalytic, catalytic, ferroelectric, and luminescent properties.

In the present work we report the results on the synthesis and characterization of organic-inorganic hybrids based on layered perovskite-like bismuth titanate

\[
\text{H}_2\text{K}_{0.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13}\cdot\text{H}_2\text{O},
\]

\[
\text{H}_2\text{K}_{0.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13}\cdot\text{H}_2\text{O}
\]
could be prepared by simple ion exchange reaction from Ruddlesden-Popper phase \(\text{K}_{2.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13}\). Organic-inorganic hybrids have been prepared by intercalation and grafting reactions. Intercalation reactions imply acid-base interaction between solid acid and organic bases (usually n-amines). Then, the preliminarily intercalated by amines compounds are used as starting materials for grafting reactions, which imply the covalent bonding between the grafting agents (usually alcohols) and inorganic matrix. In this work, we have used n-amines intercalated derivatives for reactions with n-alcohols. In particular, methylamine-intercalated hybrid was used for reactions with methanol, n-propanol and n-butanol. In case of n-butylamine intercalated compound we have added the reaction with n-hexanol, and n-octylamine intercalated derivative was used for reaction with n-decanol. The characterization of the samples was carried out by XRD, TG, and C/H/N analyses, FTIR- spectroscopy and SEM.

References

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DIRECT WRITING OF THREE-DIMENSIONAL MICROSTRUCTURES USING FEMTOSECOND LASER PULSE-INDUCED REDUCTION

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Direct-writing technology has received attention for three-dimensional (3D) micro-additive manufacturing (µ-AM). AM techniques such as selective laser sintering (SLS) and selective laser melting (SLM) has been developed for metal bulk structures. However, just downscaling of those technique is difficult because the raw metal powders are easily oxidized by downsizing the metal powders. To overcome this problem, reductive sintering of metal oxide nanoparticles has been reported [1, 2]. We have also developed femtosecond laser reductive sintering of CuO nanoparticles to form metal Cu and semiconductor Cu$_2$O microstructures selectively by controlling the laser irradiation conditions. In addition, 3D microflow sensors have been fabricated using the combination of femtosecond laser reductive sintering and 3D µ-AM techniques.

First we demonstrated the fabrication of a Cu-based micropyramid with 10 layers. The lamination was carried out using a dispenser and laser irradiation repeatedly. Figure 2 shows the fabricated flow sensor which consists of a micro bridge heater. The sensor successfully detected the flow rate in a range of 0-450 cc/min [3]. We will introduce the details about 3D µ-AM and its applications.

References
The synthesis and study of catalysts is currently an important scientific task which determines progress both in industrial development and in the field of chemistry. Structural characterization is a very important step in understanding catalysts’ action because the structure is one of the parameters that affect properties of these materials. However, when studying catalysts, one often encounters nanosized, defective materials, X-ray amorphous and close to them. Applying the usual X-ray diffraction methods based on the analysis of position and intensities of diffraction peaks to such systems can be difficult. Therefore, using special methods which take into account the specific features of X-ray scattering from small objects is required. The structure of such materials can be successfully studied by an X-ray diffraction method of the radial distribution of atoms or the radial electronic density distribution, also known as the analysis of atomic pair distribution function (PDF-analysis). This method allows us to obtain information about the short-range atomic arrangement and phase composition of materials whose coherent-scattering regions do not exceed 3 nm and even X-ray amorphous substances. The method is not widely used but is extremely relevant in connection with the development of nanotechnology and the growing interest in the structure and properties of nanoscale substances. PDF analysis is the recognized tool for studying nanoscale materials with different chemical compositions, solid amorphous materials, liquids, glasses, supported catalysts, etc. This report presents the capabilities of the PDF method and the results of the study of relevant and interesting from a structural point of view nanoscale catalysts and catalyst supports.

References

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Confinement and on-demand release of guest molecules is essential for using artificial host molecules as a molecular container. However, the strategies for the precise control of these kinetic processes have rarely been reported. We recently reported on-demand acceleration of guest exchange of a cationic cobalt(III) dinuclear macrocyclic metallohost by the replacement of the counteranion caps\[1\]. We expected that intramolecular bridging of the two cobalt ions in the metallohost would retard the guest uptake/release behavior. Here we report dynamic structural conversion of a newly synthesized cobalt(III) metallohost that has four bifunctional ligands at the axial sites. In addition, we present the guest removal and guest exchange behavior of the two kinds of structural forms.

Figure 1. Guest removal and guest exchange behavior of the two kinds of structural forms.

References
ATOMIC LAYER DEPOSITION OF LITHIUM BASED TERNARY OXIDE NANOFILMS FOR HIGH PERFORMANCE LI-ION MICROBATTERIES

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In recent years atomic layer deposition (ALD) has proved to be a successful method of fabrication and modification of electrodes for lithium-ion batteries. Tin oxide demonstrate considerable excellence over currently used materials for Li-ion battery anodes, however, lithiated tin oxides are expected to show even better performance. On the other hand layered lithium transition metal oxides (LiNiO₂, LiCoO₂) arguably represent the most successful materials for cathodes. In this research nanofilms of lithium oxide, lithiated tin oxide, lithiated nickel oxide and lithiated cobalt oxide were deposited by atomic layer deposition (ALD) using lithium hexamethyldisilylazide (LiHMDS), tetraethyl tin (TET), bis(cyclopentadienyl) nickel(II), bis(cyclopentadienyl) cobalt(II) as the metal-containing reagents and oxygen plasma as counter reagent. The temperature of deposition varied from 150 to 350°C. The monocrystalline silicon (100) and stainless steel (316SS) were used as supports. The thickness of the films was measured with spectral ellipsometry and x-ray reflectometry. The composition was studied by X-ray photoelectron spectroscopy, X-ray diffraction and time-of-flight secondary ion mass spectrometry. Morphology of the films was studied by scanning electron microscopy. It was found that layered structures of NiO-LiOₓ can be easily prepared by ALD, but nanolaminates of Li-Ni-O contain nickel in quantity by one order less than calculated on the basis of the average growth rate per ALD cycle. Nanolaminates of Li-Sn-O contain tin significantly larger quantities, but also lacking in comparison with the calculated data. Deposited Li-Ni-O and Li-Sn-O nanofilms contain significant amount of silicon and carbon as impurities of LiHMDS ligands. But impurities were not observed in pristine lithium oxide and probably are stabilized by tin and nickel oxide. Electrochemical study was carried out for the films deposited on the stainless steel. During cycling tests it was shown that lithiated tin oxide has a stable discharge capacity during 100 charge/discharge cycles, with efficiency above 99%.

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FABRICATION OF SnO$_2$ NANOPARTICLES WITH DIFFERENT MORPHOLOGICAL PARAMETERS AND THEIR IMPACT ON ORGANIC DYES DEGRADATION PROCESS

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Organic dyes from the textile, paper, cosmetic and pharmaceutical industries cause water and soil pollution worldwide. It is dangerous to the environment, the hydrosphere, people and living organisms. The most environmental friendly approach to contaminants elimination is photodegradation of using semiconductor nanoparticles (NPs) with high specific surface area. One of the promising materials is a wide band gap semiconductor SnO$_2$ (3.6 eV). There are a lot of works about application of SnO$_2$ NPs as a photocatalyst for different organic dyes photodegradation. However, to the best of our knowledge, the impact of photocatalyst shape and solution temperature on the organic dye photodegradation process is still under discussion.

Spherical NPs (SSA = 260 m$^2$/g, d = 3 nm) were obtained by chemical precipitation method. Nanorods (SSA = 38 m$^2$/g, l = 56 nm, d = 17 nm) were obtained using hydrothermal treatment (T = 260 $^\circ$C, t = 5 hours) of as-prepared samples. All samples were characterized by XRD, TEM, FTIR-spectroscopy, and SSA estimation. The efficiency of the organic dyes (methylene blue, rhodamine 6G and Congo red as typical models of pollutant) photodegradation was studied using UV-Vis spectroscopy and electrospray ionization mass spectrometry (ESI).

It has been established that for all dyes the use of spherical nanoparticles and 60 $^\circ$C are optimal in terms of the duration of the process. The impact of pH value of solution, NPs morphology and dye concentration on degradation was studied. The shortest degradation time was observed for pH=9 for all organic dyes: methylene blue – 15 minutes, rhodamine 6G – 23 minutes and Congo red – 20 minutes. Also the necessity of additional sample preparation for the Congo red dye is shown. In accordance to ESI, in optimal conditions the photodegradation processes result in the dyes full decomposition.

Acknowledgements. Scientific research were performed at the research park of St. Petersburg State University educational resource center of chemistry: Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre.
The significant interest of perovskite-type oxides over the past few decades and even until now have stemmed from their piezoelectric, catalytic and/or ionic and/or mixed ionic-electronic transport properties [1]. Because of unique structure of perovskites to tolerate of various sizes of cations at both A and B cation sublattices it is possible to search for a new electrolyte with higher conductivity and chemical stability [2, 3].

This work is devoted to the complex investigation of physicochemical properties of new compounds obtained by substitution a half of position B-cations in known perovskites LaMe$^{+3}$O$_3$ [4, 5] with zinc. Zinc oxide has been used for several reasons: the creation of oxygen deficiency; lower melting point and, accordingly, to improve the quality of ceramics; as non alkaline earth metal, that allows to increase the chemical stability.

In this work were obtained a new phases La$_4$Zn$_2$Me$_2$O$_{11}$ (Me=Al, In). The samples La$_4$Zn$_2$Me$_2$O$_{11}$ were synthesized using the solid-state reaction method. Synthesis was carried out with stepwise temperature increase to 100° increments in the range of 700–1400°C. Structure of these phases was investigated. Electrical properties of samples were studied by varying thermodynamic parameters (T, pH$_2$O, pO$_2$). The chemical stability of the samples with respect to carbon dioxide and water vapor was investigated.
Investigation of the systems with immobilized bifunctional organic molecules on inorganic core based on noble metal nanoparticles (NPs) cause a great interest due to their unique property known as localized surface plasmon resonance. Due to a high electromagnetic field concentrated in the interparticle gaps, such materials are characterized by enhanced optical performances [1-2]. In this work, we investigated the optical properties of gold and silver NPs modified by 4,4’-dimercaptostilbene (DMS) and 4,4’-disulfonylstilbene (DSS). The study of modified nanoparticles with adsorbed stilbene derivatives was carried out by the fluorescent and Raman spectroscopies together with UV-vis spectrophotometry. The different responses were revealed for NPs linked by DMS and single NPs covered by DSS. Fluorescent quenching corresponding to linear dependence on NPs concentration correlated with the Stern-Volmer equation was obtained for DSS only. Obtained Raman spectra revealed a rearrangement of adsorbed molecules when a surface coverage reaches a monolayer. Raman spectra deconvolution with Lorenz function allowed us to calculate the analytical enhancement factors for DMS.

Figure 1. Fluorescent spectra of DSS at various Au NPs concentrations.

References

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In order to elucidate the possibility to construct photoactive supramolecular systems based on symmetrical dienones 1a-c substituted with two azacrown ether moieties were synthesized. The behavior of dienones in acetonitrile in the presence of alkanediammonium ions \( \text{NH}_3\text{(CH}_2\text{)}_n\text{NH}_3^+ \) \((n = 1-12)\) was studied by UV/vis absorption spectroscopy, fluorescence and NMR \(^1\text{H}\) spectroscopy.

**Scheme 1.** Structure formulas of dienones 1a-c and salts 2

Spectra of the dienones undergo significant changes in the presence of alkanediammonium ions. The stoichiometry and stability constants of the formed complexes were determined. The dienones form 1:2 complexes with short alkanediammonium ions \((n = 1-7)\) and high stable 1:1 complexes with long ions in diluted solutions.

The results of this study can be used for directional design of photoactive supramolecular assemblies and optical molecular sensors.

Acknowledgements. This work was supported by the Russian Science Foundation (project № 19-13-00020).
We present the new approach for plasmon assisted grafting of anisotropic AuNRs with spatial selectivity, which was used for creation of NPs with amphiphilic surface. The plasmon assisted activation of IS was performed under the illumination of AuNRs with wavelength corresponded to the longitudinal plasmon resonance of AuNRs and resulted in grafting of organic moieties (Ar-(CF3)2) to AuNRs edges. The AuNRs lateral sides remains unscreened and were further grafted with diazonium salt, ADT-COOH. As result of varying substituents in the chemical structures of iodonium and diazonium salts the amphiphilic NPs with spatially divided hydrophobic (grafted to AuNRs edges) and hydrophilic (grafted to AuNRs lateral sides) chemical groups were obtained (fig. 1). Proposed approach was realized in solution and does not require the surface assistance in the spatially selective modification of AuNRs. Thus, our experimental route is potentially highly scalable and provide the possibility for powered throughput creation of amphiphilic anisotropic NPs, with chemical moieties precisely located at desired place on NPs surface.
MoO$_3$(WO$_3$)/ZrO$_2$ systems how catalysts for butene coupling reaction (isobutane alkylation and butene oligomerization for production high octane-number components to fuel) are promising [1, 2]. For a deeper understanding of their properties, it was necessary to study their catalytic and physicochemical properties in a single study.

In this work MoO$_3$(WO$_3$)/ZrO$_2$ systems are investigated which were from ZrO$_2$·nH$_2$O and different MoO$_3$(WO$_3$)-precursors. Details of the syntheses and investigation methods are given in [2].

It was revealed the genesis of MoO$_3$/ZrO$_2$ and WO$_3$/ZrO$_2$ systems is in many ways similar to each other. This is manifested mainly in slowing the crystallization of amorphous ZrO$_2$, and further affects the change in the phase state of ZrO$_2$. The introduction of MoO$_3$(WO$_3$) by impregnation method from heteropolyacids strongly stretches the crystallization process by temperature. At the same time, the presence of amorphous ZrO$_2$ makes a significant contribution to the porous structure (an increase of surface area). The composition and temperature of treatment affect the properties of the resulting catalysts most significantly. Thus, an increase in the content of MoO$_3$ also contributes to a serious reorganization of the acid cover of the surface: the exponential growth the number of Brønsted acid sites and a non-monotonic change in the content of Lewis acid sites (LAS) with a sharp fall at 9% MoO$_3$. The method of synthesis by impregnation makes it possible to obtain catalysts with the most developed porous structure and increased high LAS compared to the dry mixing method. The differences in catalytic properties are largely due to differences in the acidity of the surface. The high content of MoO$_3$ and a large supply of butenes contributes to the course of the oligomerization reaction. Reducing the supply of butenes and the introduction of MoO$_3$(WO$_3$) by impregnation contribute to the flow of alkylation of isobutane. Controlling the properties of MoO$_3$(WO$_3$)/ZrO$_2$ systems by varying the conditions of their preparation allows to regulate their physicochemical and catalytical properties.

References
CATALYTIC CRACKING OF HYDROCARBON FEED WITH BIO OXYGENATES ADDITIVE IN THE PRESENCE OF Y AND ZSM-5 ZEOLITES

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Nowadays processing of renewable biomass as an alternative to conventional oil feed draws much attention. The main drawback of such feed is high content of oxygenates which are difficult to refine by existing paths. A perspective approach could be their catalytic cracking as an additive to hydrocarbon conventional feed yielding additional quantities of C2-C4 olefins.

The goal of this work is to research trends of hydrocarbon and model oxygen containing compound (acetone, glycerin) additives catalytic cracking in the presence of Y and ZSM-5 zeolite catalysts. In order to plan such experiments a central composite rotatable plan was designed. ZSM-5 content in the catalyst varied from 0 to 20 % (here and after %mass.) and composition of bio oxygenate additive to feed were chosen as independent variables. Oxygen containing feed additive consisted of acetone and glycerin binary mixtures, total content of oxygenates in the feed was fixed at 5 % in all experiments.

It was shown that in the presence of Y zeolite the highest yield of C2-4 olefins (24,1 %) is achieved for acetone-rich additives to feed. Introduction of ZSM-5 as catalytic additive enables to achieve much higher yields of light olefins (28,5 %) for glycerin-rich feed additives. A synergistic effect was observed during catalytic cracking of hydrocarbon feed with oxygen containing additive of intermediate composition. This effect appears as a minimum in propylene and C4 olefins yield depending on feed additive composition and a maximum of gasoline yield under same conditions. This is due to condensation reactions of oxygenates and/or their intermediates yielding heavier products of gasoline boiling range. Moreover a suppression of hydrogen transfer reactions catalyzed by Y and ZSM-5 combination was shown in the presence of oxygen containing compounds.

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Available thermodynamic data on composition of equilibrium vapor over metal iodides remains scanty despite numerous investigations of thermochemistry of metal halides. The vapor over binary systems of two different metal iodides is expected to include heterocomplexes and various dimer homocomplexes in addition to the monomers. The vaporization of KI/FeI\(_2\) and KI/AgI samples was investigated in the temperature ranges between 800 to 825 K and 721 to 964 K by using the mass spectrometric Knudsen effusion method. The ions M\(^+\), MI\(^+\), MI\(_2\)\(^+\), KMI\(^+\), KMI\(_2\)\(^+\) (M=Fe, Ag), FeI\(_3\)\(^+\), K\(^+\), K\(_2\)I\(^+\), KFeI\(_3\)\(^+\), KAgI\(_2\)\(^+\) have been registered. The silver iodide was synthesized in situ as the result of interaction of silver which was using as pressure standard with iron iodide. Neutral molecules corresponding to the aforementioned ions have been found. From their partial pressures, the equilibrium constants of gaseous phase reactions were determined:

\[
\begin{align*}
{\text{KI (gas)}} + {\text{FeI}}_2 \text{ (gas)} &= {\text{KFeI}}_3 \text{ (gas)} \\
{1/2}{\text{K}}_2{\text{I}}_2 \text{ (gas)} + {\text{FeI}}_2 \text{ (gas)} &= {\text{KFeI}}_3 \text{ (gas)} \\
{\text{KI (gas)}} + {\text{AgI}} \text{ (gas)} &= {\text{KAgI}}_2 \text{ (gas)}
\end{align*}
\]

From equilibrium constants the standard enthalpies of formation KFeI\(_3\) and KAgI\(_2\) were determined (KFeI\(_3\),gas,298) = -213.9±1.2 kJ/mol and ΔfH° (KAgI\(_2\),gas,298) = -166.3±7.1 kJ/mol.

The structures of KFeI\(_3\) and KAgI\(_2\) is presented on Figure 1. The barrier height between C\(_{3v}\) and C\(_{2v}\) structure for KFeI\(_3\) is about 3 kJ/mol.
Lewis acids are widely used in organic catalysis to activate electron-excess molecules. Species with bulky substituents are of particular interest, since they can form frustrated Lewis pairs in combination with Lewis bases [1]. Also, when choosing a catalyst, it is important to estimate the strength of the Lewis acid and compare it with other compounds in order to choose the most suitable variant.

Tensimetric method allows to investigate the equilibrium between the gas and condensed phase in closed systems, thus it is possible to determine the composition of both the gas and condensed phases [2].

In this work we examined systems consisting of ionic oxophosphonium Lewis acid \([(C_3H_2(NDipp)_2N)_2PO]^{+}[B(Ar(CF_3)_2)_4]^{-}\) (LA, Dipp = 2,6-diisopropylphenyl) [3] and pyridine (Py) or acetonitrile (An). A series of tensimetric experiments were performed for this systems. From the data obtained, the gas- and condensed-phase compositions were calculated at different temperatures. It is shown that the acid forms 1:1 complex with pyridine and a solvate with acetonitrile.

A complex with pyridine is resistant towards dissociation up to 515 K, after which the irreversible autocatalitic pyrolysis began. The dissociation of solvate with acetonitrile begins at about 320 K and it is accompanied by a very small thermal effect, less than 10 kJ.

References:

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OPTICAL PROPERTIES OF SURFACE MOLECULAR-IMPRINTED TITANIUM DIOXIDE NANOPARTICLES


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Perylenediimide (PDI) dyes - acceptors of well-known organic semiconductor systems [1]. They are often used in organic photovoltaic cells in which low values of the band gap are achieved, but PDI have a tendency to self-aggregate.

The method of surface molecular imprinting [2] to create films on the surface of TiO$_2$ nanoparticles with 1-H-pyrrol-N, N′-bis (3-pentyl) perylene-3,4,9,10-bis (dicarboximide)-5-hexyl-11-1H-1,2,3-triazol-1-yl-pentanoic acid (PDI-Taz-C$_5$OOH) imprints with acceptor properties (Fig. 1) was used. The band gap of the obtained material has reduced by 0.1–0.5 eV (Table 1), and the sorption capacity after template removal with ethanol has reached 0.75 $\mu$mol/g. At the same time, molecular imprinted (MIP) material can re-bind 2 times more PDI-Taz-C$_5$OOH than unimprinted (NIP).

Table 1. Band gap ($E_g$) of NIP and MIP samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor : template</th>
<th>$E_g \pm \delta$ (P=0.95, n=3), eV</th>
<th>$\Delta \lambda$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>–</td>
<td>3.09 ± 0.01</td>
<td>–</td>
</tr>
<tr>
<td>MIP</td>
<td>1:81</td>
<td>2.62 ± 0.10</td>
<td>72</td>
</tr>
<tr>
<td>NIP</td>
<td>1:81</td>
<td>2.98 ± 0.05</td>
<td>16</td>
</tr>
</tbody>
</table>

References

Acknowledgements. This work was supported by the Foundation for Assistance to Small Innovative Enterprises (Russian Federation) (project No 52562).
The improvement of existing and development of new technologies is impossible without creating new functional and structural materials. The potential application of these materials is diverse and constantly expanding. One of the most promising nanomaterials is single-walled carbon nanotubes. Research result indicated that the addition of nanotubes to the electrolyte as a dispersed phase has a positive effect on the properties and structure of the electrochemical coating. The deposition rate increases by 2 times, the adhesion of the coating to the base is improved, coating porosity decreases [1].

Figure 1. Electrochemical copper coating with nanotubes. Image was obtained with an atomic force microscope.

Electrochemical coatings withstood climatic-mechanical tests according to GOST RV 20.39.414.1-97 and GOST 23752-79.

Reference

Acknowledgements. This work was supported by the financial support of the Innovation Support Fund. Contract №11695GU/2017.
The development of new visible-light photocatalysts is a highly attractive area in nanotechnology. Their unique photocatalytic activity under solar irradiation make them potentially of great use for efficient environmental treatment. Tin dioxide (SnO$_2$) with a band gap of 3.6 eV and rutile crystal structure is an excellent and widely investigated semiconductor material that has been used in photocatalytic researches for their high photosensitivity and chemical stability. In view of a large number of studies, doping SnO$_2$ by 3d element is considered to be an easy way to decrease a band gap value, and consequently to increase the charge separation and spread the energy range of photoexcitation. Since the mechanism and impact of doping process on electronic structure and photodegradation effect is still under discussion, the objective of this research was to study the correlation between the structure of as-prepared nanoparticles (NPs) and their photocatalytic activity.

To clarify this aspect, we used 11-33 mol% Cu, Co, Cr as dopants for SnO$_2$ nanoparticles; the influence of pH values was also studied. Bare and doped SnO$_2$ NPs were obtained by the (co)precipitation method. As expected XRD data demonstrated only rutile SnO$_2$ peaks (ISDD 00-041-1445), the crystallite sizes increased for the higher pH values. According to TEM and SSA data, the nanoparticle size does not exceed 10 nm. The changes in lattice parameters indicate the success of the doping process.

Positions of dopant atoms in crystal cell, which determines the energy spectrum, as well as densities of states were calculated using abinitio calculations in ABINIT software package. UV-Vis absorption spectra show the difference between bare and doped SnO$_2$ nanoparticles. The obtained results were in good accordance with the photodegradation tests of Methylene blue (MB) under UV and Vis irradiation. After 15 min of Vis irradiation, the degradation rate of MB reached 38 % and 85 % for SnO$_2$ and Cu-doped SnO$_2$, respectively. It is shown that the nanoparticles under study a promising visible-light photocatalyst for efficient environmental photocatalysis.

Acknowledgments. Scientific research was performed at the Research Park of St. Petersburg State University Educational Resource Center of Chemistry: Center for Optical and Laser Materials Research, Chemical Analysis and Materials Research Centre.
CRYSTAL STRUCTURE, THERMAL STABILITY AND CONDUCTIVITY OF (2E)-6-CHLORO-2-(6-CHLORO-4-METHYL-3-OXO-1-BENZOTHIOPHEN-2-YLIDENE)-4-METHYL-1-BENZOTHIOPHEN-3-ONE

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The crystal structures of Vat Red 1 (VD) crystal structures (monoclinic) derive from stacking of flat molecules arranged due to π-π interaction.¹ From the studies, the melting point of the Vat Red 1 is 409 °C and the optical band gap for VD is $E_{bg} = 2.30$ eV, and it has been calculated using powder diffuse reflectance UV–Vis spectra and the absorption edge of VD is at 539 nm. VD exhibited the highest occupied molecular orbital energies ($E_{HOMO}$), the lowest unoccupied molecular orbital energies ($E_{LUMO}$) values of -0.21959 eV and -0.13635 eV. The pristine thioindigo exhibits the $E_{HOMO}$ and $E_{LUMO}$ values of -3.05 eV and -5.86 eV.²

Fig. 1 Chemical structure of VD

Reference:
Studies in the synthesis of yttrium oxyhydroxides are relevant due to the high prospects for using these compounds as catalysts for removing organic contaminants from water, as well as the basis for nanoceramics and phosphors. The structure and particle size of materials have a significant impact on their properties and reactivity as catalysts. In this connection an important factor in synthesis of these compounds is the ability to control the structure, which allows controlling the reaction process and product quality.

In the present study the samples were obtained by the sol-gel method with hydrothermal treatment. The sol-gel synthesis was carried out at final pH values (8, 9, 10) with the introduction of malic acid and citric acid of various concentrations (0.1 M and 0.5 M). The primary hydrothermal treatment lasted for 24 hours. After the primary hydrothermal treatment the solution was adjusted to pH = 12 and subjected to repeated hydrothermal treatment within 24 hours. A study was carried out as to the effect of malic acid concentration on the structure of the samples obtained. On addition of malic acid with 0.1 M concentration, particles looking like hollow tubes 5–10 µm long and about 1–2 µm wide are formed. The wall thickness is about 100 nm. When 0.5 M acid is used, particles of a clear hexagonal shape are formed, which are not hollow. The particle length is 8–10 µm, the width is 3–4 µm, with the formation of particles of similar size.

Micrographs of a samples obtained with the addition of citric acid show hollow spheres, the surface of which is covered with pores. The pore diameter varies between 0.5–2 µm, the diameter of the spheres — 5–10 µm, the wall thickness is about 0.5–1 µm.

The analysis of the obtained diffractograms have shown that crystalline structures are formed only under the condition of repeated hydrothermal treatment with adjustment to high pH values. Analysis of the IR spectra suggests that malic acid is not included in the structure of the obtained samples, due to the absence of characteristic oscillations in the range of 1500–1750 cm$^{-1}$. For the samples obtained with the introduction of malic acid, formation of compounds with non-associated OH groups has been observed.

Acknowledgements. South Ural State University is grateful for financial support of the Ministry of Science and Higher Education of the Russian Federation (grant No 4.9722.2017/8.9).
GAS-SENSOR PROPERTIES OF 3D-MATERIALS ON THE BASIS OF CARBON NANOTUBES AND POLYAROMATIC MOLECULES

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The formation of three-dimensional (3D) carbon structures remains one of the most important challenges in nanotechnology. We suggest that the covalent cross-linking of carbon nanotubes (CNT) by polyaromatic linker molecules will enhance CNT properties, e.g. solubility, conductivity, specific surface area, porosity, sensor response, etc. Molecules of pyrene, phenylcoumarin and phthalocyanine were chosen as three types of linkers due to their polyaromatic nature, different size of their core and good solubility in organic solvents.

3D-hybrid materials were obtained by azide-alkyne cycloaddition reaction via interaction of dialkyne-substituted polyaromatic derivatives with the surface of CNT modified by azide groups, according to the reaction:

\begin{equation}
\text{N=N'N'} + \text{N=N'N'} + \text{N=N'N'} \rightarrow \text{CuSO}_4, \text{L-ascorbate, microwave 400 W}
\end{equation}

Figure 1. Scheme of 3D-materials synthesis via the reaction of azide-alkyne cycloaddition.

To compare the efficiency of functionalization method and properties of the obtained materials, hybrids with the same polyaromatic molecules were also obtained by non-covalent functionalization.

The structure of the obtained products was studied by TEM, SEM and Raman spectroscopy. Sensor responses of all hybrid materials toward NH$_3$, H$_2$S, H$_2$ and CO$_2$ were studied at different humidity. The responses of 3D-materials to ammonia were 10 times higher than those of pristine CNT and twice higher than in the case of hybrids non-covalently obtained. The possibility of selective detection of NH$_3$ in the presence of 50,000 ppm of CO$_2$ was demonstrated.

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-33-00029).
Recombinant proteins in modern biotechnology and biopharmaceutics are of great interest in this industry. Today, protein production in recombinant expression systems has several advantages, in comparison with the available alternatives, such as the treatment of animal blood serum. It is important that the Pichia Pastoris expression system is less expensive than the expression in mammalian cells. The use of Pichia Pastoris ensures the correct folding of recombinant proteins, which is very important for the analysis of the final activity of the product. Trasfferrin (TFNG) is responsible for the receptor-mediated transport of iron ions into the cell. This protein is a promising object in medical therapies of various diseases, including cancer, conjugating TFNG with therapeutic agents and using as a targeted transport inside the pathogen. Also, TFNG is an important component of serum-free media for eukaryotic expression systems. To date, the majority of serum-free media will include albumin and transferrin, obtained from the blood of animals and humans. The use of these supplementary proteins significantly increases the risks of contamination with various infectious agents, including non-enveloped viruses such as hepatitis A virus and parvovirus B19 or agents causing Creutzfeldt-Jakob disease, because during their production, the detection or inactivation of such agents is not currently are effective. The replacement of TFNG in the serum-free nutrient media used to produce modern therapeutic drugs, their recombinant analogues will eliminate the risk of contamination with biologically active impurities. In our work, we were able to obtain a strain expressing 100 mg/L unrefined protein of culture fluid.

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THE HYBRID CARBON-METAL NANOFLAKES: SYNTHESIS, CHARACTERIZATION AND RESEARCH NANOSTRUCTURE MORPHOLOGY

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The research is directed to synthesizing novel hybrid Au-Ag@C nanostructure (called nanoflakes) with unique morphology, well-controlled geometric sizes, and multifunctional properties. The flakes are deposited on the substrate-solution interface illuminated with a CW laser beam (λ = 325 nm, I = 0.5 W/cm²). The large interest of in-depth and detailed investigation of nanoflakes synthesis is determined by their following characteristics: (i) a linear birefringence caused by features of crystalline structure of carbonaceous matrix; (ii) plasmonic bimetallic clusters embedded to carbon phase and stimulating surface-enhanced Raman scattering (SERS), that can serve as efficient development for photonics, optics, and sensing technologies [1, 2]. The nanoflakes were obtained from solution of supramolecular complex (SMC) [(Au₁₃Ag₁₂(C₂Ph)₂₀)(PPh₂(C₆H₄)₃PPh₂)₃](PF₆) in aniline and acetophenone onto the different type of substrate (cover glass, quartz, polypropylene, and polyethylene terephthalate). The flakes formation is the result of laser-induced decomposition of SMC. It was demonstrated that size and shape of nanoflakes depend on parameters of laser deposition and interaction between SMC and solvent with substrate surface. The deposited structures were characterized using a scanning electron microscope (SEM) and research optical system microscope with studying of nanoflakes in the polarization light (Figure 1).

Figure 1. The SEM and optical microscope images of obtained nanoflakes

References
NEW STATIONARY PHASE BASED ON A COPOLYMER OF STYRENE AND DIVINYLBENZENE MODIFIED WITH GOLD NANOPARTICLES FOR SEPARATION PROFENS AND β-BLOCKERS

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Nanomaterials have received much attention due to their novel chemical, physical and electrical properties. Within separation science, gold nanoparticles have found a promising home, because of their long-term stability, high surface area-to-volume ratio, and ease of chemical modification. A new sorbent for HPLC based on a styrene-divinylbenzene copolymer (CSD) was synthesized by adsorption of gold nanoparticles on its surface, followed by modification through the formation of self-assembled monolayers by the reaction between gold and sulfur-containing reagent – lipoic acid with grafted lysine. Low-temperature nitrogen adsorption, diffuse reflection spectroscopy, scanning electron microscopy were used to examine physical and chemical properties of obtained sorbent. The chromatographic behavior of profens and β-blockers was studied on the sorbents depending on the composition of the mobile phase: the nature of the buffer solution, its concentration and pH, the proportion and nature of organic solvent. It was established that significant retention factors for both groups of substances are observed using the mixture of acetonitrile and buffer solution as the eluent. Herewith profens are kept longer with a lower content of organic solvent, and β-blockers, on the contrary. Hydrophobic interactions play a significant role in the retention of the studied compounds. The order of elution of profens correlates with their hydrophobicity indices logP, logD. This dependence is traced to a lesser extent for β-blockers, due to the additional interactions. The separation of the six-component mixture of β-blockers in 15 minutes and of the three-component mixture of profens in 20 minutes was carried out on the new sorbent.

Figure 1. CSD-Au-lipoic acid-lysine

Acknowledgements. This work was supported by Russian Foundation for Fundamental Research (№18-03-00742).
First isolated in 2004, graphene has sparked a great scientific interest thanks to its peculiar mechanical and electronic properties, which promise to upgrade many technologies, from microelectronics to biosensing and nano-medicine.[1] Among the many molecules that have been proposed as exfoliating agents of graphite, only a few ones successfully exfoliate and stabilize graphene in aqueous media.[2] Mechanochemistry has gained increasing importance in diverse fields of chemistry,[3] principally in the exfoliation and functionalization of nanomaterials like graphene, it has also many advantages such as shorter reaction times, higher product yields and the elimination of (harmful) organic solvents.

Here we report the development of an environmentally friendly, cheap and simple approach for the synthesis of aqueous soluble few-layer graphene, useful for biological purposes. From theoretical insight, state-of-the-art density functional theory (DFT) calculations within a super-cell slab periodic approach, and comparison with experimental result, we propose that different carbohydrates behave as melamine in a micro-solvation model where the interplay between non-covalent interactions, provides the necessary thermodynamic driving force to stabilize the graphene-water dispersions.[2] The prepared graphene have been characterized by TEM, X-ray diffraction, TGA, Raman spectroscopy. This study aims to use carbohydrates as exfoliating agents and open up new possibilities for preparing graphene materials, in large-scale, for biological applications.

References

Acknowledgements. Financial support from the EU Graphene-based disruptive technologies, Flagship project (no. 696656) and the Spanish Ministerio de Economía y Competitividad (project CTQ2014- 53600-R)
These days biocompatible pigments are actively introduced into cosmetic industry to replace apparently toxic materials such as organic dyes and inorganic compounds. In addition, the multifunctional cosmetics with a skin care effects becomes more and more popular. The pigments must be thermally stable, as the technology of cosmetic production includes high temperature treatment. The range of appropriate materials is extremely low. In our opinion, hydroxyapatite (HAp), which is the main component of bone tissue, and widely used in cosmetic industry for induction of collagen production, appears to be a promising one. It is known that doping with 3d-elements possibly leads to the color change of initially white hosts, however, the amount of articles about doped-HAp remains low. Accordingly, the present work was dedicated to the synthesis of doped HAp nanoparticles and its thermal properties.

Nano-HAP samples doped with Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cr$^{3+}$ ions (concentration ratio 10:100) were synthesized hydrothermally at 180 °C for 2 hours in the presence of two different types of hydroxide source (NaOH and NH$_4$OH). Morphological characteristics were studied with XRD, TEM methods, SSA estimation, and FT-IR spectroscopy. TGA and DSC data were collected in temperature range from 20 to 1200 °C in air.

As a result, the HAp nanoparticles were doped with Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cr$^{3+}$ ions. According to XRD, the lattice parameters of each sample have changed, which confirms successful doping. All the samples obtained with NaOH (except Cr-HAp) are tricalciumphospate (TCP), while the others are HAp. The color of the as-prepared particles indicated as a typical for salts of injected ions. The study of thermal properties showed that all samples (except for Cu-HAp prepared using NaOH) remain stable to heating up to 900 °C. In addition, several samples demonstrated the changes from the starting crystal phase to TCP under high temperature.

Acknowledgements. Scientific research were performed at the research park of St. Petersburg State University educational resource center of chemistry: Centre for X-ray Diffraction Studies, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.
ROLE OF WATER IN THE FORMATION OF ORGANOGELS WITH CYCLO(LEUCYL-LEUCYL) DIPEPTIDE

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Supramolecular gels, formed through intermolecular interactions, are a class of soft materials with promising applications in the field of materials science. Cyclic dipeptides (CDP) or 2,5-diketopiperazines (2,5-DKP) are capable of gels formation at concentrations below 1% w/v due to their structure of a molecule with two chiral centers which provides many opportunities for structural optimization through intermolecular interactions.

At the same time, the fundamental problem associated with determining the conditions for the formation of gels still remains unsolved. There are no approaches to predicting the type of solvent that can be gelled. The study of the role of solvents and their effect on the stabilization of a developing metastable material is an important topic for the development of supramolecular gels.

The present study was aimed at studying the ability of cyclic dipeptides to form gels on the example of cyclo(leucyl-leucyl) dipeptide. Solvents, including binary, were screened for their ability to induce gelation of cyclo(leucyl-leucyl). The conditions for obtaining stable organogels of cyclo(leucyl-leucyl) with a wide range of solvents were determined. The special role of water as an agent that forms intermolecular interactions for the preparation of stable gels has been established. The possibility of practical application of cyclo(leucyl-leucyl) for water purification was showed.

The results obtained in the course of research clarify the mechanism of the formation of organogels with cyclic dipeptides and can be used for preparation of new gels for solving problems of medicine, biotechnology and ecology.

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STUDYING THE ROLE OF MOLECULAR VIBRATIONS EXCITED BY UV PHOTODISSOCIATION OF OZONE MOLECULE ON POLARIZATION OF ANGULAR MOMENTA OF PRODUCING PHOTOFRAGMENTS

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Studying of a dissociation process deliver deep insight into many fundamental physical processes. Important information about dissociation dynamics, form of the potential curves, symmetry of excited states and the role of nonadiabatic interactions can be obtained from analysis of photodissociation’s cross section [1].

In this work was achieved cross section of photodissociation of molecule of prolate top type and was investigated effects of rotation and vibration of excited states. Computation was carried out using the known method of expansion over spherical irreducible tensors [2]. Angular momenta of photofragments can be oriented or aligned and it corresponds to first and second components of tensor’s rank. Usually wave function built up of spherical harmonics but in this work expansion over Wigner D-functions was proceed. Complex motion of the molecule of prolate top type was taken into account. Analysis of obtained results leads to the deep understanding of photodissociation process in the ozone molecule. Автор благодарит О.С. Васютинского за консультации и помощь при выполнении работы.

References

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LASER INDUCED MICRO-MODIFICATIONS OF OPTICAL PROPERTIES IN OXIDE GLASSES

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Femtosecond (fs) laser induced modification of oxide glasses opens new routes for precise space-selective tuning of material properties and development of functional photonic devices including integrated waveguides, optical switches, phase plates, volume optical memory, etc. In this regard, glasses doped with photosensitive agents such as noble metals and semiconductors are of particular interest due to unique optical properties of nanoclusters, nanoparticles or quantum dots that can be precisely precipitated in the confined volume of glass. Hence fs modification could become a convenient alternative to conventional nanotechnology methods for the one-step development of 3D nanostructured materials with a wide set of functionalities in sensing, photonics and data storage devices and it is crucial to understand processes which take place during the fs modification including local chemical composition change, influence of glass matrix and laser parameters. We performed fs modifications of zinc phosphate and silicate glasses doped with Ag and CdS using high power near IR femtosecond laser system PHAROS SP coupled with Aerotech 3D translation stage. We showed the possibility of simultaneous formation of luminescent silver clusters and plasmonic silver nanoparticles in phosphate glasses as well as of luminescent CdS quantum dots in silicate glasses spatially confined in micron-sized pipe-shaped domains inside glass. Also we showed that laser treatment induces micro-modification of optical properties manifested in the appearance of luminescence and absorption in the visible spectral range and homogeneous birefringence in the laser-exposed domains. Using energy dispersive X-ray spectroscopy, we showed Ag ions migration process from center to the boundary of domains as well as migration of Zn to the center. Ability to form complex 3D shapes of luminescent, plasmonic and birefringent structures embedded in dielectric transparent glass materials will pave the way for the design of nanophotonic devices and multilevel optical memory.

References

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RHEOLOGICAL ADDITIVE FOR FIRE EXTINGUISHING POWDER

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Rheological additives are a necessary component in the manufacture of fire extinguishing powders (FEP), they increase flowability, prevent caking of components during storage and give the powder hydrophobic properties. The hydrophobic silica additive currently used in FEP has several disadvantages - nano-sized particles are stable agglomerates with irregular shape \( (d_{\text{mid}} \approx 50 \text{ nm}) \) \((S1)\), which doesn’t provide uniform distribution of the additive over the surface of the fire extinguishing components and prevents free flow of the powder composition.

To increase the mobility of powder compositions, it has been proposed to use hydrophobic silicon dioxide in the form of spherical monodisperse particles of size 118 nm, were obtained by heterogeneous synthesis according to the method of Stober \((S2)\).

Silicon dioxide Aerosil 380 with an average size of agglomerates of 90 nm \((S3)\) was used together with \(S2\), individual use of which in FEP is limited due to low tamped density \(\approx 50 \text{ g/l}\). For the study, rheological additives with different ratios of hydrophobic components \(S2 / S3\) were added into a model FEP composition based on two-fractional ammonium phosphate salt with particle sizes of 200-315 \(\mu\)m \((I)\) и 0-50 \(\mu\)m \((II)\), where the average particle size is 280 \(\mu\)m and 35 \(\mu\)m, respectively. The ratio of the fractions were \(I / II = 60/40\), the ratio of ammonium phosphate and the rheological additive was 95/5.

Research of the rheological and shear properties of the powder compositions were carried out using a Freeman Technology FT4 Powder Rheometer.

The use of non-agglomerated spherical silica particles \(S2\) as rheological additive made possible to obtain more free-flow fire extinguishing powder compositions based on ammonium phosphate than using the \(S1\) additive, keeping a high proportion of fire extinguishing component (about 95%). It has been established that the combined use of \(S2\) and \(S3\) silica in additive reduces the value of the flow energy of the powder composition. When the ratio of the components of the rheological additive is \(S2 / S3: 80/20\), FEP has the lowest value of the flow energy, while the cohesion and flow function correspond to the composition with easy flowing properties.
Cubic tungsten carbide (WC$_{1-x}$) is a unique modification of tungsten carbide, which can be synthesized, according to the well-known phase diagram [1], only in an extremely narrow temperature range from ~2,700 to ~3,000 K. In addition, at slow cooling, it is extremely unstable and turns into the most common hexagonal tungsten carbides W$_2$C and WC [2]. Nonetheless, there are some reports, where its existence is shown at room temperature in the case of high-energy synthesis and superfast cooling rate of at least 10$^8$ K/s [3]. Such conditions can be achieved by implementing a direct plasma dynamic synthesis in a system based on a coaxial magnetoplasma accelerator with graphite electrodes. When tungsten is laid in the plasma formation zone, the following initiation of the arc discharge in the interelectrode gap leads to the sublimation of the precursor and its acceleration in the graphite accelerating channel. Carbon enters the plasma structure due to the electroerosion. Thus, when the plasma containing tungsten and carbon is sprayed in an inert medium, an ultrafast crystallization and formation of tungsten carbide nanoparticles occurs. In this work, by means of X-ray diffractometry, X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy it is clearly confirmed the formation of cubic tungsten carbide in the aforementioned process, as well as the product purity can reach up to 95%. Using these products, the temperature stability of the WC$_{1-x}$ phase was studied under annealing conditions in air and in vacuum. It was found that due to the process peculiarities and the material structure (the presence of a carbon shell around the WC$_{1-x}$ particles), the resulting cubic tungsten carbide has a higher range of temperature stability in the air up to 700 °C compared with known data. Vacuum annealing made it possible to detect the presence of WC$_{1-x}$ phase in the product even at temperatures up to 1500 °C.

References

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Zircon-based vanadium $\text{Zr}_{1-x}\text{V}_x\text{SiO}_4$ ceramic pigments are a modern type of pigments used in ceramic industry. They are stable at high temperatures and melted glazes due to zircon properties: its refractoriness and chemical inertness. A perspective way to solve the problem of zircon pigments cost is to use the plasma dissociated zircon (PDZ) from natural mineral as a raw material [1]. PDZ is a spheroids which consist of crystalline monoclinic zirconia grains interconnected to each other by the amorphous silica glass. Ammonium hydrofluoride used for the chemical activation of PDZ. It reacts with components of PDZ with their partial destruction. This partial fluorination caused microdefects in the structure of PDZ for more intensive interactions between defective PDZ and vanadium ions to obtain more intensively colored pigments.

A phase composition of pigments consists of V-zircon and monoclinic zirconia. V-$\text{ZrSiO}_4$ formation was confirmed by the shift of zircon phase peaks on XRD patterns. The increase of calcination temperature led to higher yield of green color in materials because of the growth of vanadium solubility in zircon structure and a more crystallization degree of zircon. Brown color of pigments were formed because of formation of green V-zircon and orange V-zirconia [2]. The pigments had blue color in the presence of mineralizer (so-called Turkish blue). However, blue color yield reduces at higher calcination temperatures. It can be explained by the fact that the mineralizer promotes the formation of not only V-zircon, but also V-zirconia.

The use of the products of fluorine-ammonium treatment for plasma-activated zircon as the raw material in the V-$\text{ZrSiO}_4$ pigments technology allows to synthesize blue and green pigments with different color characteristics depending on the degree of fluoride activation of PDZ, the amount of chromophore, the calcination temperature and the presence of mineralizer.

References

APPLICATION OF THE STATIC TENSIMETRY METHOD WITH MEMBRANE NULL-MANOMETER TO STUDY OF LEWIS ACIDITY OF (C₆F₅)₂BC₆H₂(C₆F₅)₃.

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A study of Lewis acidity is of both scientific and practical interest. Lewis acids are extensively used in organic synthesis as catalysts [1]. The question of a strength of Lewis acids remains controversial, since there is no uniform scale of Lewis acidity. The most common Lewis acidity scales are based on results of quantum chemical computations, for example, on the values of affinity energies for H⁻, CH₃⁻, F⁻, Cl⁻ anions in the gas phase [2]. Often, values obtained by different methods are not comparable. Therefore, it is important to find a parameter that can be determined by both computational and experimental methods.

In the present work the interaction between (C₆F₅)₂BC₆H₂(C₆F₅)₃ (Lewis acid, LA) and acetonitrile (Lewis base, LB) was studied by the static tensimetry method with membrane null-manometer [3]. Three experiments were carried out using different initial ratios of the LB and LA: 9.9:1, 5.6:1 and 2.3:1. In all experiments, the solid compound of 1.7:1 composition is formed at room temperature. Such composition may arise from additional acetonitrile incorporation into the crystal lattice after the complex formation due to the donor-acceptor interaction. Upon heating, the complex dissociates with the release of gaseous acetonitrile. Processes of desolvation and dissociation of the donor-acceptor bond occur as a single step, and therefore it is impossible to separate them. Quantum-chemical computations confirmed principal possibility of formation of both donor-acceptor complex and crystallosolvate. Computed dissociation enthalpies of complex and crystallosolvate are almost equal, in qualitative agreement with the results of tensimetry experiments.

References

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The development of catalysts for the reaction of partial oxidation of hydrocarbons is of great importance for the environmental safety and resource-saving technologies. Noble metals give the best effect as active component in this reaction. In this work, we prepared and characterised catalysts for the reaction of partial oxidation of hydrocarbons based on platinum supported on alumina of the bayerite series (θ-Al₂O₃). Alumina compounds were obtained through the aluminate method from aluminum. We synthesized both granular and structured catalysts. The last ones are additionally supported on the FeCrAlloy mesh. The use of alumina and described structured supports provides number of advantages [1-2]. First of all, we characterized supports, their precursors and precursors of the active component. Then the catalyst samples were prepared by impregnating the support with solutions of different precursors. Since the catalysts are synthesized in a nanoscale state, we use special physicochemical methods to investigate these substances, the support form’s influence, the active component precursor’s nature: X-ray diffraction, transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and UV-Vis diffuse reflection spectroscopy.

References

Acknowledgements. The work was supported by the Russian Foundation for Basic Research (project No 19-03-00595).
ADVANCED OXIDATION PROCESS FOR DETONATION NANODIAMOND SURFACE MODIFICATION

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An advanced oxidation process has been implemented for detonation nanodiamond purification and surface chemical modification. The treatment intended for chemical oxidation of detonation nanodiamond surface through reactions with hydroxyl radicals (·OH).

A number of samples were processed: detonation carbon, purified industrial grade detonation nanodiamond¹ and single particle hydrosols of air oxidized² and hydrogen annealed³ detonation nanodiamonds.

Comparative analysis of surface chemical composition provided by results of XPS and FTIR. Average size of primary nanodiamonds calculated by XRD data. Size distribution of detonation nanodiamond hydrosols measured by DLS. Elemental analysis provided by EDAX.

A method for obtaining uniform surface with oxygen-containing functional groups in spite of source of detonation nanodiamond was demonstrated. In some cases, advanced oxidation processing is more convenient than conventional gas-phase methods for surface modification.

References

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Zr$^{4+}$/F$^-$–SUBSTITUTED ANATASE TITANIUM DIOXIDE WITH ENHANCED ELECTROCHEMICAL PERFORMANCE

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Recently, anatase titanium dioxide is positioned as an anode material for high-rate lithium-ion batteries (LIBs). However, the sluggish transport of ions ($10^{-15}$ cm$^2$ s$^{-1}$) and electrons ($10^{-12}$ S cm$^{-1}$) serves limiting factor. A promising method to modify the titania is a cationic (substitution of part of Ti$^{4+}$ with metal ions) and anionic (partial replacement of O$^{2-}$ with non-metals) doping.

Within the scopes of the present work, the Ti$_{0.97}$Zr$_{0.03}$O$_{1.98}$F$_{0.02}$ solid solution with an anatase structure was synthesized by a template sol-gel method on a carbon fiber and investigated as an anode material for LIB.

Through a wide range of physicochemical methods, it was established that Zr$^{4+}$ and F$^-$ ions incorporated uniformly in the Ti$^{4+}$ and O$^{2-}$ sites of TiO$_2$ lattice. The difference in the ionic radii of Ti$^{4+}$ (0.604 Å) and Zr$^{4+}$ (0.72 Å) leads to changes in TiO$_2$ unit cell. At the same time, replacement of O$^{2-}$ with F$^-$ contributes to the Ti$^{3+}$ generation into the crystal lattice and affects conductivity. In particular, the conductivity of Zr$^{4+}$/F$^-$ co-doped TiO$_2$ reached $1.7 \cdot 10^{-9}$ S cm$^{-1}$, that significantly higher than only Zr$^{4+}$-doped ($8.7 \cdot 10^{-12}$ S cm$^{-1}$) and undoped TiO$_2$ (7.36 $\cdot$ 10$^{-13}$ S cm$^{-1}$) samples.

The electrode from Ti$_{0.97}$Zr$_{0.03}$O$_{1.98}$F$_{0.02}$ was tested in half-cell with a lithium counter electrode in the voltage range of 1–3 V at a current density of 1C ($C = 335$ mA g$^{-1}$). After the 35$^{th}$ cycle of galvanostatic charge/discharge the reversible capacity of Ti$_{0.97}$Zr$_{0.03}$O$_{1.98}$F$_{0.02}$ was still equal to 163 mAh g$^{-1}$, whereas Ti$_{0.97}$Zr$_{0.03}$O$_2$ sample gave only 34 mAh g$^{-1}$. Additionally, Zr$^{4+}$/F$^-$ co-doped TiO$_2$ retains a capacity of 138 mAh g$^{-1}$ even upon testing at increased current density of 5C.

Thus, it was established that co-doping with zirconium and fluorine of anatase titanium dioxide has a beneficial effect on its performance as an anode material for LIBs, including the operation under fast charge. The main reasons are as follows: i) unit cell volume increases due to the incorporation of zirconium; ii) conductivity improves after doping with fluorine.

Acknowledgements. This work was supported by the Russian Science Foundation (grant № 19-73-10017).
Bioactive and biocompatible coatings based on calcium phosphate (in particular hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) are relevant for developing new medical materials for bone implants [1].

In this work, polished titanium VT1-0 was used as a substrate. The template electrochemical synthesis was carried out using perforated coatings of xerogel titanium dioxide as a template. It was obtained by the sol-gel technology [2] and applied on a substrate by dip-coating. Depending on the synthesis conditions, various phases of calcium phosphate were obtained, including hydroxyapatite.

![Graph showing potential dependence of the ratio of phases of hydroxyapatite and monetite.]

Figure 1. The potential dependence of the ratio of the phases of hydroxyapatite and monetite.

Under certain conditions, template synthesis of the composite has been realized, perspective for bone implantation due to its structure and composition [3].

References

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Nowadays, Langmuir-Blodgett (LB) films of functional organic compounds have been attracting much attention because LB technique helps in preparation of organic assemblies with planned structure and properties. Molecules with relatively large head groups compared to alkyl chains are often used in functionalized LB films [1].

An amphiphilic Schiff base complexes have been prepared in order to research physico-chemical properties. After preparation, compression isotherms were studied in order to determine the conditions under which it is possible to transfer it to a solid substrate (\(\pi = 20\) mN/m and \(\text{pH} \approx 5\)).

![Compression isotherms of LB films based on nickel complexes with Schiff bases.](image1.jpg)

![Microphotographs of monolayers containing nickel complexes with Schiff bases.](image2.jpg)

The surface properties of monolayers were also studied by the method of Brewster angle microscopy. After a successful transfer to a solid substrate, the surface layer morphology was studied using a scanning electron microscope. The method of cyclic voltammetry was used to confirm the electrochemical properties of the substrate.

References
In recent decades, the attention of researchers has been devoted to the development of catalytic systems based on nanoparticles for using in stereo- and asymmetric catalysis\(^1\). It was established that the size, composition and shape of nanoparticles, electronic and steric properties of modifiers are important factors, which determine their catalytic characteristics. Therefore, methods for the formation of metal nanoparticles with desired sizes and shape based on using stabilizers and organic modifiers are being actively developed\(^2\). It was investigated the catalytic systems palladium-based formed from various precursors in the presence of optically active (-)-cinchonidine in the enantioselective hydrogenation of acetophenone by molecular hydrogen. During the reaction 1-phenylethanol is formed, represented by two enantiomers: R-(+) and S-(−) - phenylethanol.

It has been established that the using of palladium bis-dibenzylidene acetone as a precursor allows to create a more active system than the using palladium bis acetylacetonate (the maximum hydrogenation rates in these systems are 13.8 mmol/(L*h) and 1.4 mmol(L*h), respectively). At the same time, the enantiomeric excess 45.4% of the (S)-enantiomer was obtained with Pd(DBA)\(\text{2}\) as a precursor, while Pd(acac)\(\text{2}\) gave 14.8% ee. The additional stabilization of nanoparticles based on Pd(DBA)\(\text{2}\) by the introduction of cross-linked polyvinylpyrrolidone leads to an increase in the operating time of the catalyst and simplifies its reuse without significantly reducing the catalytic properties of the system.

References:
SYNTHESIS AND STUDY OF SYMMETRICAL AND ASSYMMETRICAL CHROMOPHORES INCORPORATING THE 4H-pyran FRAGMENT

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Organic chromophores incorporating arylvinyl fragments are widely used in the organic electronics devices (OLEDs, OFETs). New sets of symmetrical and asymmetrical conjugated structures of D-π-A-π-D and D-π-A (A-π-D-A'-D') types have been synthesized. Such spectral characteristics as quantum yields, optical bandgap values and Stokes shifts were determined. Stability towards electrochemical oxidation was also examined; simultaneously the values of HOMO/LUMO energies and electrochemical bandgaps were estimated.

The work was supported by the Russian Foundation for Basic Research (project No 19-43-590014).
FABRICATION AND SWELLING BEHAVIOR OF GHRP-2 PEPTIDE LOADED POLYMER-INORGANIC HAP/AGAROSE COMPOSITE

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The composites based on hydrogels and inorganic components excitingly attract interest as potential material for tissue engineering such as bone defects fillers due to its swelling behavior. Nevertheless, it has some drawback because of the complex crosslinking procedure and inorganic component concentration restriction. This problem can be solved by using the hydroxyapatite nanoparticles modified by the organic molecules working as a crosslinking agent.

The present study is aimed to fabrication of growth hormone-releasing peptide - 2 (GHRP-2) loaded composites based on HAP NPs synthesized under different conditions and polysaccharide agarose. Moreover, the swelling behavior of obtained compositions and release of peptide were studied.

To produce composites three types of hydroxyapatite nanoparticles synthesized by co-precipitation method were used: bare HAP NPs (HAp), HAP NPs synthesized in the presence of tartaric acid (t-HAp) and bare HAP NPs modified by succinic anhydride (m-HAp) for agarose and inorganic phase crosslinking. Synthesized HAP NPs were characterized by XRD, TEM methods, SSA estimation, and FTIR spectroscopy. It was shown that hydroxyapatite nanoparticles could extract peptide up to 94% from solution (Cp = 250 μg/ml). The peptide loaded nanoparticles (HAp@GHRP-2 and t-HAp@GHRP-2) were combine with m-HAp in ratios 50 wt.% to 50 wt.%. To fabrication composites the phase separation technique were used. The ratios of mixture HAp@GHRP-2/m-HAp or t-HAp@GHRP-2/m-HAp and polysaccharide agarose were 29 wt.%/71 wt.%, 44 wt.%/56 wt.% and 55 wt.%/45 wt.%. As expected, the composite’s swelling ratio decreased with HAP NPs mass increasing in citrate and phosphate buffers with pH=6.6. It was shown that swelling ratio for all specimens increased rapidly for the first day and achieved more than 700 wt.%. After than it decreased and reached equilibrium state for the 40 day. It was demonstrated that the peptide release started in 10 days and amount of the released peptide in citrate buffer more than in phosphate one.
THE EFFECT OF SUPPORT AND PRECURSOR NATURE ON THE PROPERTIES OF BIMETALLIC THREE-WAY CATALYSTS

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Nowadays, environmental pollution from automotive exhaust gases is one of the most important ecological problems. Over the past few decades, the use of three-way catalysts (TWC) providing simultaneous oxidation of CO and hydrocarbons along with reduction of NOx is a widespread method for neutralizing waste gases. The active components of TWC are noble metals (Pt, Pd, Rh), and various oxides (Al2O3, CeO2, La2O3, etc.) are used as a support [1]. The main problem of TWC remains their deactivation at high temperatures. The use of bimetallic alloy systems (for example, Pd-Rh) as an active component of catalyst makes it possible to reduce the impact of these negative effects due to the presence of metal-metal interaction [2].

The catalysts studied in the present work were prepared by an incipient wetness impregnation of Zr- and La-modified γ-Al2O3 and CeO2-Y2O3-ZrO2 supports with aqueous solution of corresponding nitrates, simple and double complex salts (organic and inorganic) of Pd and Rh. The samples were characterized by a complex of physicochemical methods, such as TEM, XPS and other. The catalytic activity and stability of TWC were examined by a prompt thermal aging (PTA) method and in a test reaction of ethane hydrogenolysis (HGE) [2]. It was found that the catalysts based on La-doped Al2O3 support and prepared from the nitrates are the most promising systems for further research. In this case, high-temperature reactivation of the catalyst was observed during the PTA tests. HGE results also confirm a presence of synergistic interaction between metals along with enhanced catalytic performance of the sample.

References

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CYCLOMETALATED IRIDIUM (III) COMPLEXES WITH PHENANTHROIMIDAZOLES AND VARIOUS β-DIKETONES: SYNTHESIS, STRUCTURE AND PHOTOPHYSICAL PROPERTIES

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Cyclometalated Ir(III) complexes have attracted particular attention as more stable analogs of Ru(II) dyes in dye-sensitized solar cells (DSSC). However, poor light-harvesting properties of Ir(III) photosensitizers prevent their widespread application in DSSC. Up to now, there have been 2 main approaches to improve properties of such complexes: varying cyclometalated (C^N or ‘antenna’) ligands or changing the substituents in 2,2’-bipyridine-based ‘anchoring’ ligands. Extending of conjugated π-system of antenna ligands might result in increase of molar absorbitivity coefficients in the visible region. Nevertheless, substantial improvements of photophysical characteristics might require some drastic ‘anchoring’ ligand changes. Specifically, aromatic β-diketones acting as negatively charged chelating ligands are anticipated to be very promising for constructing efficient Ir(III) dyes.

Herein, we present a comprehensive study (X-ray, NMR, MS, UV-Vis, CVA, LS) of several series of iridium (III) complexes with 2arylphenantroimidazoles and different ‘anchoring’ ligands: dibenzoylmethane (dbm), and 1-(3-methoxycarbonylphenyl)-3-thiophene-propane-1,3-dione (mtpd) (Figure 1). The most promising complexes were successfully tested in DSSC.

Figure 1. Ligands and Ir(III) complexes studied in this work.

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SYNTHESIS AND STUDY OF YVO$_4$:Dy$^{3+}$ NANOPARTICLES

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We report systematic study of Dy$^{3+}$-doped YVO$_4$ nanophosphors synthesized via modified Pechini technique. Effect of calcination temperature and doping concentration on structure and luminescence has been investigated. XRD and Raman spectroscopy revealed preparation of single-phase nanoparticles without any impurities. Synthesized nanopowders consisted of weakly agglomerated nanoparticles with average size about 50 nm. Photoluminescence spectra of YVO$_4$:Dy$^{3+}$ nanoparticles consisted of the characteristic narrow lines attributed to the intraconfigurational 4f-4f transitions dominating by the hypersensitive $^4F_{9/2}\rightarrow^6H_{13/2}$ transition. The calcination temperature variation did not affect $^4F_{9/2}$ lifetime, whereas increase of doping concentration resulted in its gradual decline. Potential application of YVO$_4$:Dy$^{3+}$ 1 at.% and 2 at.% nanopowders as ratiometric luminescence thermometers within 298–673 K temperature range was tested. The main performances of thermometer including absolute and relative thermal sensitivities and temperature uncertainty were calculated. The maximum relative thermal sensitivity was determined to be 1.8 % K$^{-1}$@298 K, whereas the minimum temperature uncertainty was 2. Thermal cycling experiments showed good repeatability of studied thermometer.

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Due to their unique properties fullerenes have a large area of potential applications in various branches of industry and medicine [1-2]. At the same time, their real applications are limited significantly because of their low solubility in water. To overcome this problem one can use the chemical modification of fullerenes. Promising fullerene derivatives are fullerenols where fullerene cores are modified by hydroxyl groups. The surface properties of solutions of a fullerenol with a large number of hydroxyl groups C60(OH)X (X = 30 ±2) were investigated by the methods of dilational surface rheology, surface tensiometry, ellipsometry, Brewster angle microscopy, transmission electron and atomic force microscopies. The surface properties proved to be similar to the properties of dispersions of solid nanoparticles and differ from those of the solutions of conventional surfactants and amphiphilic macromolecules. Although the surface activity of fullerenols with a great number of hydroxyl groups is not high and these substances do not decrease significantly the surface tension, the fullerenol molecules form a macroscopically homogeneous adsorption layer at the solution surface with a high dynamic surface elasticity up to 170 mN/m. Atomic force microscopy shows that the adsorption layer is not homogeneous at the microscale and consists of interconnected surface micro-aggregates consisting of two – three layers of fullerenol molecules. The bonds between different aggregates are weak and can be broken even by slight mechanical perturbations.

References

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SPRAY DEPOSITED FILMS BASED ON SULPHIDES OF ZINC AND CADMIUM

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The steady interest in obtaining thin films of A^{II}B^{VI} semiconductors doped with optically and electrically active impurities is due to the prospects of their application in microelectronics and laser technology. Of particular interest are materials based on CdS and ZnS, used for the manufacture of fluorescent – including electroluminescent – devices [1]. Pyrolysis of aerosols or spray pyrolysis (SP) is one of the most promising method of film deposition. Its advantages are simplicity, reproducibility, and the ability to use a wide range of precursors to produce doped and undoped films.

The aim of the work is to deposit films based on cadmium and zinc sulfides by aerosol pyrolysis and to study their properties.

According to the results of thermodynamic analysis it was found that the optimal precursors for the production of CdS films (ZnS) are cadmium nitrate (Cd(NO_3)_2), zinc nitrate (Zn(NO_3)_2) and thiourea (CH_4N_2S). The optimal conditions of the process are determined in the thermodynamic approximation. Precipitation is preferably carried out in excess of thiourea (at a ratio of 1.8:1). The temperature range of CdS formation was 525 - 1200 K, for ZnS – 880 - 1400 K.

Films based on sulphides of zinc and cadmium doped with Mn and Fe ions were deposited by the SP method. The composition of the films was determined by the band gap determined by the edge of its own absorption and the X-ray microanalysis method. The correlation between the content of dopant in the precursor solution and in the film was shown. The structure and morphology of the films were studied by X-ray diffraction and scanning electron microscopy. The effect of doping on the structure and morphology of films is shown.

References

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PLATINUM(IV) NITRATOCOMPLEXES AS EFFICIENT PRECURSORS FOR PREPARATION OF Pt\textsubscript{n}O\textsubscript{m}/CeO\textsubscript{2} CATALYTIC SYSTEM

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Carbon monoxide is a highly toxic component of modern urban agglomerations air. Under inspiration, it blockades the tissues oxygen supplying in organism so even extremely low concentration of CO (<50 ppm) in air can lead to serious dysfunctions. Due to this, efficient catalytic systems of CO neutralization at low-temperature are required.

It was determined that Pt\textsubscript{n}O\textsubscript{m} particles strongly anchored on a CeO\textsubscript{2} surface is an excellent catalyst of CO oxidation reaction at low-temperature (50-100\textdegree C). Additionally, it preserves activity at high temperature about 800\textdegree C. A distinctive feature is that platinum, in such catalyst, incorporated into CeO\textsubscript{2} surface in ionic form and securely fastened by Ce-O-Pt connection. On the other side, employing nowadays starting reagents such as chloroplatinic acid are not “oriented” towards producing of Pt\textsubscript{n}O\textsubscript{m}/CeO\textsubscript{2} systems because to generate Pt-O groups harsh conditions are required that cause full or partial reduction of ionic platinum species to metallic Pt\textsuperscript{0} particles. Ultimately it leads to irregular distribution of Pt forms on CeO\textsubscript{2} surface and lowering activity of the catalysts.

In this work, we used nitratocomplexes of Pt(IV) as precursors for preparing Pt\textsubscript{n}O\textsubscript{m}/CeO\textsubscript{2} catalysts. Such complexes seem to be a perfect predecessor because of the whole number of essential advantages:

a) platinum atoms are already located in oxygen coordination environment;

b) labile terminal nitrato groups provide a facile way for grafting on ceria surface;

c) nitratocomplexes rearrange into Pt\textsubscript{n}O\textsubscript{m} species by heating in mild conditions. Moreover, platinum nitratocomplexes with various nuclearity can be prepared ([Pt(NO\textsubscript{3})\textsubscript{6}]\textsuperscript{2-}, [Pt(OH)\textsubscript{2}(NO\textsubscript{3})\textsubscript{8}]\textsuperscript{2-}, [Pt\textsubscript{4}(\mu\textsuperscript{3}-OH)\textsubscript{2}(\mu\textsuperscript{2}-OH)\textsubscript{4}(NO\textsubscript{3})\textsubscript{10}], [Pt\textsubscript{6}(\mu\textsuperscript{3}-OH)\textsubscript{4}(\mu\textsuperscript{2}-OH)\textsubscript{6}(NO\textsubscript{3})\textsubscript{12}]\textsuperscript{2+}), therefore, Pt\textsubscript{n}O\textsubscript{m} active sites with specified n can be constructed. Our first results show that catalysts prepared by sorption of dimeric [Pt\textsubscript{2}(OH)\textsubscript{2}(NO\textsubscript{3})\textsubscript{8}]\textsuperscript{2-} complex on the ceria surface exhibit low-temperature activity (T\textsubscript{50\%} about 100\textdegree C) for CO oxidation at a high gas hourly space velocity of 240000 h\textsuperscript{-1}.

Acknowledgments. This work was supported by the Russian Science Foundation (RSF grant 18-73-0005).
Halide and polyhalide tellurium complexes attract great attention due to their intriguing physical properties. From the point of view of new materials, this area of research is very relevant, since such complexes can be used in perovskite-type semiconductors [1-2].

Anions of halide complexes can have both discrete and polymeric structure (figure 1). Currently, there is no theory to predict the structure of the product according to the initial reaction conditions.

Figure 1. Scheme of the formation of halide tellurium complexes.

In our work, we report, methods of synthesis, structural features, thermal stability and optical properties of new halide and polyhalide complex tellurium. The dependence of the structure on the reaction conditions is discussed.

References

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INVESTIGATION OF ETHANOL OXIDATION OVER COBALT CONTAINING ZEOLITE CATALYST

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Though there are many studies about the catalytic transformation of modern spirits, their work on conversion to zeolite catalysts in oxidizing environments is virtually significant. On the other hand, processes taking place over nanoparticles catalytic systems are great of interest. According to this presented paper is dedicated to development of synthesis methods of nanostructured catalytic systems, determination of their structure and morphology, and the identification of methods that can change the basic characteristics of the catalyst.

In view of this, nano complex catalyst samples were prepared by adding Co transition metal on the surface of NaX type of zeolith and their activity was studied in the process of ethanol oxidation.

The cobalt-nitrate solution on the NaX zeolite was impregnated to receive the crushed CoNaX catalyst, after that the sample was dried at 373 K and calcined at 523-573 K until full decomposition of cobalt nitrate. The obtained sample was calcined during 10 hours at 823 K. Thus, containing 1%, 2.5%, 5%, and 10% of cobalt were prepared zeolite based catalysts.

The activity of the obtained catalyst samples was studied in the reaction of ethanol oxidation by air oxygen. The process was carried out at a temperature range of 423-773K on a flow unit with a tubular reactor. The catalyst volume was 5 ml and the initial reaction volume was 2400 hours⁻¹. The ratio of initial gas reactants was taken at alcohol: air = 1:10. Analysis of primary substances and reaction products was carried out by chromatographic method.

References
SYNTHESIS OF POLYANILINE BASED NANOCOMPOSITE MATERIALS AND THEIR APPLICATION IN ELECTROCATALYSIS

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The new type of composite materials based on polyaniline doped with metal-carbon nanoparticles (NPs) PANI/M@C, where NPs embedded in polymer matrix by method of laser-induced deposition, is under investigation. These objects attract the interest in field of electrochemistry thanks to efficient performance in electrocatalytical reactions provided by combination of polyaniline matrix conductivity and metal NPs catalytic properties. Moreover, the “in-situ” polymerization of polyaniline on substrates with different geometries gives additional way to increase the electrocatalytic efficiency of the system. The role of electrode geometry is discussed in [1]. Figure 1 demonstrates the possibility of obtaining PANI films (a) and nanotubes on anodic aluminum oxide nanomembranes (b,c).

Figure 1. Polyaniline films and nanotubes.

The composition of M@C NPs is predetermined by type organometallic complex used to laser-induced deposition process, which, in its turn, determines the type of catalyzed reaction.

References

Acknowledgements. This work was supported by the German-Russian Interdisciplinary Science Center (G-RISC) project number P-2018b-30. Authors are grateful to “Interdisciplinary Resource Centre for Nanotechnology” and “Centre for Optical and Laser Materials Research” of Saint-Petersburg State University Research Park.
Synthesis of ultra dispersed carbon materials plays a significant role in the modern nanotechnologies. Nowadays the scientific community pays much attention to carbon and nitrogen compounds due to their outstanding properties [1]. There exist several methods to synthesize this material, such as CVD, laser ablation and arc discharge [2-4]. This work is focused on the synthesis of ultra dispersed graphite-like materials in DC arc discharge plasma in ambient air.

The mixture of melamine \( \text{C}_3\text{H}_6\text{N}_6 \) and graphite C in proportion of 2:1 was used as initial powder. The X-ray diffraction data obtained from the initial (a) and synthesized (b) powder are shown in Fig. 1. XRD pattern of synthesized powder (b) shows some peaks corresponding to the graphite-like structure reflections. Besides, the largest peak is wide, which indicates the presence of impurities. According to EDS analysis, the synthesized product contains carbon and nitrogen. TEM analysis also confirms the presence of graphene-like carbon structures doped with nitrogen.

![XRD patterns](image)

Figure 1. Typical XRD patterns: a – initial powder, b – synthesized powder

References
THE EFFECT OF THE SYNTHESIS PARAMETERS ON THE PROPERTIES OF β-NaYxGdyF4:Yb,Tm UP-CONVERTING NANOPARTICLES

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Fluorescent nanoparticles β-NaYxGdyF4:Yb3+,Tm3+ due to their optical properties have a great potential for applications in bio-imaging as fluorescent labels and imaging probes. We have studied the effect of the hydrothermal synthesis parameters on the luminescent properties of NaYxGdyF4 nanoparticles co-doped with Yb3+ and Tm3+. The effect of the varied concentration of Y3+/Gd3+, the effect of different pH, the effect of time stirring and temperature control on the fluorescence intensity of β-NaYxGdyF4:Yb3+,Tm3+ nanoparticles have been studied in our work. The nanoparticles with that were synthesized by hydrothermal method. The morphology of the obtained nanoparticles was studied by transmission electron microscopy. They have hexagonal structures and size of around 1000 nm. The up-conversion fluorescence of β-NaYxGdyF4:Yb3+, Tm3+ nanoparticles was measured at 980 nm excitation wavelength. The sample exhibited blue luminescence, which originated from

Acknowledgements. The measurements where performed in the “Centre for Optical and Laser materials research”, “Interdisciplinary Center for Nanotechnology”, “Centre for Molecular and Cell Technologies” and “Cryogenic department” of research park of Saint-Petersburg State University.
ORDERED HONEYCOMB-LIKE STRUCTURES NETWORK OF MnO$_2$·nH$_2$O NANOCRYSTALS FORMED ON THE SURFACE OF A Mn(OAc)$_2$ SOLUTION DROP

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The processes of depositing and evaporating solution droplets underlie method for producing electrodes of electrochemical devices. Unique conditions and effects appear when droplets of solutions of various substances evaporate. These effects lead to the structuring of the resulting products.

There is a specialty of our experiment in comparison to the previous experiment carried out by other authors. Before drying, the surface of the solution drop was treated with a gaseous reagent according to the gas–solution interface technique (GSIT) that was previously used by us to obtain nanocrystals [1], thin films and microtubes for a wide range of inorganic compounds. As the object of study, 8-40 mcL droplets of Mn(OAc)$_2$ solution applied on glass surface were selected. Ozone was a gaseous reagent. This material was chosen because manganese oxides have a great potential for practical use as electrode materials for chemical current sources, electrochemical sensors, catalysts for the oxidation of organic compounds, etc.

The first experiments showed that after treating a drop of Mn(OAc)$_2$ solution with a gaseous ozone, a light brown film forms on its surface. The observation after reaction showed that the film consists of separate “ribbons” with a width of 1-2 microns, some of which forming a network of honeycomb structures.

Figure 1. Optical (left) and scanning electron (right) microscope images of the samples obtained after drying the ozone-treated Mn(OAc)$_2$ solution drop.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-13-13018).
Protonated layered perovskite-like niobate HCa$_2$Nb$_3$O$_{10}$, relating to Dion-Jacobson phases, is the solid crystalline semiconductor compound, in which blocks with perovskite structure [Ca$_2$Nb$_3$O$_{10}$]$^-$ alternate with interlayer spaces, containing protons. This niobate is well known as a heterogeneous photocatalyst for hydrogen evolution from water and water-organic media under ultraviolet irradiation [1] that is of great importance for development of environmentally friendly technologies. Being a solid acid, HCa$_2$Nb$_3$O$_{10}$ is able to intercalate some organic bases into the interlayer space forming inorganic-organic derivatives [2]. Since photocatalytic activity of layered perovskite-like oxides strongly depends on structure and composition of the interlayer space, intercalation of amines may significantly affect it and lead to the creation of new highly efficient photocatalysts. Nevertheless, data on photocatalytic properties of hybrid inorganic-organic perovskites are practically absent.

The present work is devoted to synthesis of amino derivatives HCa$_2$Nb$_3$O$_{10}$×RNH$_2$ (R = Me, Et, Bu, Oct) and investigation of their photocatalytic activity in the reaction of ultraviolet light-driven hydrogen production from the model water-methanol solution. The derivatives obtained are characterized using modern physicochemical methods (X-ray powder diffraction, Raman spectroscopy, thermogravimetry, elemental C,H,N-analysis, scanning electronic microscopy). Measurements of photocatalytic activity are performed using chromatographic hydrogen detection with and without platinum addition as a cocatalyst. Possible reasons of the photocatalytic activity dependence on the interlayer amine are discussed.

References

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Fischer–Tropsch synthesis (FTs) has proven its ability for the conversion of synthesis gas to high value hydrocarbons (e.g. gasoline, diesel and light olefins). Some of perovskite-type catalysts ABO$_3$, where A – Ln and B – 3d-elements, have been investigated for FTs, due to the flexibility in their design and preparation.

GdFe$_{1-x}$Mn$_x$O$_3$ ($x = 0$ – 1) ultrafine perovskite powder with grain size around 40-100 nm has been prepared by sol-gel method. The catalysts have been characterized by various physico-chemical methods. The crystallinity and phase purity of the perovskites were determined by XRD. The morphology and surface characteristics of the samples were investigated by SEM+EDS and TEM, specific surface area measurements were carried out by BET method. The oxidation states of Fe and Mn were identified by XPS.

The effect of Mn-substitution on the catalytic performance and the distribution of products of hydrogenation of CO in process FTs were investigated and presented in Figure. In case of GdFeO$_3$ the content of methane and light olefins was found to be 71% and 26%. While partial or fully substitution of Fe by Mn ($x$(Mn) = 0.5, 0.8, 1) results in methane decrease to 40%, olefins increase to 35% and increase the ratio of hydrocarbons C$_5$-C$_6$. Moreover it was found that GdMnO$_3$ catalyst provides better ethylene and butylene selectivity while GdFeO$_3$ exhibits the highest catalytic activity.

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HALOGENATION OF A MULTIPLE BOND IN A METAL-ORGANIC FRAMEWORK AS A WAY TO TUNE ITS SORPTION PROPERTIES

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Post-synthetic modification of metal-organic coordination polymers is a promising way to obtain materials that are difficult to synthesize directly. The presence of easily modifiable functional groups in the initial coordination polymer makes it perspective for the synthesis of derivatives with adjustable porosity, sorption selectivity, catalytic, luminescent and other properties.

We aimed to post-synthetically functionalize the organic ligand in the aluminum fumarate A520 [1] [Al(OH)(fum)] (1) with chlorine atoms and investigate the sorption characteristics for the resulting derivative. The quantitative chlorination of 1 at room temperature was confirmed by 1H and 13C NMR spectra of digested samples, and PXRD demonstrated that overall crystal structure keeps intact. Thus, for the obtained compound the formula [Al(OH)(fumCl2)] (2) can be reliably assigned.

Sorption measurements for 2 revealed a decrease in porosity according to low-temperature (77K) nitrogen adsorption, but a more than twofold increase in the selectivity of CO2 adsorption respecting to CH4 and N2 at 273K and 298K compared to the aluminum fumarate 1. More, the preferential adsorption of acetylene over ethylene and ethane appears in the functionalized 2.

This fact can be explained by the appearance of new adsorption centers for molecules with high polarizability (CO2 and C2H2) in the chlorinated derivative, as well as the partial blocking of channels in the porous structure by bulky chlorine atoms for substrates with larger particles.

The obtained results are the first example of direct chlorination of a multiple bond in a metal-organic framework, they also demonstrate the possibilities of post-synthetic modification of ligands in coordination polymers in the synthesis of highly efficient sorbents for the separation of gas mixtures.

References
As a result of the nuclear industry activities, a large amount of waste, especially radioactive, is generated. The composition of liquid waste may include any compounds, such as highly toxic chromium (III) salts. In view of the approaching era of decommissioning of nuclear power plants, the volume of waste will grow rapidly. To maintain a clean environment, it is necessary to develop materials that can minimize the effects of harmful substances. A promising method for obtaining nanoparticles is hydrothermal synthesis, which allows to obtain nanotube morphology. The resulting nanotubes have a number of properties that make it possible to use them as sorbents.

We have performed work on filling hydrosilicate nanotubes (Ni₃Si₂O₅(OH)₄) with the pecoraite structure. Sample nanotubes were placed in buksy and filled with aqueous solutions of chloride and nitrate chromium (III) with a concentration of 0.005 M to 0.5 M. When changing the temperature-time parameters, some solutions with nanotubes were mixed using a magnetic stirrer. The contents of the other packages were filled in static conditions, also with changes in temperature and time. After the experiments, the samples were washed with distilled water and dried.

The obtained samples were investigated by XRD, IR spectroscopy and TEM. The results of the analysis show that for the best filling of nanotubes it is necessary to increase the temperature, constant mixing and the optimal concentration of aqueous solutions of chromium.

Preservation of the nanoparticles structure in experiments under various conditions suggests the use of hydrosilicate nanotubes as a sorbent for wastewater treatment of chromium (III) compounds.

References
LASER-INDUCED SYNTHESIS AND CHARACTERISTICS OF THE NANO-SIZED MoₓOᵧ FOR GAS SENSORS PLATFORM


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The development of new composite materials with specified properties such as high active surface area, small size, and high electrocatalytic activity is of great interest for many fields of science and technology, particularly, for fabrication of highly efficient gas sensors that are sensitive to concentrations of toxic and hazardous gases. The main advantages of composite sensors are their high reliability, sensitivity, and low cost [1]. The Laser-induced Chemical Liquid-phase deposition of compounds from solution (LCLD) method can be applied to receive nano-sized porous gas sensing material on the dielectric substrate. The sensing materials studied in this work are the nanostructured composites containing mixture of different molybdenum oxides. Molybdenum trioxide for instance is an important n-type semiconductor, and an effective gas sensor [2] due to its unique layered structure, where molybdenum atoms have different valences. There is a huge amount of active charge transfer centers in these structures making MoO₃ applicable in catalysis and photocatalysis as well.

In this particular study the manufacturing of nano-sized materials and testing their sensing properties was done. The composite nano-sized MoₓOᵧ materials were fabricated with LCLD method, based on the in situ laser-induced deposition of microcomposites containing molybdenum oxides with highly developed surface area from aqueous solutions on the surface of different dielectric substrates. The sensor activity of the deposits was determined for the group of reducing gases at different concentrations and temperature regions. The regeneration temperature, time response and degeneration concentration were determined for a set of samples. The selectivity of the sample was tested in the presence of a mixture of gases (NH₃, NO). Nano-sized MoₓOᵧ samples show good properties for gas sensors thanks to large surface area and huge amount of active centers.

References

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Organic molecules with high-spin ground state are of interest as building blocks for multifunctional molecule-based magnets, sensitive spin probes and organic conductors [1–3]. In search for new types of stable high-spin organic structures, we for the first time synthesized diradicals 4–6 containing exchange-coupled 1,3,5-triphenyl-6-oxoverdazyl and nitronyl nitroxide moieties.

The synthesis of diradicals were effectively carried out by using a palladium-catalyzed cross-coupling reaction of iodoverdazyls 1–3 [4] with a nitronyl nitroxide-2-ide gold(I) complex in yields up to 82%. The molecular and crystal structures of 4–6 were solved by the single-crystal X-ray diffraction analysis. The obtained verdazyl-nitroxide diradicals were characterized by ESR, cyclic voltammetry (CVA), and HRMS techniques. DFT calculations revealed triplet ground state in diradicals 4 and 6, and singlet ground state in 5.

References
Layered perovskite-like oxides are crystalline compounds, which consist of alternating layers of perovskite structure and layers with another type of structure. They are of interest because of their properties, such as ionic conductivity, superconductivity, ferromagnetism and photocatalytic activity. Usually layered perovskite-like oxides are synthesized by high temperature ceramic method [1]. However, it demands high energy consumption and leads to large polycrystalline particles of the final products, which is not desirable for their practical use as catalysts. There are alternative methods, such as hydrothermal method and sol-gel synthesis, which allow to obtain smaller particles with uniform morphology at lower temperatures.

In this research layered perovskite-like titanates $A_2Ln_2Ti_3O_{10}$ ($A = \text{Rb}, \text{K}; Ln = \text{La}, \text{Nd}$) attributed to the Ruddlesden–Popper phases were synthesized by ceramic method according to [2]. Moreover, $K_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was synthesized by sol-gel and hydrothermal methods under various conditions. The phase composition of each sample was investigated with XRD analysis. Ion-exchange properties were studied with regard to the substitution reaction of alkali cations for protons (protonation). These reactions were carried out in diluted HCl solutions with various pH and yielded three distinct phases with different substitution degree for each compound. Their cell parameters were determined by XRD analysis and the protonation degree was studied by TG analysis.

References

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2 section

POLYMER SCIENCE THE NEXT GENERATION
IMPROVEMENT OF THE TRANSPORT PROPERTIES OF ULTRAFILTRATION AND PERVAPORATION MEMBRANE BASED ON POLYVINYL ALCOHOL BY PLURONIC F127 MODIFICATION

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Among the membrane processes, pervaporation and ultrafiltration attracted the attention in the last century. Pervaporation is an applicable analytical tool for the separation of liquid mixtures containing an azeotropic, low-molecular weight and close-boiling components without additional chemicals and using less energy than conventional processes for liquid mixture separation that cannot separate these mixtures. Ultrafiltration membrane processes as alternatives to conventional methods are gaining wide attention in food processing industry; this is because it has several advantages over conventional method such as high selectivity, gentle product treatment, and lower energy consumption. One of the fastest and simplest ways to improve the properties of membrane polymeric materials is the creation of hybrid membrane. Membrane modification using Pluronic copolymers is usually performed via the introduction of Pluronic additive to the casting solution due to its amphiphilic nature, optimal hydrophilic/hydrophobic balance and high molecular weight.

In this study, pluronic F127 was used to improve the transport properties of porous membrane based on PA and supported dense membrane based on PVA. Pluronic F127 was added into porous membrane matrix that were prepared by phase inversion method. Dense composite supported membrane based on PVA and pluronic F127 have been prepared by casting thin layer of PVA solution containing pluronic F127 in the required amount into modified polyamide porous membrane. The influence of pluronic F127 addition on the structure of porous and dense membrane was studied by IR, NMR and SEM. Transport properties of dense membrane were studied in pervaporation of azeotropic isopropanol/water mixture. Transport performance and antifouling properties of porous membrane were studied in ultrafiltration of water and solution.

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In this paper, the influence of processing conditions (temperature and time) on the molecular weight and elemental composition of spruce dioxanlignin was studied.

For the reprecipitated dioxanlignins, an increase in the nitrogen content for all samples was observed with an increase in the varied parameters. It was found that during the reprecipitation of [bmim]MeSO₄ there was an increase in the molecular weight of the lignins and decrease in the degree of polydispersity with the formation of highly condensed structures. For samples obtained by reprecipitation from [bmim]Ac, molecular weight values are reduced with a decrease in the degree of polydispersity, while high-molecular fractions are degraded. The results make it possible to obtain lignin with a given molecular mass distribution, which plays an important role in the creation of new technologies for the processing of vegetable raw materials.

The work was performed using the equipment of the core facility center "Arctic" Northern (Arctic) Federal University named after M. V. Lomonosov with the financial support of the Russian science Foundation (project No 18-73-00282).
Organic compounds, whose molecules have a conjugated system of bonds, attract special attention of researchers. These compounds are promising materials for modern technology [1, 2]. Prospects for the use of these materials are far from exhausted.

Based on the $m$-phenylenediamine and aldehydes obtained new benzylidenphenylenediamines (BFDA). Polymerization of BFDA in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ produced polymers. The process of polymerization proceeds in a heterogeneous system with the formation in the first stage, the cation-radical. The resulting cation-radical recombination with the release of protons in the reaction system. Therefore, oxidative polymerization, BFDA flows through the slow (single-electron transfer).

Figure 1. Getting BFDA, polymers on their basis and their application.
PREPARATION OF NEW COORDINATION POLYMERS BASED ON TRIFLUOROACETATES OF 3D METALS

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Fluorotrifluoroacetatometalates of alkali metals are analogues of the well-known class of oxocarboxylates 3d metals formed as a result of hydrolysis. The peculiarity of their crystal structure is symmetrical polynuclear frame. The octahedral environment of the metal atom consists of four carboxylic oxygen atoms, a bridging fluoride-ion and an axial neutral ligand \cite{1}.

The latter position is of particular interest, because when replacing it with a polydentate organic ligand, it is possible to obtain a polymer MOF with volumetric cavities.

In this work, the first step was taken to obtain polymer MOF based on trifluoroacetates of 3d metals. For the first time it was shown that it is possible to obtain compounds of the studied class with axial ligands other than the trifluoroacetic acid molecule present in all previously known compounds of this class, by controlling the synthesis conditions.

For example, under conditions of sharp cooling, a compound with axial water molecules was obtained. (Figure 1). 

\[ \text{K[Co}_3(\mu_3-F)(\text{TFA})_6(\text{H}_2\text{O})_3](\text{HTFA})_4(\text{H}_2\text{O}) \]

was synthesized by dramatically lowering the temperature of the solution. Crystal cell is monoclinic (P 21/n) with \( a = 13.1069(3) \, \text{Å}, \ b = 13.9789(2) \, \text{Å}, \ c = 20.9794(3) \, \text{Å}, \ \beta = 100.598(1)^\circ, \ V = 3778.28(12) \, \text{Å}^3, \ R = 5.07\%, \ Rw = 8.90\%. \)

In the future, it is planned to obtain and crystallographically study the crystallization products of the studied compounds with organic ligands.

Figure 1. A fragment of the crystal structure \( \text{K[Co}_3(\mu_3-F)(\text{TFA})_6(\text{H}_2\text{O})_3](\text{HTFA})_4(\text{H}_2\text{O}) \).

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NETWORK FORMATION OF DNA/POLYELECTROLYTE FIBROUS AGGREGATES AT THE AIR/WATER INTERFACE

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Polycations form soluble complexes with DNA in aqueous solution due to strong electrostatic attraction between the components and allow transfer of genetic material into cells [1]. Cationic polymers represent a class of nonviral carriers which can be designed to facilitate gene delivery into target cells. The corresponding biomedical interest resulted in extensive investigations of DNA-polyelectrolyte interactions in the bulk phase of aqueous solutions [2]. At the same time, the information on surface properties of these systems is scarce.

In the given work the dynamic surface properties of DNA/poly(methylalkyldiallylammonium chloride) (PMADAAC) aqueous solutions at the solution/air interface were studied by the surface tensiometry, dilational surface rheology, ellipsometry and atomic force microscopy. The deviations of the surface properties (surface elasticity, surface tension, ellipsometric angles) of DNA/poly(dimethyldiallylammonium chloride) from the values of water were close to the error limits. Measurements of the kinetic dependencies of the surface properties of DNA/poly(methylbutyldiallylammonium chloride) and DNA/poly(methylhexyldiallylammonium chloride) solutions discovered noticeable deviations from the results for solutions of individual components indicating thereby the adsorption of DNA/polyelectrolyte complexes. These deviations increased strongly at the approach to the isoelectric point. The atomic force microscopy allowed estimation of the morphology of the adsorption layer as a function of the molar ratio and total concentration of the two components.

References

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SYNTHESIS AND CROSS-LINKING OF FERROCENE-SUBSTITUTED POLYMETHYLHYDROSILOXANES

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Self-cross-linkable ferrocenyl-substituted polymethylhydrosiloxanes are synthesized for the first time. Karstedt’s catalyst and \( \text{cis-}[\text{PtCl}_2(\text{PhCH}_2\text{CN})_2] \) are used for self-cross-linking of the ferrocenyl-substituted polymethylhydrosiloxanes by the dehydrogenative reactions between Si-H groups [1,2] (Figure). \( \text{cis-}[\text{PtCl}_2(\text{PhCH}_2\text{CN})_2] \) leads to cross-linked ferrocenyl-containing silicones (FSRs) without visible mechanical defects compared to Karstedt’s catalyst. The data reveals significant differences between FSRs and cross-linked unmodified polymethylhydrosiloxanes: FSRs have improved tensile properties (the tensile strength increased from 0.47 to 0.75 MPa) and 1.5–2.5 times lesser cross-linking degree. The surface resistivity of the FSRs is around \( 10^6 \) \( \Omega/\square \) that 10 times less than mechanical mixture of polymethylhydrosiloxane with 5 wt.% of ferrocene and 10000 times less than pure polymethylhydrosiloxane. The obtained FSRs can be potentially applied as flexible electroactive layers and antistatic surfaces for electronic and electrostatic-sensitive devices, interfaces and sensors.

Figure. Synthesis and cross-linking of the FSRs.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-20062_mol_a_ved). Measurements were performed at the Center for Magnetic Resonance, the Centre for Innovative Technologies of Composite Nanomaterials (all in Saint Petersburg State University).
Currently, one of the most important areas in modern society is the development of sustainable processes. Such processes include membrane separation processes due to the fact that these methods are environmentally friendly, use compact equipment and have low power consumption. The rapid development of membrane methods requires the search for new highly effective materials with an improved combination of physicochemical and transport properties. The obtaining novel membrane materials with improved characteristics can be easily achieved by the modification of the polymer matrix by inorganic filler that yields in developing the mixed matrix membranes (MMMs). In the present work water-soluble derivative of fullerene (polyhydroxylated fullerene or fullerenol) has been used as modifiers and cross-linking agents for sodium alginate.

The aim of this work was to develop and investigate the novel composite material based on sodium alginate modified by fullerenol for further preparation of novel environmentally friendly mixed matrix membranes with improved transport characteristics for pervaporation dehydration. The preparation methods and optimal conditions for nanocomposite were developed. Structural and physicochemical characteristics of nanocomposite material were studied by various physical and chemical methods of investigation (IR spectroscopy, scanning electron microscopy and sorption experiments).

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The rapid development of membrane technology requires the use of materials with desired properties to solve a specific technological separation problem. One of the most important ways to create membranes with optimal transport characteristics is their bulk and surface modification. The aim of this work was to create new polymer membranes with a hierarchical structure, namely, the creation of composite membranes with several polymer layers of different chemical nature. The upper selective layer was applied by interfacial polymerization. As polymeric ultrafiltration substrates were used polyacrylonitrile, polyphenylene isophthalamide, and regenerated cellulose. As an intermediate polymer layer were used chitosan, polyallylamine hydrochloride, polyphenylene isophthalamide. It was shown that the creation of multi-layers leads to an increase in the efficiency of separation of organic and water-containing binary mixtures.

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SYNTHESIS OF POLYMERIC GLYCOSILICONES VIA CUAAC AND HYDROSYLATION REACTIONS

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Glycosilicones are new class of hybrid compounds, consisting of saccharide and siloxane fragments [1]. Possibilities for synthesis of glycosilicones are limited due to incompatible solubilities of sugars (hydrophilic) and polysiloxanes (hydrophobic). Protection-deprotection steps can be used to improve saccharide solubility, but it makes synthesis more complex and can lead to side reactions. Alternative method is to perform reaction heterogeneously. In this regard high-efficient reactions such as hydrosilylation [2] and azide-alkyne cycloaddition [3] must be used to obtain good conversion.

In this work cellulose-based glycosilicones were obtained via platinum and rhodium catalyzed hydrosilylation and copper catalyzed azide-alkyne cycloaddition with “grafting to” approach. Reagents with corresponding functional groups (alkyne, azide) were obtained from epoxy-terminated polydimethylsiloxane and hydroxyethyl cellulose. Choice of catalytic reaction and catalyst influences on reaction yield and degree of substitution. Resulting compounds are insoluble in water and organic solvents. Polysiloxane grafting increased hydrophobicity of obtained glycosilicones.

References

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Macroporous monolithic materials are solid-phase sorbents characterized by a system of interconnecting pores. Their structure can provide for proteins a hydrophilic environment similar to in solution conditions, the possibility of variation of the surface chemistry and high reproducibility of the synthesis. Moreover, the 3D-structure of the macroporous materials provides the higher probe loading and, consequently, the sensitivity of analysis. Due to such positive characteristics, this class of materials is widely used in such areas as gas and high-performance liquid chromatography, solid-phase extraction and flow-through heterogeneous biocatalysis. One of the new areas of application of macroporous materials is biological microanalysis using microarray [1-2].

Nowadays, more and more studies have been devoted to the development of diagnostic systems which are utilizing aptamers instead of antibodies as probes for molecular recognition of proteins and nucleic acids. Aptamers are a class of small oligonucleotide ligands increasingly growing in importance in the face of contemporary detection challenges. Compared with traditional ligands such as antibodies, aptamers have advantages including smaller sizes, lower manufacturing costs, none or low immunogenicity, versatile chemical modifications, extensive targets and batch-to-batch reproducibility.

In this work, a series of macroporous monolithic materials in the thin-layer form was obtained by the photoinitiative free radical polymerization. The influence of the polymerization mixture composition and polymerization conditions on the physico-chemical characteristics of obtained materials was investigated and material’s average pore size via the correct choice of porogen mixture was optimized. The developed materials were tested for the analysis of glycosylated hemoglobin using aptamer as a probe.

References
Molecular imprinted polymers (MIPs) represent the polymeric matrices bearing the artificial stereospecific recognition sites that are complementary to the template in shape, size and spatial position of the functional groups. Such site formation occurs in the process of copolymerization of functional and cross-linking monomers around the template, followed by the removal of latter from ready-to-use matrix. MIPs are very attractive for extraction of both low-molecular weight compounds and biological objects, such as viruses, proteins and cells.

The aim of this work was to synthesize molecular imprinted cryogels based on 2-hydroxyethyl methacrylate (HEMA) and poly(ethylene glycol) diacrylate (PEGDA) and to investigate the properties of materials obtained. Polymer nanoparticles (NPs) based on lactide-poly(ethylene glycol)-5000 copolymer, representing the experimental model of virus, were prepared by nanoprecipitation and then modified with α-chymotrypsin (NPs-CHTR). The particle size and ζ-potential were analyzed by dynamic light scattering (DLS). The HEMA-PEGDA matrices imprinted with NPs-CHTR were synthesized by cryo-copolymerization of monomers in the presence of these particles as templates. The process was carried out in water with application of ammonium persulfate/N,N,N',N'-tetramethylethylenediamine as initiator system at 24 h and -13 °C. Non-imprinted cryogels were synthesized at same condition for application as control materials (NIP). The effect of synthetic condition (molar ratio of functional monomers/cross-linking agent and concentration of monomers in the system) on mechanical characteristics of obtained materials was studied. The morphology of the matrices was investigated by SEM and X-ray microtomography. The cryogels were tested as the stationary phases for recognition of protein and nanoparticles.
THE EFFECT OF MULTIVALENT COUNTERIONS CHEMICAL STRUCTURE ON IONIC POLYELECTROLYTE COMPLEXES FORMATION

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The negative charged polyelectrolytes such as polyacrylic acid are able to form complexes with multifunctional counterions. They are used as carriers for the targeted drug and genes delivery, as medical imaging agents and antibacterial coatings. Currently, complexes of polyacids with inorganic ions and oppositely charged polymers are widespread in the literature; however, there is almost no information about low molecular weight organic compounds as counterions for polyelectrolyte complex formation.

In the present work the ionic complexes between polyacrylic acid with different molecular weight (Mn = 2000 and Mn = 26700) and multivalent organic counterions. Amines having fixed number of amino groups and different number of methylene groups were chosen as counterions. The possibility of the water-insoluble complex formation was determined by the turbidimetry, and the pH ranges within which such complexes are stable were studied. The influence of the different parameters on the characteristics of the forming complexes was investigated: the molecular weight of the polymer, the number of methylene groups in the amine, the ionic strength, the polarity of the medium. The stoichiometric composition of the complexes was equal to the reagent ratio in the starting mixture which was shown by NMR-spectroscopy. The size and ζ-potential of the complexes particles in the solution were estimated by the DLS method. Morphology of the complexes resulted from fast non-equilibrium adsorption on mica was studied by AFM and it was shown that the complex particles have vesicular structure. Moreover, SEM was used to investigate the morphology of the complexes in the form of solid precipitates and particles isolated from the colloidal solutions.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-03-00629 A) and resource centres of St. Petersburg State University: Centre for Magnetic Resonance Research Centre, Interdisciplinary Resource Centre for Nanotechnology, Chemical Analysis and Materials Research Centre.
RAFT-POLYMERIZATION OF 2,2,3,3-TETRAFLUOROPROPYL METHACRYLATE

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In recent years, control radical polymerization methods have been widely used to synthesize (co)polymers with a given architecture. Reversible addition-fragmentation chain transfer (RAFT) polymerization can be applied to a wide range of monomers unlike the rest of techniques; therefore, it is a more versatile technique for the synthesis of amphiphilic copolymers [1]. Fluorinated (co)polymers draw the attention of scientists due to some of their properties such as thermic and chemical resistance, atmospheric sustainability and low surface energy [2]. Controlled (co)polymerization of fluorine (meth)acrylates has not received proper attention in literature yet.

This work dwells on the issues of controlled synthesis of polymers based on 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA).

Polymerization of 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA) was carried out. Initially, the effectiveness of different chain transfer agents was investigated (AIBN was used as initiator, benzene was used as solvent). It was estimated through analyzing the curves of the molecular mass distribution of polymers at different conversions. It turned out that 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) and 4-cyano-4-[(dodecylsulfanyl-thiocarbonyl)sulfanyl]pentanoic acid (CDTPA) are more effective in RAFT polymerization of TFPMA which is confirmed by the linear increase of MW and the decrease of polydispersity with the rise of conversion. The chain transfer constants (C_tr) of CPDT and CDTPA were estimated by GPC measurement. End-groups of PTFPMA were defined by MALDI-TOF MS/MS. Further, polymerization of TFPMA in the presence of polymeric chain transfer agent PTFPMA was carried out. Then, amphiphilic block-copolymers were obtained using acrylic and methacrylic acid, and glycidyl methacrylate.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-03-00843).
INTERACTION OF REACTIVE OXYGEN DERIVARIVES WITH NITRIC OXIDE IN THE MODEL REACTION OF tryptophAN PHOTOOXIDATION

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The interest in short-lived biologically active simple molecules, in particular nitrogen oxide and active forms of oxygen (ROS), is due to the fact that such compounds act as regulators at various levels of the organization of living organisms. Nitric oxide is a multifunctional signaling molecule that controls intracellular and intercellular processes in organisms. ROS are a necessary component of the vital activity of the cells and the organism as a whole.

The interaction of nitric oxide and its derivatives (such as dinitrosyl complexes of iron (DNIC) with active forms of oxygen leads to the formation of reactive metabolites of nitric oxide and its compounds - peroxynitrite, nitrogen dioxide, NO₂Cl and, which are important components of the immune response in humans and animals. Such interaction can lead to formation of NO and NO⁺ in biosystems and determine not only cytotoxic, but also regulatory and regenerative processes in living organisms.

The photogeneration of ROS is the basis of oxidative destruction of pathological cells and tissues (malignant neoplasms as well as infected wounds, burns, trophic ulcers) in the method of photodynamic therapy (PDT).

In this work the influence of DNIC with thiol-containing ligands and dimethylglucamine salt of chlorin e6 (photoditazine, PD) on the rate of photosensitized oxidation of organic substrate, tryptophan. Also, the DNIC-PD system was investigated in the presence of the amphiphilic polymer-Pluronic F-127. It is shown that in the presence of DNIC, the rate of photodegradation of PD is increased, but the introduction of Pluronic F-127 into the system the rate constant of photodegradation of PD is decreased. It is the fact opens up the possibility of simultaneous use in the treatment of wounds of photodynamic therapy and DNIC without losing the effectiveness of PDT.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (RFBR) (project No. 17-02-00294A).
SYNTHESIS OF SUPRAMOLECULAR COMPLEXES OF (CO)POLYSILOXANE WITH Fe(III), Co(II) AND Ni(II)

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Synthesis of new supramolecular (co)polysiloxanes with electroactive centers and creation on their basis materials with the most important properties (self-healing, electrical conductivity, flexibility, bioinertness, etc.) is challenging task.1,2
In the study new supramolecular complexes of (co)polysiloxane with Fe(III), Co(II) and Ni(II) were synthesized. The PDMS oligomer with 2,6-pyridinedicarboxamide groups was prepared by condensation reaction between bis(3-aminopropyl)-terminated poly(dimethylsiloxane) (Mn = 850) and 2,6-pyridinedicarbonyl dichloride to give a colourless viscous liquid. The obtained copolysiloxane was subsequently crosslinked into solid by Fe(III), Co(II) and Ni(II) chlorides. The structures of the synthesized copolysiloxane were studied by NMR spectroscopy. Molecular mass characteristics of the copolysiloxane were determined by gel permeation chromatography (Mw=48000, Mn=32500). The redox-active properties of supramolecular complexes of copolysiloxane with Fe (III) and Ni(II) using cyclic voltammetry have been established. Electrophysical characteristics of the synthesized supramolecular complexes of copolysiloxane with Fe(III) and Ni(II) were investigated using high-frequency impedance (conductivity $10^{-10}$Sm/cm at 1kHz).

References

Acknowledgements
This work was supported by the Russian Foundation for Basic Research (project No 18-33-20062_mol_a_ved). Measurements were performed at the Center for Magnetic Resonance, the Centre for Innovative Technologies of Composite Nanomaterials (all in Saint Petersburg State University).
Complication of the architecture of amphiphilic copolymers by introducing additional blocks and branching into the structure of macromolecules expands the possibilities for creating on their basis wide range of nanostructures of different morphology that cannot be achieved in the case of linear diblock copolymers. In this respect, molecular brushes – graft copolymers with densely grafted side chains – are of particular interest.

In this study the well-defined amphiphilic molecular polyimide (PI) brushes with hydrophilic polymethacrylic acid (PMAA) side chains and amphiphilic block-copolymer poly(methacrylic acid)-block-poly(methyl methacrylate) (PMAA-block-PMMA) side chains were synthesized by the “grafting from” approach in combination with ATRP method. For that, PI brushes with poly(tert-butyl methacrylate) (PTBMA) side chains were obtained initially. PI brushes with block-copolymer side chains were synthesized by chain extension of MMA from living chain ends of PI-g-PTBMA. At the last step, the target amphiphilic PI brushes with hydrophilic PMAA blocks in side chains of various composition were obtained by acidic hydrolysis of TBMA units. Conditions of the controlled synthesis making it possible to adjust grafting density, length and distribution of side chains were determined.

It was found by TEM and DLS that depending on the composition, size and distribution of side chains the amphiphilic molecular PI brushes possess different self-assembly behaviour in selective solvents.

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INTERACTION OF SMALL ANIONIC LIPOSOMES COMPOSED OF EGG LECITHIN AND CARDIOLIPIN WITH POSITIVELY CHARGED BIODEGRADABLE POLY(N-VINYLCAPROLACTAM-CO-VINYLAMINE) MICROGELS

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Adsorption of liposomes, spherical particles composed of a lipid bilayer, on a microgel particle is an example of a multiliposomal system potent for drug delivery applications (Figure 1). Such constructs have been proposed in the literature as a versatile platforms for a combination therapy of different types of diseases ranging from tumors to infections and auto-immune deficiencies. Liposomes have been previously immobilized on polymer stars, inorganic colloids, polycationic brushes. These and similar systems either do not concentrate a large enough amount of liposomes or contain toxic components and have, thus, only theoretical significance.

In the present study liposomes were adsorbed on biodegradable biocompatible microgels synthesized by RAFT copolymerization of N-vinylcaprolactam and N-vinylformamide with consequent hydrolysis of amide groups in the copolymer. Thus obtained macromolecules were cross-linked with poly(ethylene glycol) diacrylate to yield microgels of effective diameter 200 nm [1].

Liposomes were then adsorbed on these microgel particles and the complexes were characterized with DLS and laser microelectrophoresis. The composition of a saturated complex was estimated. Effect of adsorption on the permeability of the lipid bilayer was studied with use of doxorubicin-loaded liposomes. As the last step, effect of ionic strength on the interaction was investigated.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-33-01190) and the Russian Science Foundation (project No 19-43-04104).
One of the important objects of application of fibrous nanomaterials obtained by electroforming (EF) are chemical current sources, where they can be used as interelectrode separators [1, 2].

The aim of our work was to study the effect of the properties of polymer solutions on the process of EF and the porous structure of the resulting fibrous material for use as a separator in a sealed lead-acid battery.

For the formation of fibrous materials, the following polymers were selected: polyvinylidene fluoride (F-2M, company "Galopolymer Kirovo-Chepetsk", TU 2213-012-13693708-2004) and polystyrene (PS, company "Nizhnekamskneftekhim" TU 2214-126-05766801-2003). The solubility of polymers F-2M, PS and their mixture in a solvent based on dimethylformamide (DMFA) and butyl acetate (BA) in different ratios was estimated using computational and experimental methods [3]. Physicochemical properties of the obtained polymer solutions, such as viscosity, electrical conductivity, and surface tension, are investigated. The fibrous material was obtained by capillary-free EF method at the NSLAB 200S plant. The influence of physical and chemical properties of polymer solutions and technological parameters of electroforming on the porous structure, air permeability, surface density and thickness of the obtained materials was estimated. It was found that an increase in the pore size leads to an increase in the viscosity of polymer solutions. The resulting fibrous materials have been tested in models of lead-acid batteries (SKA) as separation materials such as "sandwich". It is shown that the use of the proposed separation materials increases the efficiency of oxygen ionization in a sealed SKA.

References
NOVEL FLUORINE-CONTAINING NORBORNENE-TYPE POLYMERS FOR MEMBRANE GAS SEPARATION

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One of the promising approaches to obtain thermally and chemically stable materials for efficient gas separation is the synthesis of polymers based on fluorine-containing norbornene derivatives. In order to reveal new correlations between polymer structure and membrane properties the synthesis of a series of novel fluorine-containing tricyclononenes was executed [1]. A series of exo-tricyclononenes was synthesized via stereo- and regio-specific thermal [2σ+2σ+2π]-condensation of the quadricyclane with fluoroalkenes. The synthesized monomers were then successfully subjected to ROMP in the presence of 1st generation Grubbs catalyst.

Figure 1. Novel fluorine-containing metathesis polytricyclononenes

Gas separation properties of new polymers were studied and influence of different fluorine-containing substituents on gas-transport parameters was estimated. Membranes based on the new polymers showed increased selectivity of gas separation for different CH₄-containing gas mixtures.

References

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MULTIBLOCK COPOLYMERS WITH MIXED LINEAR-BRUSH TOPOLOGY WITH BRUSH-TYPE CENTRAL BLOCK

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Multicomponent copolymers containing more than three thermodynamically incompatible blocks attract increased attention due to the possibility of formation of microstructures in films and selective solvents. An important task of modern polymer chemistry is the synthesis of multiblock copolymers with controlled length and architecture of each of the blocks. Currently, approaches based on the combination of several methods of controlled polymerization are often used in the synthesis of such copolymers. Combination of blocks with radically different structure, such as aromatic and aliphatic blocks, is especially of great interest, since it opens up the possibility of varying the properties of copolymers.

In the present work we synthesized new three-component pentablock copolymers PMMA-block-PCL-block-(PI-graft-PMMA)-block-PCL-block-PMMA with mixed linear-brush topology with central block of grafted polyimide with PMMA side chains. Targeted block copolymers were synthesized using a combination of ROP and ATRP. Obtained copolymers were analyzed using 1H NMR and IR spectroscopy, SEC with triple detection and sedimentation-diffusion analysis.

Acknowledgements. This work was supported by the Russian Ministry of Education and Science [grant number 14.W03.31.0022 (Megagrant of the Government of the Russian Federation)].
ARENEDIAZONIUM TRIFLATES FOR POLYLACTIC ACID SURFACE MODIFICATION

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Polylactic acid (PLA) is a biodegradable, biocompatible and eco-friendly biopolymer which nowadays is widely used in different medical applications as surgical sutures, bone screws, scaffolds, and thin coatings for implants [1]. However, such materials have significant limitations due to hydrophobic behavior of PLA surface and a lack of reactive side-chain groups [2].

We proposed an effective and simple method for PLA surface modification by arenediazonium triflates which allows to control surface wettability. The proposed approach includes treatment of thin PLA films surface with water or water with ethanol solutions of arenediazonium triflates under ultraviolet irradiation (254 nm). We obtained a range of previously unknown arenediazonium triflates ArN₂⁺TfO⁻ and investigated its structure and properties by IR, NMR, TGA/DTA/DSC [3]. Modified films were investigated by optic goniometry to determine the effect of different functional groups of arenediazonium triflates on PLA surface hydrophilicity/hydrophobicity. We have found that treatment with 4-carboxyarenediazonium triflate increases surface hydrophilicity up to 45.6° and [1,1'-biphenyl]-4-diazonium triflate increase surface hydrophobicity up to 100.9° in comparison with pristine PLA surface – 74.1°. Scanning electron microscopy was used for morphology survey of modified films surface. Chemical composition of coatings formed onto PLA surface was examined by X-ray photoelectron spectroscopy to assume the coating formation mechanism.

References


Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No. 17-03-01097).
PRODUCTION OF UHMWPE USING THE CATALYTIC SYSTEMS BASED ON TI (III/IV) TETRAHYDROFURANATES

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The processing of UHMWPE is complicated due to its high melt viscosity and is usually conducted by solution method. Another opportunity to process UHMWPE is solvent-free method developed by Smith¹,² and modified by Rastogi³. In this work, we report catalytic systems based on titanium (III/IV) tetrahydrofuranates that are able to produce UHMWPE, suitable for solvent-free processing techniques.

Figure 2. Two types of catalytic systems for production of UHMWPE

These systems catalyze ethylene polymerization with activities up to 1840 kg PE/mol Ti⁻¹·h⁻¹·atm⁻¹. The obtained UHMWPE reaches $M_w$ up to 7.9·$10^6$ Da and has very low bulk density, less than 0.1 g/cm³. That is one of the crucial prerequisites for solid-state formation of tapes from UHMWPE nascent powder. All UHMWPE powders with $M_w$ higher than 2·$10^6$ Da were transformed into tapes by solid-state method described by Ozerin⁴. For the resulting tapes, the highest breaking strength of 2.1 GPa has been achieved.

References

Acknowledgements. This work was financially supported by Russian Science Foundation (Project No. 16-13-10502, Ti (IV) catalytic studies, UHMWPE processing and evaluation) and Russian Foundation for Basic Research (Project No. 17-03-00234, Ti (III) catalytic studies).
Thermo- and pH-responsive poly-(dialkylamino)alkyl(met)acrylamides differing in the structure of the monomer (Figure 1) were synthesized using method of radical polymerization at 70°C. Molecular masses and hydrodynamic radii of scattering objects were determined in chloroform solutions by static and dynamic light scattering. The buffer solutions of polymer were studied using light scattering and turbidity methods. Acidity of solutions changed from pH = 7.00 to 13.00. Temperature dependences of optical transmission, intensity of scattered light and hydrodynamic radii of scattering species and their fraction in solutions were obtained in temperature interval from 15 to 70 °C.

Figure 1. Structures of monomers.

Table 1. Phase separation temperatures $T_1 / T_2$, °C at $c = 0.800$ g/dl for studied polymers.

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Acknowledgements. This work was supported by Russian Foundation for Basic Research (project № 18-33-00576 mol_a).
HIGHLY EFFICIENT METHOD FOR PRODUCING TRANSPARENT AND HYDROPHOBIC SILICA AEROGELS

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In recent years, there has been an increased interest in porous materials, which is related to their applicability in different areas of science, medicine and technology. Aerogels, silica aerogels in particular, have special abilities: (1) high specific surface area and porosity, with a low density; (2) high insulation and soundproof rates; (3) optical transparency; (4) low permittivity; (5) low Young's modulus; (6) thermostability and other.

There are several successive stages that are carried out when obtaining silica aerogels: (1) sol–gel synthesis - wet gel forming; (2) aging and the formation of a lasting gel; (3) workup - preparing the gel for drying (including replacement one solvent with another, the catalyst and byproducts removal etc.); (4) drying - manufacturing an aerogel from the wet gel.

At the same time, we can highlight a number of critical technological problems, that are cost- and time-consuming, in the production of silica aerogels: duration of formation (1) and aging (2) of the gel (one to several days); use of excess amounts of acidic and/or alkaline catalysts/reagents; need to change one solvent in the gel pores to another and other stages of drying preparation (3); duration and high cost of the drying stage.

This work is aimed to solving these problems - developing a new method for obtaining aerogels, based on highly efficient, simple, commercially available and cheap catalytic system. This system will reduce the number and duration of technological stages of the process and will allow for preparing aerogels with tunable transparency, hydrophobicity and mechanical strength (Figure 1).

Figure 1. Transparent (a, b) and fluorescent (c, d) aerogels.

Acknowledgements. This work was supported by the Ministry for Science and Higher Education of the Russian Federation, Grant of the Government of the Russian Federation No. 14.W03.31.0018.
Thermoresponsive star-shaped eight-arms (poly-2-isopropyl-2-oxazoline)–block-(poly-3-(2-oxazoline) propionic acid) (Fig. 1) was synthesized using a “grafting from” approach. Molar mass of sample was about $M_w = 22000$ Da. The aqueous solutions of polymer were studied using light scattering and turbidity methods. The solution concentration was equal to 0.005 g·cm$^{-1}$. Acidity of solutions changed from pH = 2.2 to 12.4. The temperature dependences of optical transmission, intensity of scattered light and hydrodynamic radii of scattering species and their fraction in solutions were obtained in temperature interval from 15 to 55 °C.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-03-00356).
Primary amino group is very suitable functionality for chemical modification of natural polysaccharides in comparison with OH-group. The most common way to introduce primary amino group in macromolecule of sodium hyaluronate is partial deacetylation of sodium hyaluronate. However, this approach requires hard conditions and leads to partial depolymerization of the hyaluronic chain [1]. Herein, we report new one-pot route to introduce amino functionality into macromolecule of sodium hyaluronate (Scheme 1). The first stage consists in preparation of cetyltrimethyl ammonium (CTA) salt of hyaluronic acid, which is soluble in DMSO. The salt interacts with Boc-protected amino acid in the presence of DCC and NHS, followed by deprotection of amino functionality. The change of cetyltrimethyl ammonium cation (CTA) to \( \text{Na}^+ \) proceeds by dialysis of the prepared polymer against sodium chloride solution. Then, after dialysis against water to remove excess of sodium chloride, the obtained polymer was freeze-dried.

![Scheme 1. Introduction amino functionality into macromolecule of sodium hyaluronate.](image)

The obtained polymer was characterized by \( ^1\text{H} \) NMR and infrared spectroscopies and also by elemental (C, H, N) analysis.

References

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USAGE OF DISPERGATORS-MONOMERS TO INCREASE AGGREGATIVE STABILITY OF SYNTHETIC LATEXES

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It is showed that one of the reasons of synthetic latexes coagulation and coagulum formation is destabilizing influence of stable macroradicals on polymer-monomer particles [1]. Electron density of macroradicals leads destabilization of hydrate adsorption layer and to latex coagulation during storage period if adsorption layer protection is insufficient and monomer conversion rate is high [2]. Full termination of macroradicals by inhibitors of radical polymerization increases latex stability. EPR research showed reaction between stable radicals of EPR marker and living macroradicals inside polymer-monomer particle.

Stabilizing ability and surface activity of naphthalene dispersing agents lowers with increase of its polycondensation rate. Naphthalene dispersing agents lower critical micelle concentration of surfactant, prolong micellar stage of polymerization, increase emulsifier saturation of adsorption layer and macroradicals termination rate in polymer-monomer particles during polymerization.

Dispersing agents-monomers we synthesized showed similar effect and are able to built-in polymeric chain thus reducing concentration of no biodegradable naphthalene compounds in waste waters. Dispergators monomer are proposed as a replacement of existing dispersive agents.

References
TITANIUM (III) AS AN ACTIVE PARTICLE IN THE POLYMERIZATION OF ETHYLENE AND VARIOUS METHODS OF ACTIVATION OF TITANIUM (III/IV) POST-METALLOCENE COMPLEXES TO OBTAIN UHMWPE

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As a result of this work, the catalytic activity of non-metallocene complexes of titanium (III) and (IV) (Figure 1) was compared during the polymerization of ethylene. Also the oxidation state of the transition metal in these complexes before and after their activation by aluminum (Et₂AlCl, Et₃Al₂Cl₃, EtAlCl₂, Et₃Al) and magnesium (Bu₂Mg) organic compounds or their binary mixtures was determined. The activation process for both complexes was studied by EPR, NMR, and UF-Vis spectroscopy.

Figure 1. structure of complex Ti (III) and Ti (IV).

Both systems, Ti (III) and Ti (IV), catalyze ethylene polymerization with activities up to 4500 kg PE/mol Ti⁻¹·h⁻¹·atm⁻¹. It was found that the complexes of titanium (III), are two times more active than ones of Ti (IV). Obtained UHMWPE reaches Mₘ up to 7.2·10⁶ Da and has very low bulk density, less then 0,1 g/cm³. That is one of the crucial prerequisites for solid-state formation of tapes from UHMWPE nascent powder. All UHMWPE powders with Mₘ higher than 1,6*10⁶ Da were transformed into tapes by solid-state method described by Ozerin [1]. The highest breaking strength of 2.9 GPa has been achieved for the resulting tapes.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No. 16-03-10502) and Russian Foundation for Basic Research (Project No. 17-03-00234).
Pervaporation is a promising method for the separation of liquids in the bioprocessing, petrochemical and pharmaceutical industries. This method allows to separate closely boiling and thermally unstable components, as well as azeotropic mixtures and mixtures of isomers. Pervaporation is an environmentally-friendly method of separation, for its implementation does not require expensive equipment and high energy consumption. The rapid development of pervaporation requires the search for new high-performance membrane materials with desired properties.

In the present work the novel membranes based on polyvinyl alcohol were prepared by bulk modification. Bulk modification was carried out by introducing the metal-organic framework UiO-66(NH$_2$)-EDTA into the PVA matrix. The improvement of the transport properties of polymer membranes occurs due to the porous structure of the metal-organic frameworks.

The study of the physicochemical properties of the membranes was carried out by scanning electron microscopy, IR spectroscopy and thermogravimetric analysis. Contact angle was using for study of the surface properties of the membranes, the degree of swelling was study by the gravimetric method.

The transport properties of the developed membranes were studied by pervaporation separation of the azeotropic mixture of isopropanol - water (88/12 wt.%). All developed membranes were highly selective for water (more than 95 wt.% water in the permeate). The introduction of UiO-66(NH$_2$)-EDTA into the PVA matrix leads to significant changes in both the physicochemical and transport properties of polyvinyl alcohol membranes.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-73-20060). The experimental work was facilitated by equipments from Interdisciplinary Resource Centre for Nanotechnology, Chemistry Educational Centre, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Magnetic Resonance Research Centre, Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Nanophotonics Centre and Centre for Geo-Environmental Research and Modelling (GEOMODEL) at St. Petersburg State University.
CURRENTLY, ONE OF THE MOST IMPORTANT AREAS IN MODERN SOCIETY IS THE DEVELOPMENT OF SUSTAINABLE PROCESSES. MEMBRANE SEPARATION METHODS ARE RELATED TO SUCH PROCESSES DUE TO THE FACT THAT THESE METHODS ARE ENVIRONMENTALLY FRIENDLY, USE COMPACT EQUIPMENT AND HAVE LOW POWER CONSUMPTION. ONE OF THE MOST POPULAR MEMBRANE PROCESSES FOR THE SEPARATION OF LOW MOLECULAR WEIGHT COMPONENTS IS THE PERVERSATION, WHICH ALLOWS THE SEPARATION OF AZEOTROPIC MIXTURES, MIXTURES OF ISOMERS AND THERMALLY UNSTABLE MIXTURES. THE RAPID DEVELOPMENT OF THIS METHOD REQUIRES THE SEARCH FOR NEW HIGH-PERFORMANCE MEMBRANE MATERIALS WITH DESIRED PROPERTIES.

IN THE PRESENT WORK THE NOVEL MEMBRANES BASED ON POLYPHENYLENE ISOPHTHALAMIDE (PA) WERE PREPARED BY BULK MODIFICATION. BULK MODIFICATION WAS CARRIED OUT BY INTRODUCING THE METAL-ORGANIC FRAMEWORK UIO-66(NH2)-EDTA INTO THE PA MATRIX. THE IMPROVEMENT OF THE TRANSPORT PROPERTIES OF POLYMER MEMBRANES OCCURS DUE TO THE POROUS STRUCTURE OF THE METAL-ORGANIC FRAMEWORKS.

THE STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF THE MEMBRANES WAS CARRIED OUT BY SCANNING ELECTRON MICROSCOPY, IR SPECTROSCOPY, NMR SPECTROSCOPY. ALSO CONTACT ANGLE AND SWELLING DEGREE OF THE MEMBRANES WERE MEASURING.


ACKNOWLEDGEMENTS. THIS WORK WAS SUPPORTED BY THE RUSSIAN SCIENCE FOUNDATION (PROJECT NO 17-73-20060). THE EXPERIMENTAL WORK WAS FACILITATED BY EQUIPMENTS FROM INTERDISCIPLINARY RESOURCE CENTRE FOR NANOTECHNOLOGY, CHEMISTRY EDUCATIONAL CENTRE, CENTRE FOR DIAGNOSTICS OF FUNCTIONAL MATERIALS FOR MEDICINE, PHARMACOLOGY AND NANOELECTRONICS, MAGNETIC RESONANCE RESEARCH CENTRE, THERMOGRAVIMETRIC AND CALORIMETRIC RESEARCH CENTRE, CENTRE FOR X-RAY DIFFRACTION STUDIES, CHEMICAL ANALYSIS AND MATERIALS RESEARCH CENTRE, NANOPHOTONICS CENTRE AND CENTRE FOR GEO-ENVIRONMENTAL RESEARCH AND MODELLING (GEOMODEL) AT ST. PETERSBURG STATE UNIVERSITY.
Nowadays, the essential improvement of the transport properties of polymer membranes can be achieved by the modification of the polymer matrix by inorganic filler that yields in developing the mixed – matrix membranes (MMMs). The introduction of inorganic filler in the polymer matrix of the membrane allows getting tailoring properties. MMMs combine the simplicity of processing polymer membranes with the superior transport properties of inorganic particles.

In the present work the novel membranes based on polyvinyl alcohol were prepared by bulk modification. Bulk modification was carried out by introducing the metal-organic framework FeBTC into the PVA matrix. The improvement of the transport properties of polymer membranes occurs due to the porous structure of the metal-organic frameworks.

The study of the physicochemical properties of the membranes was carried out by scanning electron microscopy, IR spectroscopy, and thermogravimetric analysis. Contact angle was using for study of the surface properties of the membranes, the degree of swelling was study by the gravimetric method.

The transport properties of the developed membranes were studied by pervaporation separation of the azeotropic mixture of isopropanol - water (88/12 wt.%). All developed membranes were highly selective for water (more than 95 wt.% water in the permeate). The introduction of FeBTC into the PVA matrix leads to significant changes in both the physicochemical and transport properties of polyvinyl alcohol membranes.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-73-20060). The experimental work was facilitated by equipments from Interdisciplinary Resource Centre for Nanotechnology, Chemistry Educational Centre, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Magnetic Resonance Research Centre, Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Nanophotonics Centre and Centre for Geo-Environmental Research and Modelling (GEOMODEL) at St. Petersburg State University.
Today, biosensors are increasingly used in medicine by which wide range of relevant biological molecules can be conveniently detected or quantified. The desire for miniaturization of devices makes researchers to look for new materials. One of solutions was to use organic semiconductors as biological sensors. Such materials have properties that could be interested from the point of view of flexibility, ease of processing, biocompatibility and mixed ionic and electronic conductivity.

Thus, the aim of the work was to create electrically conductive core/shell particles that are promising for creating sensory films on their basis.

For the polymerization of the electrically conductive layer from 3,4-ethylenedioxythiophene (EDOT), it is necessary to obtain stable particles with a diameter of 5-10 μm with a surface layer enriched in sulfo groups. The paper shows several ways of forming the polymer core such as copolymerization of styrene with sodium 4-vinylbenzenesulfonate by emulsion and dispersion polymerization, as well as inverse suspension polymerization of sodium 4-vinylbenzenesulfonate.

As a result, particles with a diameter range of 250-650 nm were synthesized by emulsion polymerization, 300-650 nm by dispersive polymerization, 5-10 μm by inverse suspension polymerization. At the same time, the concentration of sulfo groups in the surface layer of particles obtained by inverse polymerization was 145-300 μmol/m², which is 1000 times greater than that for particles obtained by emulsion and dispersion polymerizations. Therefore, such particles are of the greatest interest for further research.

The forming of electrically conductive shell was carried out by polymerization of EDOT in the presence of various initiators: K₂S₂O₈ and FeCl₃. As a result, it turned out that the initiating system has a strong effect on the system, for example, particles aggregated and formed a flake-like precipitate in the presence of FeCl₃, but during polymerization in milder conditions, in the presence of K₂S₂O₈, the particles saved their spherical shape.
Platinum (0) and (II) complexes, notably cis-[PtCl\(_2\)(BnCN)]\(_2\) and Karstedt’s catalyst, are used for self-cross-linking of the polymethylhydrosiloxanes by the dehydrogenative reactions between Si–H groups\(^1\). The cross-linking is carried out using a one-component system at RT in air. Karstedt’s catalyst leads to the formation of Si–Si cross-links, obviously, by dehydrogenative coupling and Si–O–Si cross-links by oxygenation or autoxidation of Si–Si bonds. The cis-[PtCl\(_2\)(BnCN)]\(_2\) results in predominantly Si–O–Si cross-links. The cis-[PtCl\(_2\)(BnCN)]\(_2\) allows creating high-quality silicone rubbers without visible mechanical defects (bubbles and cracks) in comparison with hyperactive Karstedt’s catalyst. Swelling measurements and SSNMR demonstrated that cis-[PtCl\(_2\)(BnCN)]\(_2\) forms silicone rubbers with a 1.5–2 times lower cross-linking degree than in the case of Karstedt’s catalyst. This cross-linking approach can be used to obtain new Si–H-containing silicone materials, in particular, for creation heterogeneous reducing agents.

![Figure](image.png)

**Figure.** Cross-linking of polymethylhydrosiloxane.

References


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The influence of crosslinking conditions and the type of crosslinking agent from a series of diglycidyl ethers of glycols (1,4-butanediol, ethylene glycol, glycerol and polyethylene glycol) on the morphology, swelling degree, hydrodynamic characteristics and sorption capacity of supermacroporous monolithic materials (cryogels) based on polyethylenimine (PEI) have been investigated. We have found that diglycidyl ether of 1,4-butanediol (DGE-1,4-BD) with a ratio of crosslinking agent (CA): PEI 1:4 is the most effective crosslinking agent at -20 °C. Using confocal scanning microscopy, it was shown that the cryogel has a homogeneous pore structure with an average size of 106 µm (Fig.1A). Static sorption capacity of the sorbent for copper (II) ions was 2.21 mmol/g.

Figure 1. Crosslinked PEI cryogel (DGE-1,4-BD:PEI =1:4): confocal SEM image (A); breakthrough curve of copper (II) ions sorption (B).

Breakthrough curves of copper (II) ions sorption on PEI cryogels were obtained at a flow rates 120-300 bed volume (b.v.)/h. The monolithic sorbents provided removal of copper down to the lowest acceptable limit (<1.0 mg/l) with effective dynamic sorption capacity of 1.5 mmol/g at flow rate up to 250 b.v./h (Fig.1B).

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Polymerization of Dopamine on Air/Water Interface

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Poly(dopamine) has attracted interest recently as a universal surface modification agent in a broad range of biotechnological, electrochemical and nanotechnological applications [1]. One of the most common way of the polydopamine synthesis is dopamine oxidation in its aqueous solution. Dopamine hydrochloride is easily oxidized and undergoes spontaneous polymerization in a slightly alkaline environment. Oxygen from the air acts as an oxidant. The reaction proceeds spontaneously under mild conditions. Polymerization leads to changes of the solution color from almost colorless via light brown to dark brown. The polymer film is formed on the surface and polymer grains are formed in the bulk. The dynamic surface properties of polymer film at the air-water interface during formation were studied by dilatational surface rheology, ellipsometry and Brewster angle microscopy (BAM). The dynamic surface elasticity was measured as function of time and concentration by the oscillation ring method. It was shown that there is a significant increase of the elasticity for solutions with concentration from 0.75 g/l to 2 g/l. The highest values of the dynamic surface elasticity (~ 60 mN/m) were obtained for solutions with a concentration of 1 g/l. These values are comparable with those for solutions of globular proteins [2] indicating that the film consists of separate domains. The high surface elasticity is due to the interactions of relatively rigid domains of the polymer film. This assumption is supported by BAM images. Different steps of the growth of the film are observed. At first, the heterogeneity of the film increases gradually at the approach to equilibrium. The higher the initial concentration is, the faster the polymerization takes place and the thicker is the formed film. The dynamic surface elasticity decreases for dopamine solutions of 2 g/l and 5 g/l. For these solutions, the thickness of the polymer film reaches about 80 nm. In this case the film could break under its own weight. The cracks in the film lead to weakening of the mechanical properties of the layer.

References

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SYNTHESIS AND MACROMOLECULAR REACTIONS OF SILICON-CONTAINING POLYENES

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Organosilicon polymers are widely used as precursors of ceramics, photocurable polymers, crosslinking agents, membrane materials, etc. This study aimed at the synthesis of new silicon-containing multiblock copolymers, which could be of potential interest for gas separation. New copolymers built from glassy norbornene blocks and amorphous blocks of organosilicon olefins were synthesized using the cross-metathesis macromolecular reaction between polyenes [1]. The parent polynorbornene (PNB) and poly(1,1-dimethylsilapentene-3) (PSiP) were prepared by ROMP of norbornene and 1,1-dimethylsilacyclopentene-3 (SiP) in the presence of Grubbs’ Ru-catalysts of 1st (G1) or 2nd (G2) generation. Poly(1,1,3,3,5,5-hexamethyltrisiloxanyl-5-dcenylene) (PSiO) was obtained by ADMET polymerization of bis(5-hexenyl)-1,1,3,3,5,5-hexamethyltrisiloxane) (SiO). The cross-metathesis between PNB and PSiP or PSiO was carried out in the presence of G1 and G2.

Figure 1. Macromolecular cross-metathesis reaction

New NB-SiP and NB-3SiO copolymers with various degrees of blockiness were obtained and characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR, DSC, IR, and GPC. It was shown that their thermal properties depend on the composition and average block length and can be regulated by adjusting the cross-metathesis conditions.

References

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PHYSICO-MECHANICAL PROPERTIES OF POLYSTYRENE COMPOSITES FILLED WITH DIFFERENT TYPES OF PARTICLES

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Rapidly growing applications of composite materials in industry stimulate analysis of various aspects of their mechanical behavior. The aim of this work was the study of the influence of various types of (nano)fillers on physico-mechanical properties of polystyrene (PS) based composites. Block samples of composites filled with different types of particles (MMT, HNT, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CB, CNT, Mica) were obtained by melt technology. The concentration of particles amounted to 0, 5, 10, and 20 wt\%. Rheological characteristics of composite melts were determined using the rheometer Physica MCR 301 (Anton Paar), the influence of the particles concentration on the mechanical properties of composites in tension was studied on Instron system. The dispersion of particles in the polymer matrix was estimated from the micrographs of cryo-cleavage surfaces of the composite samples, taken using a Carl Zeiss Supra-55 scanning electron microscope. The mechanical properties were studied in uniaxial tension and three-point bending tests. Basing on the data obtained, the strength at break, strain at break and elastic modulus of composites were determined.

It was shown that the introduction of MMT, CNT, and Al\textsubscript{2}O\textsubscript{3} cause an increase in material viscosity by an average of 2 to 5 orders of magnitude over the pure PS. This increase is indicative of the formation of a network structure between the polymer and filler particles. The introduction of more rigid particles were shown to provide an increase in the elastic modulus of composites. HNTs were shown to be most promising among the considered alumosilicate inclusions demonstrating substantial increase of elastic modulus with concentration along with acceptable aggregation even at 15% concentration. The best results though were obtained with carbon nanoparticles (CNT and CB). At the same time, it should be noted that composites containing CB demonstrate higher strength than pure PS.

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POLYMER-STABILIZED NEMATIC LIQUID CRYSTAL FOR BEAM DEFLECTOR DEVICE

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The beam deflector device is a necessary part of the holographic display system and LIDARs. One of the fastest approaches to modulate optical phase shift in time is based on the use of nematic liquid crystals (LC). Under the action of the electric field, the Fréedericksz transition from the planar state to the homeotropic state is observed (Fig. 1), giving rise to the phase shift between the ordinary and extraordinary rays.

The main problem of these systems is relatively slow relaxation time. One possible solution is the stabilization of the nematic by a polymer network, which allows increasing Frank’s elastic constants, thereby reducing the relaxation time. In this work mesogenic (capable of LC phase formation) or non-mesogenic monomers (1.5-5.0%) and UV photoinitiator are introduced into the highly birefringent LC-mixture and polymerized, resulting network stabilized liquid crystal.

![Freedericksz transition for nematic phase](image)

The series of monomers were studied, with variable concentration of monomers and initiator and different conditions of UV-irradiation. The samples were characterized by polarization microscopy and by the electro-optical setup (the turn-off time was determined).

Some regularities for monomers and irradiation condition are established. It is shown, that for the polymer-stabilized system, it is possible to obtain relaxation time, which is four times better (10 ms) than in pure LC.

Acknowledgements. This work was supported by the Samsung Advanced Institute of Technology
Aromatic polyimides (PIs) have an excellent combination of thermal and mechanical properties and cater for numerous applications. However, current demand for PI materials requires an ongoing improvement of the said properties. Incorporation of nano-components into polymer matrices has been proved to enhance functional properties of the resulting composite. Recently, nanocomposites based on the PI matrices have been being under intensive study. Nevertheless, there are still many issues in the design of such nanocomposites, not solely in processing, but also in understanding interactions between the polymer matrix and nanoparticles and the functional response of the final material.

In this work, we tackled these issues. We have prepared nanocomposite films based on a number of aromatic PIs doped with CeO$_2$ nanospecies. The latter have a fascinating feature of changes in charge-states Ce$^{4+}$ to Ce$^{3+}$, thereby affecting the properties of the composite. The thermal analysis of the nanocomposites under study in air and in inert atmospheres reveals that ceria nanoparticles enhance thermal properties of the composites based on only such PIs which contain SO$_2$-group in the elementary units of their chains. The reason behind this enhancement is suggested. The mechanical and thermomechanical properties of the nanocomposite films are also reported. Results obtained provide new options for the design of polyimide nanocomposite materials with enhanced thermal stability.

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Age-related macular degeneration and diabetic retinopathy are among the most common ocular diseases that lead to vision loss. These pathologies are characterized by proliferation and migration of epithelial cells and increase in vascular permeability and inflammation. [1]. A key role in the regulation of these processes plays vascular endothelial growth factor (VEGF).

In the last decade, a great number of studies were focused on the development and testing of anti-VEGF therapy in vitro and in vivo. One of the most promising approaches is an intracellular delivery of small interfering RNA, which is capable of knocking down the VEGF gene. [2] The major obstacles for RNA delivery are poor cellular uptake, insufficient targeting of RNA molecules and their instability under physiological conditions. To overcome these problems polymer particles can be applied as nanocarriers for siRNA.

This work is devoted to the creation of biocompatible polypeptide nanoparticles based on lysine, glutamic acid, phenylalanine and isoleucine. The target copolymers were obtained using ring-opening polymerization of corresponding N-carboxyanhydrides. The obtained nanoparticles were characterized by nanoparticle tracking analysis and dynamic light scattering and their morphology was studied by a transmission electron microscopy. Transfection and cell cytotoxicity of the nanoparticles were studied in vitro.

The experiment of intracellular delivery of siRNA encapsulated in polymer particles was carried out and the VEGF gene knockdown was successful.

References

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COORDINATION POLYMERS OF 1-AZOLYL ADAMANTANE 3-CARBOXYLIC ACIDS.

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Coordination polymers have been a subject of intensive research in the past decades. A wide variety of organic spacers have been utilized to link coordinating functions together, including adamantane. Adamantane derivatives attract the attention of researchers for the construction of coordination polymers because of their conformational rigidity and thermal stability, but most of the works are related to 1,3-adamantane dicarboxylic acid as a dicarboxylate linker. Here we prepared an orthogonally substituted adamantane derivates 3-(triazol-1-yl) or 3-(tetrazol-1-yl) adamantane carboxylic acids. Several coordination polymers were prepared and their a range of their properties was studied. One of the polymers was found to act as a catalyst in Chan-Evans-Lam arylation of imidazoles with boronic acids. Influence of the reaction conditions on the geometry of complexes is also observed.

Figure 1. Reaction of the ligand formation and two examples of obtained complexes.

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CHROMATOGRAPHIC EVALUATION OF THERMAL STABILITY OF POLY (3-TRIBUTOXYSILYLTRICYCLONONENE-7)

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Thermal stability is one of the most important parameters of the stationary phases in gas chromatography. However, there are no common procedures for determination of this characteristic for the newly developed polymers being the candidates for utilization in GC as the stationary phases. The present work is devoted to the evaluation of process of thermal ageing of poly (3-tributoxysilyltricyclononene-7) (See Figure. 1) using chromatographic method.

Figure.1. The structure of the metathesis poly(3-tributoxysilyltricyclononene-7)

The polymer was placed into the quartz capillary and then the following procedures were performed:
1) efficiency and selectivity of the native polymer used as a stationary phase were determined;
2) the accelerated thermal ageing of the polymer was performed at 200°C for 7 h;
3) efficiency and selectivity of the aged polymer used were evaluated.

The efficiency of the original polymer was more than 15 000 theoretical plates per column for the best chromatograms. This value practically did not change after column heating, meaning that poly(3-tributoxysilyltricyclononene-7) might be used as a stationary phase in GC at temperatures up to 200°C.
NOVEL MUCOADHESIVE GRAFT-COPOLYMERS FOR THE TREATMENT OF ANTERIOR SEGMENT OCULAR DISEASES

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Topical administration, mostly in the form of eye drops, is employed to treat anterior segment diseases. Upon administration, precorneal factors and anatomical barriers negatively affect the bioavailability of topical formulations. Mucin present in the tear film plays a protective role by forming a hydrophilic layer that moves over the glycocalyx of the ocular surface and clears debris and pathogens [1]. Tear film displays a rapid restoration time of 2–3 min, and most of the topically administered solutions are washed away within just 15–30 s after instillation. Thus, the colloidal nanosized carriers have been widely explored to overcome various static and dynamic ocular barriers.

Novel drug delivery strategies such as bioadhesive particles and gels were developed to sustain drug levels at the target site. In this work we aim to develop novel mucoadhesive thermo-responsive hybrid polymer carriers for topical non-invasive application to improve drug delivery to the anterior segment of the eye. The polymers based on natural polysaccharides and thermo-responsive pNIPAAm chains were obtained via RAFT polymerization. Physico-chemical properties were widely studied. Nanoparticles and polymer gels were successfully obtained using thiol-chemistry approaches. The encapsulation and release of dexamethasone and ³H-propranolol were studied and optimized for ocular delivery. Finally, the in vitro retention study of polymers on the corneal epithelium was done using mucin binding affinity assay.

References

Acknowledgements. This work was supported by the Megagrant №14.W03.31.0025.
The uncontrolled release of antibiotics into the environment with wastewaters of pharmaceutical production, hospitals, livestock and poultry farms has been recently recognized as a serious danger to human health. Due to the low efficiency of municipal wastewater treatment facilities towards many classes of antibiotics, the search for new approaches and materials for efficient removal of antibiotics from wastewaters of pharmaceutical plants and drinking water is the urgent problem.

Fluoroquinolones are widely used antibiotics, having high chelating ability with respect to ions of divalent and trivalent metals. Earlier, we have developed a method of fabrication of metal-affine sorbents based on carboxyalkyl chitosan cryogels crosslinked with hexamethylene diisocyanate [1].

In this work, the kinetics and dynamics of ciprofloxacin sorption, as the most common fluoroquinolone, by metal-affine sorbents based on cross-linked carboxyethylchitosan (CEC) containing Cu (II) and Al (III) ions have been studied. Using kinetics data, we have shown that the sorption of ciprofloxacin on the CEC-Cu (II) cryogels takes place in the external diffusion mode that is determined by the highly developed porous structure of the sorbents and good accessibility of all active sorption centers. The dynamics of ciprofloxacin sorption was investigated on Cu(II)-containing metal-affine sorbents at flow rates up to 40 bed volumes per hour (b.v. /h). Effective dynamic sorption capacity was calculated from breakthrough curves assuming that sorption was efficient if 99% of ciprofloxacin was recovered. We have shown that effective dynamic sorption capacity of CEC-Cu (II), crosslinked with epichlorohydrin, reaches 0.42 mmol/g at a flow rate of 10 b.v. /h and pH 7.5 for initial ciprofloxacin concentration 2·10^{-4} mol/l.

References
PREPARATION AND PERVAPORATION PERFORMANCE OF SULFONATED COPOLYIMIDE.

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Polyimides containing high-polar groups, especially sulfonated polyimides, recently became an object of interest due to their potential application as a material for diffusion membranes [1]. Usually, they are being considered as a suitable material for proton exchange membranes. The presence of mobile hydrogen atoms in sulfonic groups of a polymer ensures the availability of proton-conductivity when the polymer is swollen in a protonic solvent. However, there are only a few articles where the transport properties of sulfonated polyimides in the processes of membrane liquid or gas separation were studied [2,3].

A novel sulfonated copolyimide was synthesised via polycondensation of 4,4’-Diaminobiphenyl-2,2’-disulfuric acid (BDSA), 4,4’-oxydianiline (ODA) and 5,5’-[1,3-Phenylenebis(oxy)]bis(2-benzofuran-1,3-dione) in m-cresol. The chemical structure of the obtained polymer was confirmed with NMR spectroscopy. Thermodynamical properties of obtained films were characterised by the methods of differential scanning calorimetry and thermal gravimetric analysis.

For the investigation of transport properties of obtained copolymer dense films were prepared and tested in the process of pervaporation of methanol/toluene mixtures at 20, 40 and 60 °C. Obtained films showed great values of permeability and selectivity in the wide range of mixture compositions and are considered as a potential pervaporation membranes material for effective methanol/toluene mixtures separation.

References
ETHYLENE POLYMERIZATION AND COPOLYMERIZATION WITH HEXENE-1 ON CATALYTIC SYSTEMS BASED ON TI (IV) FLUORINATED SALEGININ COMPLEXES

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Earlier we have reported catalytic systems based on Ti (IV) complexes with OO-type ligands that are effective both in polymerization and copolymerization of olefins [1,2]. These systems were further tested in tandem catalysis to yield LLDPE. In this work, we report new Ti (IV) complexes with fluorinated ligands that can form effective catalysts for olefin polymerization and copolymerization.

Figure 1. Catalytic systems.

The best results in ethylene polymerization have been shown by the catalytic system 1/Et2AlCl/Bu2Mg. The activity reached 1600 kg PE/mol Ti-1·h-1·atm-1 and the resulting polymer (UHMWPE) was formed into tapes with breaking strengths up to 2.6 GPa. However, the catalytic system 3/Et2AlCl/Bu2Mg was superior to other systems in ethylene copolymerization with hexene-1 (activity up to 4500 kg/mol Ti-1·h-1·atm-1). The studies of copolymers properties are in progress.

References

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Water-swellable polymer composites combine remarkable mechanical characteristics with the ability of swelling in water [1]. The ability of the composite to swell in water is provided by water-absorbing components (WAC). One of the main drawbacks of such composites is the insufficient interfacial interaction of particles of the hydrophilic WAC and the hydrophobic elastomer matrix. This leads to the leaching of the WAC from the matrix of the composite and the reduction of its mechanical characteristics. In this regard, it is important to find a way to enhance the interfacial interaction in water-swellable polymer composites to improve the integrity of the material.

A possible solution to this problem may be the creation of water-swellable composites using chlorosulfonated polyethylene, due to its reactivity [2, 3]. Thus, the purpose of this work is to study the possibility of enhancing interfacial interactions in water-swellable polymer composites based on chlorosulfonated polyethylene, as well as to study their properties.

Chlorosulfonated polyethylene, high-pressure polyethylene, ethylene-vinyl acetate copolymer, and Na-carboxymethylcellulose as a WAC were used as components of the composite. The composite was obtained in a two-rotor mixer for 10 minutes, under conditions of high shear rates (100 rpm) and at 190 °C providing an increased value of the decay rate constant of sulfonyl chloride groups in chlorosulfonated polyethylene.

As a result of the study of the sample surface by scanning electron microscopy, the best interaction of the particles of the WAC with the polymer matrix was found. This is reflected in a decrease in the leaching of the WAC after exposure to water. These compositions have high mechanical characteristics (6-8 MPa) in combination with the possibility of achieving high degrees of swelling.

References:
DEVELOPMENT OF SILICON BASED COMPOSITE PHOTOCURABLE NANOMATERIALS FOR 3D LASER PRINTING

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Laser 3D printing is the technology of additive manufacturing of models, prototypes and products from liquid photo-curing compositions. The method is based on the irradiation of a liquid photopolymer mixture with a laser or other optical radiation to create digital models.

Organosilicon compounds are used as objects of study, their advantage is that the objects obtained from them with the help of 3D printing are bioinert and can be turned into ceramic by pyrolysis [1]. In the work using IR-Fourier, NMR spectroscopy, solubility and swelling tests, thermogravimetric analysis were investigated photocuring of polydimethylsiloxanes with terminal acryloxy and methacryloxy groups, as well as photo curing of 3-glycidoxypropyltrimethylsilane. Possible mechanisms of their photocuring are proposed.

Composites based on these compounds with nanostructured fillers, such as silicon dioxide, yttrium oxide doped dysprosium and carbon nanotubes, were obtained. These composites were studied using Raman scattering and scanning electron microscopy. The formation of new chemical bonds for a composite based on photocured 3-glycidoxypropyltrimethylsilane and oxide nanoparticles has been found.

References
Modification of known polymers by incorporation of different fillers is a perspective method to create new materials with improved characteristics. Nowadays branched polymers are actively studied, particularly polymer brushes. Incorporation of polymer brushes not only changes the matrix polymer structure but also allows varying of polymer composition properties. The objects of the present work are composite materials based on poly(m-phenylene-iso-phthalamide) (PA) and copolyimide brush that is regularly grafted polyimide with side poly(methyl methacrylate) chains (PI-PMMA). The aim of the work is to study influence of PI-PMMA as filler on a structure, physical, mechanical, thermal properties of composite materials PA/PI-PMMA. Morphology of test composite films was studied by scanning electron microscopy. Interactions between polymers were defined using viscometry, dynamic light scattering and IR-spectroscopy. Length of the side PMMA chains influences significantly on interactions between the matrix and polymer brush and mechanical properties of the composite films. Particular attention was paid to stable microphase separation in the compositions. It was revealed that the film compositions have microphase separation with uniform distribution of polymer brush there but dense durable films containing polymer brush with concentration up to 30 wt% were obtained. Membranes based on compositions PA/PI-PMMA were prepared for pervaporation of methanol-hexane mixture and gas separation. It was found that the test membranes are effective materials for pervaporation and gas separation.

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Due to its uniquely low coefficient of friction, as well as its ability to maintain its value over a wide temperature range, polytetrafluoroethylene (PTFE) attracts the attention of tribologists around the world. Interest as a tribological material does not subside due to the fact that the matrix easily responds to all sorts of modifications by introducing a variety of fillers. The aim of the work is to study the complex of various types of fillers on the physicomechanical and tribological characteristics of composites based on PTFE. The objects of study were PTFE and composites based on it, containing as fillers carbon fibers (CF) or basalt fibers (BF) with functional additives, FORUM® nano-dispersed powder and activated aluminium oxide ($\text{Al}_2\text{O}_3$). FORUM® was used as a functional additive to reduce the friction coefficient, and $\text{Al}_2\text{O}_3$ - to improve the adhesion interaction at the interface. Characteristics of the shape and size of the particles, and the chemical composition of the filler significantly affect the properties of the mixture. CF improve compressive strength, making it more resistant to wear. Test samples were obtained by dry mixing the components, followed by cold pressing to form them, after which they were sintered in a muffle furnace at a temperature of 375 °C and calibrated to correct the shape of the samples and eliminate the effects of thermal shrinkage during sintering. Mechanical activation technology was used in a planetary mill Activator-2S (Russia). The main technical characteristics were obtained by standard methods: "Compression test method" (GOST 4651-2014), "Method of determining the friction coefficient" (GOST 11629-2017), "Elastic modulus" (GOST 9550-81). The results of the study showed that the use of complex filling in a certain combination leads to a significant improvement in the properties of composites based on PTFE: the compressive strength increases by 40-80%, a high degree of crystallinity is observed in the composite with 18 wt.% BF and 0.5 wt.% $\text{Al}_2\text{O}_3$, the wear resistance increases up to 1500 times in contrast to the initial PTFE. Thus, new promising formulations of polymer composite materials (PCM) based on PTFE for tribological purposes with enhanced performance characteristics have been obtained.
EVOLUTION IN THERMOMECHANICAL PROPERTIES OF POLYCAPROLACTONE BASED MULTIBLOCK POLY(URETHANE-UREA)S DEPENDING ON THE STRUCTURE

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Segmented polyurethanes are block-type copolymers with [A-(B)ₖ] structure, where A is a hard block, and (B)ₖ is a soft one. The role of soft blocks can act as aliphatic glycols, which have ether and ester groups in their structure, while hard blocks are usually represented by aromatic diisocyanates with diols or diamines. The resulting urethane and/or urea groups contribute to microphase separation and the formation of a domain structure in multiblock copolymers. Currently, materials based on segmented polyurethanes are widely used as rigid and flexible foams, elastomers, functional coatings, adhesives and sealants.

In this work, the synthesis was carried out and the structure and properties of segmented polyurethanes were investigated. A combination of 4,4’-methylene diphenyl diisocyanate (MDI), 2,4-diisocyanato-1-methylbenzene (TDI), 1,3-phenylenediamine (MF) and bis[4-(4-aminophenoxy) phenyl] sulfone (BAPS) was used as hard aromatic segments. The soft segments were polycaprolactone (PCL) with a molecular weight of 530 g/mol and 2000 g/mol. The synthesis was carried out according to a two-stage scheme. The first stage of the process was accompanied by the formation of urethane. The second one was urea formation as a result of the interaction between isocyanate and amine groups. The structure of the obtained multiblock copolymers was confirmed by IR and NMR spectroscopy. The deformation-strength properties and the effect of changes in the system of hydrogen bonds with an increase in the molecular weight of the flexible segment were studied. It was shown that polyurethanes (MDI-PCL2000-MDI) BAPS and (MDI-PCL530-MDI) BAPS are thermoplastic elastomers: the flow stress reaches 50 MPa, the elongation at break is up to 900%. The thermal properties of the obtained materials were studied by TGA, DSC and DMA methods. The values of the glass transition temperature in copolymers range from -52°C to 66°C, the destruction temperature is 256-298°C.

References
GEL ELECTROLYTES BASED ON CHITOSAN, CHOLINE CHLORIDE AND DIBASIC ACIDS

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The progress in electrical transportation systems and an increasing number of electronic devices leads to the intensive search of new effective and environment friendly materials for construction of power sources. One of the important directions in this field is the elaboration of solid polymer electrolytes (SPEs), in particular, based on the natural polymers (such as chitosan or cellulose) [1]. In the last decade, ionic liquids and their particular type - deep eutectic solvents (DESs) have been actively studied due to their unique physicochemical properties such as relatively high conductivity, thermal stability and wide working potential window and natural origin [2]. Combining of the natural DESs and natural polymers into one system is a promising way to obtain renewable low toxic SPEs.

This research focuses on the investigation of the relationship between the structure and electrical properties of the chitosan-DES films. The choline chloride and the raw of dibasic acids (oxalic (OA), malonic (MA) and succinic (SA)) were used for obtaining of DESs. The films with various DESs were prepared by solution casting method and final films contained 50 wt% of DES. Electrical impedance spectroscopy at various temperatures was performed and specific conductivity (σ) was calculated. It was found that values σ for OA and SA were significantly higher than ones for samples prepared with MA. This allows to suggest the formation of enriched DES network of ionically conducting channels inside the film prepared with OA and SA. This leads to the significant enhancing of the ionic conductivity at ambient temperature from 7.2×10⁻⁸ S/cm for film with MA up to 6.3×10⁻⁵ S/cm and 7.2×10⁻⁵ S/cm for ones containing SA and OA respectively.

References

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THE INFLUENCE OF MEDIA AND LIPOsome COMPOSITION ON LIPOsome-MICROGEL COMPLEX FORMATION AND STABILITY

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Recent reviews on drug delivery systems outline that further development of such systems should result in embedding stimuli-sensitivity and ability to carry several therapeutic agents simultaneously. These requirements can be satisfied with the system composed of liposomes bound to a thermosensitive microgel. Microgels of certain composition may undergo significant decrease in size upon heating which may lead to release of encapsulated drug. Investigation of complex behavior in media with different pH and ionic strength values is important for complete understanding of the system’s properties.

We have experimentally demonstrated that anionic liposomes made of egg lecithin and 30 mass % phosphatidylserine can be adsorbed on the surface of cationic thermosensitive microgel synthesized from 3-((N,N-dimethylamino)propylmethacrylamide, N-isopropylacrylamide and N,N-methylenebisacrylamide. Liposomes stay intact upon adsorption and for complex properties description liposome-to-microgel mass ratio is used. The process of complex formation was investigated in media with different ionic strength values. It was shown that with an increase of ionic strength the rate of aggregation in liposome-microgel mixtures slows down until it stops completely at 120 mM indicating that no interaction between oppositely charged particles occurs at this value of ionic strength. Interestingly, the same trend was observed in the range of pH = 4.75 – 7.2 when the microgel’s protonation degree changes from 1 to 0.7. To study the role of liposome composition, a series of liposomes composed of variable mass ratio of egg lecithin and cardiolipin were used. With all the samples, the above-described procedures were performed including complex formation at different liposome-to-microgel ratios and in the media with different values of ionic strength using the relevant ratio chosen. It was shown that the quantity of cardiolipin in the lipid bilayer determines the maximum value of ionic strength at which liposome-microgel complexes can be formed.

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SYNTHESIS AND VISUALIZATION OF NOVEL HELICAL BOTTLEBRUSH POLY(PHENYLACETYLENE)S

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The precise design of structurally complex polymers is increasingly important for their unique physical properties in recent year. In particular, various kinds of topologies based on helical polymers have recently drawn great attention from not only academia but also industry because of their valuable potential application, such as chiral separation and asymmetric synthesis for pharmaceuticals [1]. Recently, we have developed a novel catalytic system capable of inducing living polymerization of various phenylacetylene derivatives. This finding opened new fields of synthesizing structurally complex helical polymers.

Here, we report the formation of the structurally complex polymers based on helical polymers. We have synthesized poly(phenylacetylene)-based bottlebrush polymers by a “grafting from” method, which were obtained quantitatively and their molecular weight distributions were very low. AFM analysis revealed that the polymers have well-controlled bottlebrush structures (Figure 1). We also describe the chiroptical properties of bottlebrush polymers bearing chiral groups on the side brush chain.

This is the first example of bottlebrush poly(phenylacetylene)s. We are convinced that these complex structures might allow the development of new functional chiral materials.

![AFM image of bottlebrush polymers.](image.png)

References
Polymyxins represent a group of peptide antibiotics. The limiting side effects of polymyxin’s administration are their nephrotoxicity and neurotoxicity due to the increased dosage required for the achievement of therapeutic action. In turn, the reason for higher dosage application is a fast inactivation of the peptide drug in the bloodstream [1]. To overcome the aforementioned disadvantages, the use of polymeric drug delivery systems can be a matter of choice. This work proposes the creation of delivery systems for polymyxins based on self-assembled biodegradable particles from amphiphilic copolymers of amino acids. Currently, this class of nanoparticles attracts increased attention of the scientific world, both in terms of basic research and in terms of commercial application [2]. A series of the random amphiphilic copolymers based on aspartic/glutamic acid and isoleucine were synthesized by ring-opening polymerization of α-amino acid N-carboxyanhydrides. Molecular weight characteristics and composition of copolymers were determined using gel permeation chromatography and quantitative HPLC-MS analysis of amino acids. According to the data of transmission electron microscopy, the obtained amphiphilic copolymers formed spherical particles. The characteristics of particles were determined by the method of dynamic and electrophoretic light scattering. The cytotoxicity of the obtained particles was evaluated in a wide range of concentrations and the stability of the particles was studied in the model and culture media. A technique for HPLC analysis of polymyxins B and E was developed, and the features of antibiotic’s encapsulation into the obtained polymer particles were studied. Such important parameters as encapsulation efficiency and maximum drug loading were determined. The release profile of polymyxins in a model solution was also studied.

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References
APPLICATION OF AFM AND LAZER INTERFEROMETRY FOR MORPHOLOGICAL RESEARCH OF THIN-FILM BIOPOLYMER MATRIXES

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In recent years, optical research methods are widely used in pharmacology, medicine and biotechnology to characterize new materials and objects. AFM and laser interferometry has become the most common and successfully used tools for the study of surface properties in tissue engineering to repair damaged tissues of a living organism [1]. Directed growth and controlled development of mesenchymal stem cells are realized using matrices and scaffolds capable of supporting cell proliferation [2].

The aim of the work is to study the characteristics of the structure and biological properties of biodegradable polymer matrices with anti-inflammatory activity, created on the basis of chitosan in combination with polypeptides secreted by mesenchymal stem cells, and promising for the development of materials for biomedical purposes. The optimal conditions for the production of thin-film biopolymer matrices by the method of irrigation with acetic acid solution of chitosan, cross-linked by genipine onto an aluminum plate and further use of spin-coating, are determined. A non-invasive assessment of structural features (surface topography, microrelief character, heterogeneity of polymer structure) and biological properties (biocompatibility, adhesiveness, immunogenicity, thrombogenicity, etc.) of the obtained thin-film matrices using super-resolving laser modulation microscopy and AFM was carried out. The phase images of biopolymer samples were obtained which could be interpreted as a two-dimensional projection of their three-dimensional structure.

References

Acknowledgements. This work was supported the Russian Science Foundation (grant № 18-29-17059).
Silicone resins are three-dimensional polymers with residual functional groups [1]. They are widely used as varnishes, paints and electrical insulation coatings due to a complex of unique properties: high thermal and thermal oxidative stability, resistance to ultraviolet radiation, a wide range of operating temperatures, bio-inertness, manufacturability, etc.

The traditional method of resin production is hydrolytic copolycondensation of trifunctional and difunctional organochlorosilanes, where trifunctional create a three-dimensional net, and difunctional improve mechanical properties. However, such methods of production have drawbacks: compositional heterogeneity, complexity of control of material properties and poor reproducibility.

This paper presents regular copolymers (i.e. with a regular arrangement of functional and non-functional fragments). The functional fragment [2] contains functional groups and is responsible for the formation of a three-dimensional polymer net; the non-functional fragment provides the product with the necessary set of physicochemical properties (Fig 1).

Thus, the properties of the polymer are set by its chemical composition, and not by an empirical selection of the conditions of the hydrolytic co-condensation reaction, as in the case of the traditional method.

References

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NEW SYNTHETIC METHODOLOGIES IN ORGANIC AND BIOMEDICAL CHEMISTRY
The development of efficient and selective methodologies is of prime importance to achieve the goals of green chemistry. Hydrogen borrowing (hydrogen auto-transfer) reactions are considered to be eco-friendly, atom economic alternatives to conventional synthesis methods since they result in only water as a side product. Moreover, they allow for the utilization of widely available alcohols as substrates that can also be derived from renewable resources. These catalytic methods received huge attention in the last decades, employing noble\textsuperscript{[1]} and earth-abundant metals.\textsuperscript{[2]}

Herein, we show our recent developments in the $N$-alkylation of amines with alcohols using Ni, Fe and Ru based catalytic systems \textit{via} the hydrogen borrowing approach. More specifically, we have developed a highly active and easy-to-prepare Ni based catalyst system\textsuperscript{[3]}, that is \textit{in situ} generated from Ni(COD)$_2$ and KOH under ligand-free conditions. Moreover, novel methodologies using Ru and Fe complexes for the synthesis of $\beta$-amino acid esters and $N$-substituted heterocycles will be presented.\textsuperscript{[4]}

Additionally, we demonstrate our recent achievements regarding the use of doped porous metal oxides as catalysts in catalytic conversion of lignocellulose and lignocellulose derived chemicals to higher-value building blocks including amines \textit{via} cross-coupling and hydrogen borrowing reactions.\textsuperscript{[5]}

References
L-Alpha glycercyolphosphorylcholine (alpha-GPC) is part of the nootropic drug group. It is used to treat cognitive impairments of various etiologies. One of the main methods for the synthesis of choline alfoscerate is the catalytic transesterification of 95% lecithin with methanol, using 1-propylamine as a catalyst [1].

In this paper, we studied the catalytic activity of diethylamine for the transesterification of a 35% solution of lecithin in soybean oil while changing various reaction conditions. The determination of the completeness of the conversion of lecithin (Rf = 0.43) and the authenticity of α-GPC (Rf = 0.05) is carried out by thin layer chromatography in eluent chloroform: methanol: acetic acid: water in a volume ratio of 5: 2.5: 0.8: 0.4 respectively. The results showed that at room temperature and the same mole ratios, diethylamine and 1-propylamine exhibit similar catalytic activity. The reaction rate was slightly increased by the influence of ultrasound with a frequency of 45 kHz. Heating to the boiling point (water bath temperature 80 °C) leads to a significant increase in the reaction rate. In addition, it was found that when methanol contains more than 5% water, is observed a decrease in the reaction rate and the formation of an insoluble precipitate — a mixture of carboxylic acid amides.

![Figure 1. Synthesis of choline alfoscerate.](image)

References
Ketoacetylenes are useful intermediates in the synthesis of diverse heterocycles through dipolar cycloaddition or nucleophilic addition-elimination mechanisms. However, there are no literature data on the biological activity of the molecules composed of these fragments. Assuming that ynone fragment could be involved in hydrogen bonding with nucleobases, the aim of this work is to evaluate cytotoxicity of calixarene tetraketoacetylenes with variable arrangement of ynone units and their DNA binding ability.

1 1,3-alternate
2 partial cone
Surface pressure–area isotherms of ynone 1 on water (C = 0.1 mg/mL in CHCl₃) without and with DNA (5–50 mg/L) and A375 lung cell viability in the presence of ynone 1. In this work, ketoacetylene derivatives of calix[4]arene on the lower rim in 1,3-alternate (1) and partial cone (2) stereoisomeric forms have been synthesized and characterized. DNA binding studies at the air–water interface have shown that the monolayer of calix[4]arene 1 is expanded in the presence of 5 mg/mL of calf thymus DNA, which indicates incorporation of the nucleotide. Furthermore, no cytotoxicity of calixarenes 1 and 2 towards human lung cell line (A375) has been detected, which is a promising result from the viewpoint of DNA detection using ketoacetylene units preorganized on a calixarene scaffold.

The work was supported by the Russian Foundation for Basic Research (project no. 17-53-10016-KO-A).
Despite the physiological function of the cytokines of the IL-17 family in innate and adaptive immunity, dysregulated production of these cytokines has been shown to play a role in developing autoimmune and inflammatory conditions. The IL-17 family of cytokines contains 6 structurally related cytokines. IL-17A, the most extensively studied member of this family, has been implicated in the pathogenesis of autoimmune and inflammatory diseases such as psoriasis and rheumatoid arthritis. As a result, blocking the interaction of IL-17A with its receptor, IL-17RA, has emerged as an effective strategy in the treatment of diseases of this nature [1].

Inhibition of protein-protein interactions with small molecules presents many difficulties for medicinal chemist and IL-17A with a very large protein-protein interaction interface and no distinct small-molecule pocket, has certainly proved one of the most difficult targets in small-molecule drug discovery. Monoclonal antibodies targeting IL-17A or its receptor have shown remarkable efficacy in autoimmune disorders. Secukinumab, a monoclonal antibody interacting with IL-17A, for instance, has been approved for the treatment of psoriasis and the search for finding more monoclonal antibodies is still ongoing. However, so far no small-molecule inhibitor of IL-17A has made it to the pharmaceutical market [2].

Here, we report the computer-aided development of small-molecule inhibitors of IL-17A. Biophysical assays of these compounds revealed the outstandingly high affinity of some of the compounds synthesized. Moreover, we could unambiguously define the binding site by a cocrystal structure of one of our small molecule binding to IL17A.

References


Acknowledgements:
This work was supported by the the NIH grant (2R01GM097082-05).
One of the most important problems of pharmaceutical and supramolecular chemistry is design of new, non-toxic macrocyclic structures to stabilize and prolong the action of proteins with antitumor activity. New generations of water-soluble amphiphilic nanocontainers (capsules) can act as encapsulation systems. The use of amphiphilic macrocycles that promote the formation of self-associates will contribute to the encapsulation, compaction, and metered release of the drug. This will significantly reduce drug toxicity, as well as lead to a prolonged action of a therapeutic agent to slow its release.

Functionalization of structure of macrocycles by terpenoid fragments will increase biocompatibility and increase the efficiency of interaction with tumor cells. The structure of the obtained compounds was characterized by a complex of physical methods – $^1$H, $^{13}$C, NMR and IR spectroscopy, mass spectrometry, individuality was confirmed by TLC. The ability of the compounds to form self-associates was studied by the DLS method. It was shown that the compounds obtained in water form nanoscale aggregates.

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A NEW STEREOSELECTIVE SYNTHESIS OF BIOLOGICALLY ACTIVE NATURAL 5Z,9Z,13Z-EICOSATRIENOIC ACID

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Unsaturated carboxylic acids attract chemists’ and pharmacologists’ attention owing to the broad spectrum of biological properties they exhibit. For example, it was found that di-, tri-, and polyenoic acids containing a 1Z,5Z-diene moiety in the molecule, which are isolated in micro quantities from sea sponges and gymnosperm seeds, exhibit antiviral, antimicrobial, antitumor, antimalarial, and antituberculosis activities, and are also used as biologically active additives to reduce appetite in the treatment of obesity [1-3].

We developed an original procedure for preparation of natural 5Z,9Z,13Z-eicosatrienoic acid (20:3) (5) using the new reaction that we developed, namely, Ti-catalyzed cross-cyclomagnesiation of oxygenated and aliphatic 1,2-dienes induced by Grignard reagents, in the key stage of the synthesis.

Scheme 1.

Using flow cytometry, the new molecules were shown for the first time to be efficient apoptosis inducers in the HeLa, U937, Jurkat, and K562 cell cultures and to have dose-dependent effect on the S and G2 phases of the cell cycle.

References

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SELECTIVE MULTICOMPONENT APPROACH TO THE NEW 5-(4-HYDROXY-6-METHYL-2-OXO-2H-PYRAN-3-YL)-CHROMENO[2,3-B]-PYRIDINE SCAFFOLD

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Cyano-functionalized chromeno[2,3-b]pyridines inhibit mitogen-activated protein kinase-activated protein kinase 2 (MK-2) and suppress the expression of TNFα in U937 cells [1], and also increase the level of phosphorylated coflin in HCA2 cells, making chromeno[2,3-b]pyridines possible therapeutic option in the treatment of Werner syndrome [2].

In the present study we found multicomponent synthesis of 5-C substituted chromeno[2,3-b]pyridines from salicylaldehydes 1a-i, 2-aminoprop-1-ene-1,1,3-tricarbonitrile and 4-hydroxy-6-methyl-2H-pyran-2-one (Fig. 1). In small amount pyridine–ethanol catalyst/solvent system chromeno[2,3-b]pyridines 2a-i was obtained in 45-85% yields (4h, reflux).

Figure 1. Multicomponent assembling of salicylaldehydes 1a–i, 2-aminoprop-1-ene-1,1,3-tricarbonitrile, and 4-hydroxy-6-methyl-2H-pyran-2-one into chromeno[2,3-b]pyridines 2a–i.

This new facile and efficient procedure found by us utilizes simple equipment; it is easily carried out, final compounds do not require additional purification and isolation step consists only from filtration followed by washing with a small amount of ethanol.

References

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SYNTHESIS OF 2-AMINO-6-METHYPYRIMIDIN-4(3H)-THION DERIVATIVES AND THEIR PLANT GROWTH STIMULANT ACTIVITY

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The pyrimidine derivatives exhibit a wide diversity of biological activity. The pyrimidine nucleus is a part of natural compounds – nucleic acids, vitamins, strong poisons (tetrodotoxin), coenzymes, as well as a number of medicines (barbiturates, antitumor agents, pyrimidine sulfamides, antibiotics) [1]. A series of pesticides that are widely used in agriculture have been synthesized on the basis of pyrimidine [2]. At the same time, judging by the literature data, compounds with a combination of the pyrimidine ring with other pharmacophor heterocycles, in particular, with azoles and azines, have been poorly studied.

The purpose of this work was to develop accessible and effective methods for the synthesis of novel pyrimidine derivatives, as well as compounds with combination of pyrimidine with azole and azine rings in the molecule and study their biological activity in terms of searching for new environmentally friendly pesticides or plant growth regulators.

A large number of new compounds were synthesized by the functionalization of 2-amino-6-methylpyrimidine-4(3H)-thion at the expense of 2-amino group and the exocyclic sulfur atom of the pyrimidine cycle.

All synthesized compounds demonstrated a stimulating effect on plant growth. The substances that in the experiment showed the activity higher than 80% (compared to heteroauxin) were selected for additional study and further field trials.

References
PHOSPHORYLATION OF 2-THIOPYRIMIDINE DERIVATIVES

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As the object of the study, we chose compounds of a number of 2-thiopyrimidines, since representatives of this class are well known as biologically active compounds. The initial pyrimidines were obtained by us in the course of a three-component one-pot reaction (Figure 1):

![Figure 1. Synthesis of 2-thiopyrimidine derivatives.](image1)

We found that in the course of further functionalization of the obtained 2-thiopyrimidines with chloroethynephosphonate (Figure 2), the corresponding 3-phosphorylated thiazolopyrimidines are formed as final products. The formation of the final phosphonates proceeds with high chemo- and regioselectivity with high yields. The structure of the obtained products of bicyclic structure was established by ¹H, ¹³C, ³¹P nucleus NMR spectroscopy, and also proved by X-ray structural analysis.

![Figure 2. Reaction of chloroethynephosphonates with obtained 2-thiopyrimidines.](image2)

Acknowledgements. This work was supported by Ministry of Education (project No 4.5554.2017/8.9) with using the resources of Engineering Centre of SPbSIT (TU). The reported study was funded by RFBR according to the research project № 18-33-00430.
Aminoimidazoles have a remarkably broad utility in medicinal chemistry: anti-inflammatory, antiviral, antimicrobial, anesthetics and can be used as antidepressants and analgesics. Recent new drug developments from imidazole derivatives show better effects and less toxicity. Therefore, the search for new biologically active heterocyclic analogs of imidazole is an important task in the field of medical chemistry [1].

The reaction of the synthesis of imidazole derivatives consists in the aminating of propargylamides and their cyclization catalyzed by zinc triflate [2]. We obtained compounds with various aromatic and aliphatic substituents both in the amine and imidazole fragments (Fig. 1).

![Chemical structure](image)

Figure 1. Reaction.

In order to minimize the imidazoldine derivatives formed during the reaction, we carried out a selection of the catalyst, as well as the ratio of the reactants. The highest yield was achieved with a ratio of urea to amine of 3:1 and using zinc triflate as a catalyst. On aromatic ureas, ZnCl also showed a good yield, but the desired product was not formed with aliphatic ureas using ZnCl. The structures of the synthesized compounds were confirmed using $^1$H, $^{13}$C NMR spectroscopy and HRMS.

References
In this study we have developed a practically convenient, three-component approach to $N$-hydroxytetrahydroisoquinolonic (THIQ) acids via a variant of the Castagnoli-Cushman reaction involving in situ cyclodehydration of homophthalic acid with concomitant formation of an oxime in refluxing toluene with azeotropic removal of water. Using hydroxylamine acetate or $O$-benzylhydroxylamine in lieu of the hydroxylamine hydrochloride typically employed to prepare oximes was key to the success of the reaction.

For prepared $N$-benzyloxy THIQ acids decarboxylation and debenzylation reactions were additionally investigated. Five selected cyclic hydroxamic acid compounds produced in the course of this study have been profiled and confirmed as ligands for $Fe^{3+}$. Thus, a new, practically simple and flexible approach to potential iron overload disease treatments or analogs of bacterial siderophores for antibiotic delivery has been validated[1].

References


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META-FUNCTIONALIZATION OF NAPHTALENE PROTON SPONGE VIA THE USE OF SCHLOSSER’S SUPERBASE

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Lithiation of 1,8-bis(dimethylamino)naphthalene (DMAN) with Schlosser’s superbase (n-BuLi–t-BuOK) in the presence of TMEDA in hexane was examined (Scheme 1). It has been shown that, compared with previously studied n-BuLi–TMEDA or t-BuLi–TMEDA mixtures, this reagent provides much more selective meta-lithiation. A variety of 3-substituted and 3,6-disubstituted derivatives of DMAN has been prepared in a good to reasonable yield after quenching the reaction mass with different electrophiles. A possibility of further functionalization of thus introduced meta-substituents to synthesize more complex 3-substituted derivatives of DMAN is also demonstrated.

Scheme 1.

The influence of bulky trimethylsilyl substituent on the selectivity of metatation of dimethylaniline and anisole is studied. Neighboring SiMe₃ group forces dimethylamino and methoxy groups to occupy conformation with unshared electron pair turned towards silicon atom. This forced conformation prevents NMe₂ groups from providing DOM-effect, facilitating meta-metallation, while OMe group demonstrates more rotation freedom supporting ortho-metallation.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project 16-33-60030).
Octahedral rhenium cluster complexes \([\{\text{Re}_6\text{Q}_8\}\text{L}_6]^n\) (Q = S, Se, L = organic or inorganic ligand) possess promising properties such as X-ray contrast due to high local concentration of heavy elements, luminescence in NIR region and redox activity. Usually such complexes are not soluble in water or not stable in water solution. One of known water-soluble rhenium cluster complexes are compounds containing 1H-benzotriazole as a terminal ligand. Moreover, these clusters are stable in water solution at physiological pH, which in combination with physicochemical properties is promising for biomedical applications. Thus, it was suggested to obtain new octahedral rhenium cluster complexes with typical triazoles, namely 1,2,3-triazole (1,2,3-trzH) and 1,2,4-triazole (1,2,4-trzH) and investigate their physicochemical and biological properties.

In this work, we studied the interaction of the hydroxide octahedral rhenium cluster complexes \(K_4[\{\text{Re}_6\text{Q}_8\}(\text{OH})_6]\) (Q = S, Se) with 1,2,3-triazole and 1,2,4-triazole. Reactions were carried out in the melt of pro-ligands in sealed glass tube at 200 °C. During this study, anionic cluster complexes \([\{\text{Re}_6\text{Q}_8\}(1,2,3\text{-trz})_6]^4^-\) and \([\{\text{Re}_6\text{Q}_8\}(1,2,4\text{-trz})_6]^2^-\) were obtained, which are easily soluble in water and in many organic solvents. All obtained compounds were investigated by a set of physicochemical methods ( multinuclear NMR- and IR-spectroscopy, elemental analysis, mass-spectrometry, etc.). Furthermore, their luminescence and redox properties were studied, as well as biological effects using MTT test, flow cytometry and confocal microscopy.

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UNSYMMETRICAL BACTERIOCHLORINS WITH PERFLUOROCARBON SUBSTITUENTS: SYNTHESIS AND PROPERTIES

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Bacteriochlorins belongs to the novel generation photosensitizers (PS) for photodynamic therapy of cancer with effective NIR absorption (range 700-800 nm). The application of bacteriochlorins with fluorocarbon emulsions – delivery system of oxygen and PS - requires their modification to impart solubility in the fluorocarbon phase. We used the approach previously developed on the example of porphyrin and chlorin structures [1, 2].

\[
\begin{align*}
\text{R} & = \text{F} \text{F} \\
\text{OCH}_2\text{C}_n\text{F}_{2n+1} \\
\text{TsN}_2\text{H}_3, \text{K}_2\text{CO}_3 & \quad \text{pyridine, reflux}
\end{align*}
\]

Figure 1. Bacteriochlorin synthesis

In the report will be considered the design of fluorinated bacteriochlorins, its synthesis and properties.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-315-00432).
Rhodium (III) hydroxocomplexes prepared by treating of the rhodium chlorocomplexes by alkali water solution exhibits catalytic activity in a number of organic and inorganic reactions. The polycondensation of the hydroxocomplexes which accelerates with the increasing of temperature, rhodium concentration and decreasing of alkali concentration may influence the catalytic activity. The technique allowing the reproducible production of various mixtures of rhodium (III) hydroxocomplexes is developed and used for catalysts preparation. For this, a solution of K$_3$RhCl$_6$ (0.005M) in NaOH (2M) is kept at room temperature for 20 min to produce exclusively [Rh(OH)$_6$]$_3^-$ ions which undergoes a polycondensation reaction at 60°C for 30 min giving a mixture of hydroxocomplexes with a number of rhodium atoms from 1 to 4. The deposition of complexes to the surface of Al$_2$O$_3$ is carried out by dropwise addition of Ca(NO$_3$)$_2$ which saves the distribution of species obtained at the previous step. The catalysts consisting of highly dispersed Ca$_x$[Rh(OH)$_y$] salt mixture deposited from two abovementioned solutions were tested for activity in benzaldoxime to benzamide rearrangement at 140°C in water. The experiments show that polynuclear species are at least 3 times more active than [Rh(OH)$_6$]$^{3-}$ but they are degrade in progress of the reaction.
Organotin compounds demonstrate wide range of their biological activity including anticancer properties.

The aim of the work is the synthesis of Sn (IV) carboxylates based on bile acids and the study of their cytotoxic activity. Organotin carboxylates of the general formula $R_3Sn(LCOO)$ and $R_2Sn(LCOO)_2$ were synthesized (where $R = Me, Ph$; $L$ is fragments of cholic ($L^1$), deoxycholic ($L^2$), lithocholic acid ($L^3$)). Compounds were characterized by $^1H$ and $^{13}C$ NMR and elemental analyzes. Cytotoxicity activity in vitro of the compounds was studied on A549, WI38, MCF-7, SW480, and HCT-116 cancer cell lines in the MTT test. It was shown that all compounds possess high cytotoxicity, IC$_{50}$ values in the range of 0.2 - 8 μM were found. The toxicity of $R_2Sn(L^2COO)_2$ is one order lower than that of $R_3Sn(L^2COO)$ (1.3 and 0.3 μM, respectively). The study of the cell cycle and by flow cytometry showed that the compounds block the cell cycle in the G2/M phase. Analysis of the apoptotic profile showed that diphenyltin derivatives induce apoptosis more intensively than triphenyl derivatives (the number of apoptotic cells was 25% and 21%, respectively) (Fig. 1).

![Fig. 1. Apoptotic profile of cancer cells HCT 116 after treatment with $R_2Sn(L^2COO)_2$ (a) and $R_3Sn(L^2COO)$ (b) at 2 and 0.4 μM respectively after 24 h.](image)

References


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TWO-PHOTON FLUORESCENCE ANISOTROPY INVESTIGATION OF TRYPTOPHAN DISSOLVED IN SOLUTIONS WITH DIFFERENT VISCOSITY

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Tryptophan is an amino acid naturally existing in proteins which are now widely used as a fluorescent probe for investigation of proteins in solutions and cells [1]. We present an experimental study of two-photon excited polarized fluorescence in tryptophan in water-propylene glycol solutions with different viscosity and polarity. The fluorescence was excited within a two-photon absorption scheme. The excitation wavelength was varied in the range of 385–510 nm and the fluorescence was detected by a time-correlated single photon counting (TCSP) system by two independent detectors. Fluorescence decay signals were described by a bi-exponential model [1-2]. The fluorescence decay parameters: fluorescence lifetimes τ₁, τ₂ weight coefficients, rotational correlation time τ_rot, anisotropy parameter r₀, and total intensity were extracted from experimental data by means of the computer code based on Python 3. The results obtained demonstrate the dependence of these parameters on the viscosity of the solvents and wavelength of the absorbed radiation.

References
ZrO$_2$/NiO: A RECYCLABLE CATALYST FOR 4-COMPONENT FUSION TO PRODUCE NOVEL 1,4-DIHYDROPYRIDINES AND THE MECHANISTIC STUDY

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Among the heterocyclic compounds, N-heterocyclic scaffolds in general acquired more prominence in the medicinal and pharmaceutical chemistry [1]. In particular, 1,4-dihydropyridines (1,4-DHPs) are the privileged scaffolds of biological importance[2]. In this we are presenting Nickle oxide loaded on zirconia (NiO/ZrO$_2$) as an expedient catalyst for the synthesis of ten novel unsymmetrical 1,4-dihydropyridine derivatives at room temperature is studied. The Lewis acidic nature of the catalyst proved excellent for the one-pot four-component reaction with excellent yields of 93-98% in 20 minutes. Mechanistic studies show that that enamine and imine are the two possible pathways for the formation of 1,4-dihydropyridines with high selectivity. Catalyst reusability up to 6 cycles and reaction at room temperature (RT) makes this protocol green and economical. The single crystal structure of 5-methyle derivative observed as a single colorless block-shaped crystals, corresponds to a triclinic cell. This is the first report of using NiO/ZrO$_2$ as a catalyst in the multicomponent fusion in one-pot reaction system.

![Figure 1. Synthesis of novel 1,4 dihydropyridines.](image)

References

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INFLUENCE OF CO-CRYSTALLIZATORS ON STABILITY OF β-GLYCINE

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In the past two decades, the issue of polymorphism has become acute in the drug market. It was shown that solubility and, as a consequence, biological activity largely depend on the polymorphic modification for many substances. In accordance with the rules governing the requirements for the production and use of food and drugs for each medicinal substance should be necessarily contain the information about all the available polymorphs. This makes it all studies on finding polymorphic modifications, deciphering their structure, studying thermal stability, as well as possible transformations during storage and at different stages of the processing chain very important. Polymorphic modifications can be obtained by different ways: by changing the conditions of crystallization or storage, by varying temperature and pressure, by various solid-phase transformations – phase transitions and chemical reactions, and also by mechanical action. Thus, we can conclude that the problem of controlling the polymorphism of medicinal substances is one of the most popular areas of modern pharmaceutical science. It should be noted that most of the works describing the polymorphism of drugs is devoted to the identification of various polymorphic forms, their mutual transitions and biological activity. At the same time, the development of methods for stabilizing certain thermodynamically unstable modifications is practically neglected, which makes this work relevant.

Thus, this work is devoted to studying the influence of the method of preparation of polymorphic modifications on the kinetic parameters of polymorphic transitions. In the present work, metastable β-glycine polymorph was obtained by a method of rapid removal of the solvent, as well as by crystallization with various co-crystallizators, such as glucose, sodium chloride and potassium iodide. Polymorphic phases and their time stability were investigated by X-ray powder diffractometry. It was found that β-glycine obtained by co-crystallization with glucose is more stable form than simple β-glycine. It was shown that β-form of glycine has bigger dissolution rate than α-form by dissolution kinetics studies.

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Donor-acceptor cyclopropanes 1 (DACs) are a broad class of substituted three-membered carbocycles. They are known for their capability to undergo small ring opening to act as 1,3-zwitterionic synthons. Our group developed a quiet different type of reactivity of DAC – the use of 2-arylcyclopropane-1,1-dicarboxylates (ACDC, 1) as sources for generation of 1,2-zwitterions 2 in the presence of GaCl₃ [1].

Now we demonstrate a new approach for using ACDC 1 in reactions with acetylenes in the presence of GaX₃. We have been developed a new strategy for assembly of substituted (3-haloallyl)malonates 3, dihydronaphtalenes 4 and lactones 5 [2]. As the result all discovered processes proceed with a high regio- and diastereoselectivity and good yields of products obtained. Reaction conditions and features of these processes will be discussed.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 14-13-01054-P) and Russian Foundation for Basic Research (project No 18-33-20180).
Donor-acceptor cyclopropanes (DACs) are remarkable building blocks widely used in contemporary organic synthesis. Most commonly, DACs are used as sources of 1,3-zwitterion intermediates, which are then used in reactions with a broad range of substrates, including 1,3-dipoles, for example organic azides [1]. Recently, we discovered a new type of reactivity of DACs 1, which consists in generating 1,2-zwitterionic intermediates 2 under the action of Lewis acids, in particular, gallium halides [2]. It was interesting to study the reactions of these intermediates with 1,3-dipoles, in particular with nitrones, azides and diazocompounds.

It was found the interaction of 1,2-zwitterion with benzylazide and methylidiazooacetate lead to products 3 and 5 respectively. Nitrones does not react with compound 2, however, it participates as a ligand in the dimerization of zwitterionic intermediates giving unknown dimer 4a. As the result all discovered processes proceed with a good yields of products obtained. Reaction conditions and features of these processes will be discussed.


This work was supported by the Russian Foundation for Basic Research (project No 18-33-01000).
Adamantyl-containing compounds with cumulated double bonds, such as isocyanates, isothiocyanates and isoselenocyanates, are frequently used in the synthesis of biologically active compounds.

We developed new and enhanced known methods for the preparation of adamantyl-containing heterocumulenes of the following structure A:

One-pot method for the preparation of isocyanates from carbon acids based on the Curtius reaction was developed, which allows to increase yield and decrease the potential explosiveness of the process. New one-stage syntheses of adamantyl-containing isocyanates and isothiocyanates based on the reaction with 1,3-dehydroadamantane were introduced [1]. New reaction of adamantyl-containing amines with phenylisothiocyanate leading to corresponding adamantyl-containing isothiocyanates was discovered [2].

New 1,3-disubstituted ureas and diureas B – potent soluble epoxide hydrolase (sEH, E.C. 3.3.2.10) inhibitors were synthesized based on heterocumulenes A. The effect of substituents in adamantyl moiety on the properties on inhibitors was investigated. Inhibitory activity of the most potent compounds reaches IC$_{50}$ = 0.4 nM [3]. For the most potent inhibitors the affinity constants and microsomal stability were evaluated.

References

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REACTIVITY OF NEW «AZOLE-INCLUDING» ANHYDRIDES IN THE CASTAGNOLI-CUSHMAN REACTION

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The Castagnoli-Cushman reaction (CCR) is a reaction of cyclic anhydrides of dicarboxylic acids with imines 1 (fig. 1). At this moment succinic (2), glutaric (3) and homophthalic (4, HPA) anhydrides are the most popular substrates for CCR. HPA is the most reactive in CCR from all known anhydrides.

![Figure 1. The Castagnoli-Cushman reaction.](image)

Figure 1. The Castagnoli-Cushman reaction.

We have developed a group of new azole-annulated anhydrides as substrates for CCR (fig. 2). It was suggested to name this group «azole-including» anhydrides [1]. Results of the CCR with anhydrides 8-11 explained the influence of electronic effects of azole heterocycles to reactivity of anhydrides [1,2]. For «indole-including» anhydrides 11-13 the influence of the position of the electron withdrawing substituents in indole ring to reactivity of anhydrides was shown [3].

![Figure 2. «Azole-including» anhydrides.](image)

Figure 2. «Azole-including» anhydrides.

References

Acknowledgements. The reported study was funded by RFBR according to the research project № 18-33-00758.
A new class of electrochromic compounds 9 containing conjugated pyridinium fragments was synthesized by 1,3-dipolar cycloaddition. Their electrochemical characteristics were studied by CVA, electrochromic cells were made, and their spectral properties were studied from 0 to 2 V. All compounds colored from colorless to brown at 1.5 V.

Figure 1. Synthesis of target compounds, pictures of electrochromic device, CVA curve of 9c.

Acknowledgements. The reported study was funded by RFBR project (project No 18-33-01253).
The development of new chemosensors is an actual problem, since the rapid identification of organic structures of various structures is an urgent task of modern organic chemistry.

We have proposed an approach to the synthesis of novel polytargeted chemosensor 1 based on 4-(trifluoromethyl)pyridine, containing an acceptor tricyanobutadiene fragment (TCPy). These structures were obtained by trifluoropentane-2,4-dione heterocyclization with dimer of malononitrile. Synthesized TCPy 1 can form salts with various organic bases. As a result, compounds 2 are obtained, possessing solid-state fluorescence. Photoluminiscence maximum of salts can be varied by the used organic base. This can be observed using toluidine isomers as example (Fig.1).

Figure 1. Synthesis, and solid state fluorescence of toluidine salts of TCPy.

It has been found that the application of TCPy 1 as chemosensors is quite wide, since these structures form fluorescent salts with one-, two-, three-, and four-substituted amines, with various biomolecules, as well as with metals.

Acknowledgements. The work was supported by a grant from the Russian Science Foundation (Project № 17-13-01237).
1,3,4-OXADIAZOLES BASED ON ARYLIDENESULFONAMIDES: THE NEW CLASS OF POTENT AND ISOFORM-SELECTIVE MONOAMINE OXIDASE INHIBITORS

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Good potency inhibitors of human monoamine oxidase (hMAO) isoforms may be useful for the treatment of depression and Parkinson’s disease. The series of 1,3,4-oxadiazole benzenesulfonamides 4 have been synthesized by cyclization of N,N'-diacylhydrazines 3, which consists in the reaction of dehydration [1-2]. Also the compounds 4 were obtained by cyclocondensation of the sulfonyl chlorides 7.

Figure 1. Reaction of synthesis of benzenesulfonamides 4.

The obtained compounds 4 were evaluated as potential inhibitors of hMAO-A and B. The most potent MAO-B inhibitors of these compounds have value IC50 = 0.00272; 0.04841 and 0.07943 µM. These potencies are in the same range as those of reference MAO inhibitors used in the clinic.

References
Pyrrole and indole fragments are an important structural parts of a wide range of natural compounds and biologically active substances. \(N\)-Vinylpyrroles are one of the universal types of reactive carriers of the pyrrole moiety. We investigated the reactions of \(N\)-vinylpyrroles and indoles with various 1,3-dipoles: nitrones, azomethine imines, nitrileoxides. [1, 2]

Figure 1. Reactions of \(N\)-vinylpyrroles and indoles with 1,3-dipoles

It was found that for the considered reactions different pathways are possible, depending on the conditions of conduction and the structure of the initial compounds. This makes it possible to obtain both (3+2)-cycloaddition products, and polycyclic products of formal (3+3)-cycloaddition then Lewis acids are used as catalysts.

References

Acknowledgments. NMR, HRMS and XRD studies were performed at the Saint Petersburg State University Center for Magnetic Resonance, Center for Chemical analysis and materials research and X-Ray Diffraction Center, respectively.
EXPLORATION OF S_N^E-APPROACH TOWARD FUNCTIONALIZED NITROXIDES AND NITRONYL NITROXIDES

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An actively using of conjugated nitroxides in the molecular design of magnets, spin labels, and redox active materials stimulates the development of ways of their preparing. In this work we demonstrated the possibility of obtaining functionalized nitronyl nitroxides by regiospecific substitution of fluorine in polyfluorinated arenes by a 4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl lithium derivative [1–3].

It was shown that the interaction of tert-BuNH₂ with perfluoroarenes and the subsequent oxidation of the resulting arylamines by m-CPBA leads to formation of new nitroxide radicals. The complexation reaction of Cu(hfac)₂ with the synthesized paramagnets gives complexes with ferromagnetically coupled spins.

References

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1,3-DIPOlar CYCLOADDITION OF NINHYDRIN-DERIVED AZOMETHiNE YLIdes WITH CYCLOPROPENES. STEREO- AND REGIOSELECTIVE SYNTHESIS OF SPIR0[CYCLOPROPA[A]PYRROLIZINES] AND 3-AZASPIR0[BICYCLO[3.1.0]HEXANES]

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3-Aza[bicyclo[3.1.0]hexanes] and related nitrogen heterocycles with a cyclopropane moiety are of great importance for organic and medicinal chemistry. As a result, it is not surprising that many efforts have been made to develop new protocols for the synthesis of these heterocycles.

In the past two years, our research group has demonstrated that 1,3-dipolar cycloaddition methodology can be extended to the synthesis of complex spiro[cyclopropa[a]pyrrolizines] and 3-azaspiro[bicyclo[3.1.0]hexanes] [1,2,3].

In this work, we aimed to explore expandability of this method by utilizing ninhydrin-derived azomethine ylides in cyclopropene 1,3-dipolar cycloadditions. Differently substituted cyclopropenes, including unstable substrates, were found to be highly reactive in these reactions affording the corresponding 1,3-dipolar cycloadducts with full regio- and stereoselectivity in impressive yields (up to 96%). The studied reactions are IED-controlled processes in which high regio- and stereoselectivity result from orbital control and second-orbital interactions as it has been disclosed by DFT calculations.

Figure 1. 1,3-DC reactions of ninhydrin-derived ylides to cyclopropenes.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Project No 18-33-00464).
SYNTHESIS OF 1-(PYRIDINE-2-YL)-2-AZABUTA-1,3-DIENES AND THEIR TRANSFORMATIONS INTO NITROGEN-CONTAINING HETEROCYCLES

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Functionalized 2-azabuta-1,3-dienes are attractive organic substrates for the synthesis of nitrogen-containing heterocycles (1,3- and 1,4-oxazine, dihydropyrazine and dihydropyrimidine derivatives), which can be formed by 1,4-electrocyclization or various 1,6-electrocyclizations involving azabutadiene fragment [1]. To study 1,6-electrocyclization of azabutadienes with participation of C=N bond of the aromatic pyridine cycle, we choose 1-(pyridine-2-yl)-2-azabuta-1,3-diene 3, which were supposed to be obtained by Rh(II)-catalyzed reaction of [1,2,3]-triazolo[1,5-a]pyridine derivatives 1 with 2H-azirines 2.

![Reaction scheme](image)

Figure 1. Reaction scheme.

It was found that properties of the 1-(pyridine-2-yl)-2-azabuta-1,3-dienes 3 are very different and depend on its substitution pattern. Some derivatives 3 (R¹ = CO₂Me) are stable and do not undergo any cyclizations. On the contrary, in the presence of a cyano group in the azabutadiene (R’ = CN) or a methyl group (R¹ = Me) 1,6-electrocyclization into 4H-pyrido[1,2-a]pyrazines 4 is the main direction of cyclization. In some cases, the 1,6-electrocyclization is reversible (R¹ = Ar) (Fig. 1).

References.

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SYNTHESIS OF AMIDES OF CARBOXYLIC ACIDS WITH AN IMIDE AND ALICYCLIC FRAGMENTS

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A search for new compounds capable of improving the properties of seeding material, increasing the productivity, and enhancing the resistance of crops to phytopathogens, drought, and cold is currently a topical problem in the optimization of agriculture. It is known that compounds containing an amide fragment possess a high biological activity and constitute a wide spectrum of fungicidal, insecticidal, and herbicidal preparations [1, 2]. However, at present, there are problems associated with the stable resistance of pathogens to available preparations, large amounts of wastes during their production, and, as a consequence, harmful effects on the environment. Thus, the search for, and the creation of, compounds free from these shortcomings is a timely task in the chemistry of pesticides [3]. Some compounds containing an imide fragment that are known to possess biological activity and low cytotoxicity have found application as growth-regulating reagents [4].

Our work is devoted to the synthesis of amides of carboxylic acids containing an imide and cycloalkenyl fragments. We synthesized several potentially bioactive compounds in which we combined the active structure of an amide with imide and cycloalkenyl fragments.

![Reaction Diagram](image)

1. DMSO, K₂CO₃, amino acids
2. DMSO, K₂CO₃, amine

R = H, iPr, iBu, -CH₂Ph
R’ = morpholine, cyclohexylamine, aromatic amine

Figure 1. Reaction

N-Substituted imides of alicyclic dicarboxylic acids were obtained in the in situ reaction of the corresponding amines with the products of the reaction of anhydrides (I) and (II) with natural amino acids in the equimolar ratio in the presence of a 1% solution of K₂CO₃ in DMSO. This method makes it possible
to obtain target compounds with high yields over a short time without intermediate isolation and with the use of readily available reagents.

References
OXIDOVANADIUM COMPLEXES WITH DIIMINE LIGANDS: SYNTHESIS AND PHYSICOCHEMICAL STUDIES

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Oxido complexes containing the V⁴⁺=O and V⁵⁺=O moieties are ubiquitous in the coordination chemistry of vanadium. They demonstrate efficient catalytic oxidase reactivity in various transformations. [1-2].

Figure 1. The structure of complexes 1-3.

This work is devoted to the study of reactions of VX₃ (X = Cl, Br) or VCl₃(thf)₃ with diimine ligands, such as 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen), 4,4'-di-tert-butyl-2,2'-dipyridyl (dbbpy), bis(imino)acenaphthene (dpp-bian) in acetonitrile in air, which lead to the formation of molecular complexes [VOCl₂(dpp-bian)] (1), [VOCl₂(H₂O)(dbbpy)] (2), and polymeric compounds [VOX₂(LNN)] (X = Cl, Br; LNN = bpy, phen) (3). Magnetic and redox properties were investigated for the obtained compounds. Complexes 1-3 exhibit high catalytic activity in alkane oxidation reactions, and complex 2 catalyzes cyclooctene oxidation [1-2].

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-03-00155).
A novel class of heterogeneous catalysts with an uniform distribution of Brønsted acidic centers was easily created by simple mixing of aqueous solutions of the tetrahydrochlorate of tetrakis(4-aminophenyl)methane and disodium 2,6-naphthalenedisulfonate acid salt in a ratio of 1:2, respectively (Figure 1). The structure of the formed salt was established by X-ray diffraction analysis.

Scheme 1.

According to the local X-ray spectral analysis the distribution of functional groups within the samples of CAHOC is uniform. CAHOC catalyzed epoxide ring opening reactions with MeOH, t-BuOH, H2O and Diels-Alder reactions (Scheme 3). In all the reactions CAHOC functioned as a heterogeneous catalyst and could be easily recovered from the reaction mixture and reused several times.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-53-05004 Арм_а).
One-pot Fe(II)/Au(I)-catalyzed protocol for the 4-propargylisoxazoles to methyl nicotinates derivatives transformation have been developed in our research group few years ago [1]. Further extension of this approach yielding symmetrical and unsymmetrical 2,2'-bipyridines have been reported by us recently [2]; later bipyridines turned out to be quite interesting as the ligands for luminescent complexes based on transition metals.

Little is known about properties of the same complexes of terpyridines, but in terms of chemical logic and minor accumulated evidences, one could suppose these substances to possess higher QY and other interesting optical properties. Here we wish to present the latest results of our investigation giving a way to titled compounds.

Figure 1. Schematic representation of proposed approaches to 2,2’-bi/2,2’:6’,2’’-terpyridines synthesis

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-33-00182).
Ti-Mg-CATALYZED REACTION OF $N,N,N',N'$-TETRAMETHYLDeca-2,8-DIYNE-1,10-DIAMINE WITH Et$_2$Zn


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Carbometallation is an efficient method of regio- and stereocontrolled synthesis of olefins. This work demonstrates that carbozincation of $N,N,N',N'$-tetramethyldec-2,8-diyne-1,10-diamine results in the selective formation of a bis-alkylidene cyclohexane derivative. Previously, we have shown that Zr-catalyzed cycloalumination of $\alpha,\omega$-bis(aminomethyl)alkadiynes results in the selective formation of a bis-alkylidene cyclohexane derivative [1]. Similarly, the reaction of $N,N,N',N'$-tetramethyldeca-2,8-diyne-1,10-diamine with 2.5 equiv. of Et$_2$Zn in the presence of 10 mol. % Ti(O-iPr)$_4$ and 20 mol. % EtMgBr carried out in diethyl ether at room temperature for 18 h and followed by deuterolysis or hydrolysis affords bis-alkylidene cyclohexane 1 and 2 derivative (Figure 1).

Figure 1. Carbozincation of $N,N,N',N'$-tetramethyldeca-2,8-diyne-1,10-diamine

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-73-20128) and Russian Foundation for Basic Research (project No 18-03-00817).
Polymorphism of organic, especially chiral, compounds is of great interest and value for modern crystallography, physical chemistry, process, and patent law. Since the free energy of different polymorphs of the same substance is different, all their physicochemical properties are different, that is, melting point, solubility, stability, hygroscopicity, pharmacodynamic and pharmacokinetic properties, and so on. Therefore, bioactive substances are particular attractive from the point of view of guided polymorph search. In this abstract, we reported crystallization and heterogeneous equilibria and transitions of four racemic N-substituted 4-arylsulfanyl-3-chloro-5-hydroxy-3-pyrroline-2-ones consisting an unsaturated $\gamma$-lactam ring that is an important pharmacophore group. As a result, in this series of compounds, a unique “conglomerate-conglomerate” polymorphic pair and a pair of packing polymorphs were found. All individual crystalline phases were studied by means of single crystal and powder X-ray diffractions. Their phase behavior was carefully investigated using heat flux differential scanning calorimetry, temperature-resolved solid-state vibration spectroscopy and hot-stage microscopy.

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SYNTHESIS OF \textit{N}-PYRIDYLUREA COPPER (II) COMPLEXES

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Complexes of copper (II) are widely used substances, especially in medicine as antimicrobial, antiviral, anti-inflammatory, as well as antitumor agents. Moreover, they are catalysts for several organic reactions. One of frequently used ligand motif in such complexes is pyridine and its substituted analogues. Our group has recently developed a mild method of \textit{N}-pyridinyl substituted ureas synthesis, using pyridine-\textit{N}-oxides and dialkylcyanamides [1]. These substances can be used as bidentate ligands for copper (II) complexes. We have synthesized several kinds of such complexes depending from CuCl$_2$ amount: \textit{i}) square planar, with only one urea ligand; \textit{ii}) octahedral, with two urea ligands and two chlorides; \textit{iii}) square pyramidal cationic with two urea ligands and one chloride. They were characterized by IR spectroscopy and HRMS as well as single crystal X-ray diffraction data.

![Figure 1. Preparation of \textit{N}-pyridylureas and they complexing.](image)

References

Acknowledgements. Physicochemical studies were performed at the Research park of Saint Petersburg State University.
Organic boronic acids have wide application in C,C and C,X- cross-coupling reactions and in medicinal chemistry [1]. However, many of them have limited stability, which complicates their usage in organic synthesis. Here, we have developed novel three-component condensation reaction between boronic acids, tris-oximes 1 and primary halides under mild conditions, leading to ate complexes 2. This is very unusual process in the chemistry of oximes, which rarely undergo cyclotrimerization reaction (Scheme). Heterocage complexes 2 have thermal stability up to 250°C, they are resistant to air-moisture and do not undergo hydrolysis in neutral and alkaline media. Thus, boradamantanes 2 may be considered as protective groups for unstable boronic acids.

Furthermore, the developed boronate-triol condensation was efficiently used in the design of fluorophore-labeled natural molecules (peptides, steroids), supramolecular assemblies, modified polymers, boronic acid scavengers, solid-supported organocatalysts, and biodegradable COF-like materials [2-3].

Scheme. Synthesis of stable ate complexes 2.

References

Acknowledgements. This work was supported by RFBR (Grant № 18-33-00647).
STUDY OF THE REACTIVITY OF $\beta$-HYDROXYPYRROLES

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Highly functionalized pyrroles have found various applications in organic synthesis, pharmaceutics and material science. Last year, highly substituted $\beta$-hydroxypyrrroles have unexpectedly become very accessible compounds due to the new method for their preparation that appeared [1]. However, chemistry of these compounds remains poorly studied, and their synthetic potential is not clear.

In the present work we report three highly selective transformations of synthetically accessible $\beta$-hydroxylated pyrrole-3-carboxylates 1 and pyrrole-2,4-dicarboxylates 2, which proceed under mild conditions to afford high yields new pyrrolin-3-one or pyrrole derivatives in high yields. Thus, a variety of pyrrol-3-yl sulfonates 3 and 2-aminopyrrolin-3-ones 4 were prepared using appropriate sulfonylating agent and “amine/halogenation agent” mixture respectively. The base-mediated reaction of pyrroles 1,2 with triflyl chloride provides the oxidative homocoupling products, bipyrrolinones 5. The conditions which enable the control of the diastereoselectivity of the reaction in favor of one or the other of the two isomers were found. The mechanism of this new reaction is discussed.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project № 17-13-01078). This research used resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies, and Chemistry Educational Centre of the Research Park of St. Petersburg State University.
TANDEM UGI/INTRAMOLECULAR DIELS-ALDER REACTION OF N-ALLYL FURALDIMINES

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The tandem Ugi/Diels-Alder reaction is one of a myriad of post-condensational modifications of the classic Ugi reaction. First reported in 1999, the UDA reaction provides a simple route to complex bridged tricyclic products [1]. In the present study we expanded the scope of the UDA methodology by incorporation of the dienophile in the amine and not in the acid counterpart.

These UDA reactions proceeded smoothly to provide compounds 1 as nearly equimolar (the diastereomeric ratio being 1:≤2) mixtures in good combined yields. These compounds can be involved in further modifications such as dehydrative aromatization to provide isoindolines 2 or intramolecular alkylation [2] to provide fused piperazinediones 3. These reactions are currently under investigation in our laboratories.

References

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Ru(II)-ARENE OXALATE COMPLEXES WITH BEXAROTENE AND LOMIDAMINE LIGANDS

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A significant sector of the anticancer drugs market is occupied by platinum-based compounds — cisplatin and its analogues. Ruthenium compounds, as the most promising alternative to platinum complexes, have a number of advances over classical platinum drugs, such as reduced general toxicity and different major targets. Ru(II)-arene compounds can be modified using biologically active ligand to achieve selective targeting of a cancer cell, selective accumulation or preparation of dual action drug.

The use of anionic chelating ligand, such as oxalate ligand instead of halide, has already been used to overcome solubility and stability problems, in the case of platinum-based compounds and titanocene analogues. For example, replacing two chloride ligands in RAPTA-C compound by oxalate ligand yielding complex that resistant to hydrolysis. This modification has a significant effect on the chemical and biological properties of the compound.

In our study new Ru(II)-arene oxalate compounds with lonidamine and bexarotene moiety were prepared. All complexes were characterized by NMR, ESI-MS and elemental analysis. Compounds were found to be stable in aqua and DMSO-containing solution. Antiproliferative activity of new compounds was investigated against SW480, A549, MCF7, WI-38 and HCT-116 cell lines by means of standard MTT colourimetric assay.

This work was supported by the RSF (project № 19-13-00084).
It has been recently shown that cinnamonitrile (3-phenylpropenenitrile) reacts with various arenes in the superacid CF$_3$SO$_3$H (TfOH) forming two types of compounds, 3-aryl-3-phenylpropanenitriles and 3-phenylindanones [1]. We continued this study and showed that substituted 3-arylpropenenitriles 1a-d in the same reaction in TfOH gave products of hydroarylation of the double bond C=C, 3,3-diarylpropanenitriles 2, and products of their further cyclization, 3-arylindanones 3. This reaction may proceed with an intermediate formation of cations A and B. The latter reacts with arenes Ar’H giving rise to species C, hydrolysis of which results nitriles 2. On the other hand, cations C bearing enough nucleophilic aryl rings Ar and Ar’ may undergo cyclization into species D, which form indanones 3 upon hydrolysis. This reaction is a novel method for the synthesis of nitriles 2 and indanones 3.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-001718).
HYDRATED IMIDAZOLINE RING EXPANSION (HIRE): RAPID ACCESS TO THE DIARENE-FUSED 1,4,7-TRIAZECINE RING SYSTEM

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Medium-sized rings have applications in a number of scientific fields, ranging from medicinal chemistry and supramolecular chemistry, to catalysis and nanotechnology. Such ring scaffolds (>8) generally have sufficiently well-defined conformations to bind to target receptors, but are more flexible than their smaller ring analogues. However, their use in these areas is limited by an important factor: large ring systems are very often difficult to make. Traditional end-to-end cyclisation reactions of long linear precursors are typically unpredictable and impractical processes. In contrast, the expansion of smaller ring systems is an attractive alternative way to synthesize such compounds [1].

One of the most promising ways to obtain such compounds is the hydrolytic imidazoline ring expansion (HIRE) methodology [2]. The reactions resulted in the facile formation of a rare medium-sized ring system that has an emerging utility in bioactive compound design. Thus, when primary aminoethanols are used, we get imidazoline-fused diazepines, and using of secondary aminoethanols leads to the formation of 10-membered lactams [3].

References

Figure 1
The Diels-Alder reaction is widely used in organic synthesis due to its simplicity, reproducibility and high atom economy. The Diels-Alder reaction between furans and alkynes results in the formation of 7-oxabicyclo[2.2.1]heptene scaffolds, which are used as a framework for a wide range of bioactive compounds and intermediates for the synthesis of other types of useful organic substances [1].

The phenomenon of thermodynamic and kinetic control is unique in organic chemistry since it allows alteration the direction of the reaction pathway by varying temperature. But on the other hand, the practical application of the kinetic/thermodynamic control is seriously hindered or rendered impossible by the formation of isomers [2].

Herein we report an interesting case of kinetic and thermodynamic control in the Diels-Alder reaction between hexafluorobutine and sulfamides on the basis of bis-(N,N)-furfurylamine. Depending on conditions, products of kinetic (3 a-e) or thermodynamic (4 a-e) control could be obtained in excellent yields.

*Figure 1. Synthesis of “pincer” and “domino” adducts.*

Synthesized products represent a promising class of novel potentially bioactive substances and were submitted on biotesting.

**References**


Funding for this research was provided by the Russian Science Foundation (RSF) (project No. 18-13-00456).
Great attention in modern pharmaceutical industry is paid to the problem of their targeted delivery directly to the affected organs, tissues and cells. Among many methods, the development of drug preparations containing lipids. Non-toxic amphiphilic derivatives of macrocyclic compounds have recently been used as lipid analogues. Pillar[n]arenes are new class of paracyclophanes, which have a number of attractive properties, i.e., ease of synthesis and functionalization possibilities. It was shown earlier, that substituted pillar[5]arene can form either host-guest complexes, or supramolecular associates, capable to targeted delivery of drugs.

We have synthesized the amphiphilic pillar[5]arene bearing DETA fragment. The presence of a single tail-group has opened wide opportunities for controlling the supramolecular associates formation in the form of various structures, i.e., pseudotaxanes, supramolecular polymers and SLNs all of which utilize only one type of the macrocycle. Water-insoluble macrocycle 3 forms the SLNs with controlled shape and size, stable in water. The simultaneous synthesis of the SLN with fluorescein made it possible to create the SLN-Flu particles containing luminescent marker, but not able to luminescence themselves. The light amplification is observed only when they interact with the DNA. This makes it possible to use the SLN-Flu as luminescent probes.

Figure 1. Synthetic scheme of the fluorescein-loaded SLN based on monoamine pillar[5]arene 3: i – ethylbromoacetate, K₂CO₃, KI; ii – DETA, EtOH/toluene (1:1), iii – THF/water.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-13-01208).
The present work is focused on the relevant issue of developing various biomedical composite materials. Composite materials were obtained in two stages: 1) using hydroxyapatite (HA) and 2) a pore-forming agent. NaCl forms ceramic frames that are calcined and subsequently soaked in distilled water to obtain porous ceramics. The resulting porous ceramic substrates are impregnated with a solution of poly(lactic-co-glycolic acid) (CLG) in chloroform under ultrasound exposure. The detailed obtainment and identification procedures of these materials have been described in the previous work [1].

Table 1. The ratio of components in composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>K1</th>
<th>K2</th>
<th>K3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content of NaCl at stage 1, wt.%</td>
<td>10</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Content of CLG in composites, wt.%</td>
<td>5</td>
<td>7</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 2. Characteristic of the diffusion of composites and hydroxyapatite

<table>
<thead>
<tr>
<th>Sample</th>
<th>After impregnation</th>
<th>Before impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K1</td>
<td>K2</td>
</tr>
<tr>
<td>Diffusion coefficient, D \cdot 10^{-7}, m^2/s</td>
<td>0.66</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The open porosity was confirmed by an experiment with the Franz diffusion cell. Diffusion coefficients for the composites were calculated both before and after CLG impregnation. After CLG impregnation, the diffusion coefficients decrease by 2-3 times, which correlates with a decrease in porosity during impregnation. Macroporosity of composites increases depending on the content of a pore-forming agent.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project number 17-03-00698\19).
The abuse of antibiotics was lead to appearance of resistant strains of bacteria and search of novel antibacterial agents is important. Mannich bases were found to possess broad spectrum of activities such as antibacterial, antifungal, antiviral and antimalarial [1]. Complexing to metals could increase the pharmacological effects and overcome the toxicity and side effects of these organic ligands [2]. Bismuth(III) compounds have been used for centuries in the treatment of a variety of microbial infections due to their high efficacy and low toxicity. Thus bismuth(III) complexes with Mannich bases present a promising field of search for compounds useful in producing such antibacterial agents.

Figure 1. Synthesis of Mannich bases.

Mannich bases of sterically hindered phenolic compounds were synthesized according to methods reported previously (Figure 1) [2]. Bi(III) complexes with Mannich bases were prepared and characterized by means of elemental analysis, TG/DTA, FT-IR, UV-Vis, XRD and conductivity measurements. They were isolated from acidic medium where phenolic ligands are protonated, and thus no bonding between the ligand and bismuth(III) was observed. The bismuth(III) ions are coordinated by chloride ions forming complex chloride anions. The charge of this ion is compensated with protonated phenolic ligands (ionic interactions). According to the results of pharmacological screening bismuth(III) complexes demonstrate high antibacterial and antifungal activities and may be considered as potential chemotherapeutic agents.

References
Cationic azaheterocyclic compounds are widely used in the chemistry of materials, as well as in synthetic organic chemistry as precursors of various nitrogen-containing heterocycles and acyclic substances. This work describes a new highly efficient synthetic method of preparation of 5-amino-2-methyl-1,2,4-oxadiazolium salts from aminonitrone and isocyanide dibromides [1]. The reaction proceeds under mild conditions, utilizing simple and easily accessible reagents. In the framework of this study, 16 new 5-amino-2-methyl-1,2,4-oxadiazolium salts were obtained in high yields (65–95%).

The charged character of these heterocyclic systems makes them suitable substrates for reactions with nucleophiles, and 5-cyclohexylamino-2-methyl-3-phenyl-1,2,4-oxadiazolium bromide, taken as a model compound for the reactivity study, reacts rapidly under mild conditions with hydroxylamine, hydrazine, or benzamidine, to give 5-cyclohexylamino-3-phenyl-1,2,4-
oxadiazole (88%), 5-cyclohexylamino-3-phenyl-1,2,4-triazole (95%), and 2-cyclohexylamino-4,6-diphenyl-1,3,5-triazine (64%), respectively. Treatment of the oxadiazolium salt with excess water provides N-benzoyl-N’-cyclohexylurea (95%).

All of these compounds were unknown before, and in this work, they were characterized by HRESI+MS, IR, and \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR spectroscopies. In addition, six species were additionally characterized by single-crystal X-ray diffraction (XRD).


This work was financially supported by the Russian Science Foundation (grant 17-73-20004). Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).
Various structures of sulfonamides had been holding the limelight of synthesis chemistry for a long time. Their structural diversity has led to the expansion of the action’s spectrum of drugs of this class. Recently many new containing two sulfonamide functions drugs have been synthesized. It allowed to increases their biological activity.

Based on the previously developed method for creating a sulfonamide function by Diels-Alder reaction using aniline derivatives, we synthesized compounds containing two sulfonamide fragments, as well as a fused and an isolated biaromatic fragment.

![Figure 1. Synthesis of \(\alpha\)-naphthylamine based sulfonamides](image1)

![Figure 2. Synthesis of 1,5-diaminonaphthalene based sulfonamides](image2)

![Figure 3. Synthesis of 4,4’-ethyleneedianiline based sulfonamides](image3)

The structure of compounds 5-13 is confirmed by the data of FTIR, NMR. The structure of compound 11 is finally established by XRC.
FORMYLATION OF THIOPHENE FRAGMENTS IN THE SYNTHESIS OF POLYFLUORATED TRIARYLPYRAZOLINES-BASED CHROMOPHORES

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It was previously shown that aldehydes based on polyfluorosubstituted triarylpyrazolines can be used as donor blocks in synthesis of donor-acceptor NLO dyes [1, 2]. In this work, an attempt was made to elongate the polymethine chain of chromophore by including a thiophene fragment. For this purpose, Wittig condensation of aldehyde 1 and thiophene 2 was used for the synthesis of compound 3, which was then subjected to formylation. When the reaction was carried out in BuLi/DMF system the molecule 3 was destroyed. Vilsmeier formylation led to dialdehydes 4 and 5.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-13-10156).
Donor-acceptor organic molecules with conjugated polyene bridge are being investigated because of their nonlinear optical properties due to the charge separation [1].

Previously a range of thiophene-based dyes with dendroid substituents was made [2]. Here we expand that range by the synthesis of such dye with novel dendroid structure (TAFS) and analysis of possible byproducts.

Novel nonlinear dye 3 was obtained from corresponding aldehyde 1 by the condensation with TCP and further acylation. The major product of condensation is 4, due to the equilibrium formation of TCP, so the target compounds 2 was isolated with a rather low yield.

Chromophore 3a showed second-order susceptibility of 60 pm/V (polycarbonate film, 20% wt.), $\lambda_{\text{max}}$ 936 nm (CHCl$_3$).

References
SYNTHESIS OF 2,2'-SPIROBI[INDENE] AND 5,5'-SPIROBI[CYCLOPENTA[B]THIOPHENE] AND THEIR MODIFICATION VIA STILLE REACTIONS

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High-efficient organic light-emitting diodes (OLEDs), organic light-emitting transistors (OLETs) and organic electrically driven lasers require materials combining efficient electroluminescence and high semiconducting properties. However, synthesis of such compounds is challenging since the dense packing that is crucial for improved semiconducting properties causes quenching of luminescence due to the aggregation effects.

Herein we develop synthesis and study properties of linear conjugated spirocyclic compounds – 2,2'-spirobi[indene]s and 5,5'-spirobi[cyclopenta[b]thiophene]s – which combines rod-like structure with the orthogonality of two independent π-systems.

The synthetic route to spirocyclic dihalogenide 5 includes the sequential alkylation of malonic ester with the corresponding halogenides 2, hydrolysis of the obtained ester 3, and the intramolecular acid-catalyzed cyclization of the resulting acid 4 in the presence of polyphosphoric acid (PPA). Spirocyclic dihalogenide 5 was further decorated with linear conjugated systems based on thiophene or phenylene-thiophene moieties via Stille reactions.

DFT and TD DFT quantum chemical calculations were used for theoretical study of ground and excited states of the molecules obtained. As a result, it was shown that spiroconjugation could be effectively used for design materials with specific optical and electronic properties.

Acknowledgements. This work was supported by Russian Science Foundation (project № 19-13-00327).
CHARGE TRANSFER COMPLEXES OF LINEAR ACENES WITH A NEW ACCEPTOR PERFLUOROANTHRAQUINONE. THE INTERPLAY OF CHARGE TRANSFER AND F···F INTERACTION.

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Two charge transfer bicomponent 1:1 crystals of polycyclic aromatic hydrocarbons (anthracene and tetracene) with a new acceptor molecule (perfluoroanthraquinone) were grown by slow evaporation from solutions in toluene. The perfluoroanthraquinone molecule exhibits structural reorganization from folded geometry to planar structure upon complex formation. The co-crystals exhibit charge transfer bands in the UV-Vis spectra. In both crystals π-π stacks of alternating donor and acceptor molecules are observed. In the tetracene-perfluoroanthraquinone complex face-to-face stacking is the prevailing intermolecular interaction, which results in the “ideal” ring-over-bond mutual orientation of the donor and acceptor molecules. Meanwhile in the complex of anthracene-perfluoroanthraquinone multiple interactions (stacking, F···H, O···H, F···F) of similar energy are observed as revealed by the R. Bader’s QTAIM method. This results in a significant shift of the molecules from the supramolecular arrangement favorable for the charge transfer and in polymorphic modifications of the anthracene-perfluoroanthraquinone complexes as determined by X-ray single crystal diffraction and DSC. The charge transfer degree was estimated to be equal to 0.04 and 0.08 e in anthracene and tetracene complexes, respectively, which complies with interplanar distances of 3.5 Å in anthracene complex and 3.3 Å in tetracene complex and perfect ring over bond arrangement in the latter.
3,7-Diazabicyclo[3.3.1]nonanes (aka “bispidines”) represent a very useful group of compounds that could possess multifunctional properties. For example, earlier we investigated copper complexes with bispidine-based chelates which could be used for diagnostic and medication of pathological diseases using PET [1]. In addition, molecules with bispidine backbone are promising as catalysts. The unsolved problem of such chelates is how to binding them to a vector for targeted delivery of a drug, or to solid support.

In this work, the role of sterical hindrance in the selective transformations of the sixth position in 5,7-dimethyl-1,3-diazaadamantanes was studied. We performed a series of reactions and showed that, indeed, the sterical hindrance of sixth position by two adjacent methyl groups highly restricted its reactivity. So, only a limited scope of modifications is proved to be synthetically useful for the creation of linking group at sixth position (Scheme 1).

Scheme 1. Synthetically useful reactions for modification of the sixth position of 5,7-dimethyl-1,3-diazaadamantane derivatives.
In future, this work could help in expanding the synthetic strategy for drug’s linking to a diazaadamantane, which itself is a precursor of variable bispidine derivatives.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-73-20090).
SYNTHESIS OF NOVEL TYPES OF TETRACYCLIC HYDROXAMIC ACIDS VIA THE CASTAGNOLI-CUSHMAN REACTION


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Hydroxamic acids are widely applied in medicinal chemistry as metalloenzyme inhibitors and drug-carriers. In addition, hydroxamic acids are often used as metal chelating agents for development of colorimetric or fluorimetric chemosensors. This work aimed to construct novel fluorescent tetracyclic hydroxamic acids by cyclization of the Castagnoli-Cushman reaction (CCR) products followed by post-modifications. The CCR products were obtained from homophthalic anhydride (HPA) and aryl-substituted oximes. Two types of cyclizations were studied: intramolecular esterification (Fig.1) of salicylic oxime derivative and Fridel-Crafts acylation (Fig.2). As a result, we accomplished the synthesis of three novel isoquinolinocoumarines using the first protocol. The structure of products was confirmed by 2D-NMR spectra and X-ray analysis. The reactions of aromatization for these compounds were also studied. The second synthetic approach was studied for two CCR products (Fig.2), which allowed to obtain one novel tetracyclic hydroxamic acid with five-membered cycle.

![Figure 1](image1)

![Figure 2](image2)

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-73-00074).
Porphyrin photosensitizers (PPS) are macro heterocyclic pigments with peculiar physico-chemical properties which determine their extensive use in the medicine and catalysis. It should be pointed out that water-soluble porphyrins and their analogues – chlorins – may form complexes with surfactants, that boosts their photodynamic and photocatalytic activity. In particular, polyvinylpyrrolidone (PVP) increases the photosensitizing activity of PPS in 3-5 times [1]. The new tendencies in the improvement of the photodynamic therapy (PDT) efficacy in the treatment of hard-to-heal purulent wounds, trophic ulcers, infected burns, are exhibited in a combination of PDT with the effects of biologically active substances – enzymes, vitamins, natural bactericidal polymers, accelerating the healing process[2]. As one of such substances, chitosan (CT), a biologically active and bactericidal polysaccharide, is considered. However, the preliminary experience of its application as a polymer component in complex with PPS in model processes of photosensitized oxidation of organic substrates unambiguously indicated a diminished efficiency of PPS-CT systems. The objective of this study is to select the optimal ratio of the components in the three-component complex PPS-PVP-CT, which exhibits high photocatalytic activity in the temperature range of PDT sessions, on the example of a model (test) process of tryptophan oxidation in an aqueous medium. Also, the use of photoditazin-CT-PVP complexes in the treatment of model wounds of laboratory animals have shown effectiveness, in particular their use reduces the activity of inflammatory processes and increases the proliferation of fibroblasts, neoangiogenesis, growth and maturation of granulation tissue.

References

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NEW “ONE-POT” TECHNOLOGY FOR PRODUCING OLEANOLIC ACID FROM PLANT RAW MATERIALS BY SUBCRITICAL WATER (SBW)

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Oleanolic acid (OA) is one of the most common pentacyclic triterpenoid compounds, mainly occurring in various plant sources (more than 1,600 species of plants). The object of investigation used in the roots aralia (Aralia mandshurica Rupr.). Using the roots of a plant for therapeutic purposes related to their content of up to 5% of triterpene saponins - aralosides (I) [1-2].

Developed and studied «one - pot» technique for obtaining OA (II) from the roots of the Aralia in subcritical water environment. Procedure «one-pot» processing aralia roots in SBW were performed using a reactor (autoclave) [3]. The efficiency of the proposed method of obtaining OA in subcritical water environment studied in the temperature range from 140 to 230°C. It is established that «one - pot» equipment for subcritical water environment allows for output OA, comparable to the yields of traditional methods, without the use of - or catalytic additives. Time cost of the proposed approach reception OA is 16 times less than the traditional two-step process of getting OA (Fig. 1).

Figure 1. Scheme preparation of oleanolic acid from roots aralia.

References

Acknowledgements. This work was financially supported by the internal grant of the Southern Federal University (project No VnGr-07/2017-04).
THIOMETHYLATION OF 2-HYDROXY-1,4-NAPHTHOQUINONES:
SYNTHESIS OF QUINONE-CARBOHYDRATE CONJUGATES

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1,4-Naphthoquinones comprise an important class of organic compounds that are widely distributed in plants, marine invertebrates, fungi, and bacteria. These compounds attract the attention of researchers due to a wide range of pharmacological properties including antibacterial, antiviral, trypanocidal, anticancer, antimalarial, and antifungal activity. In particular, dioncoquinone B (1) and related compounds 2-5 isolated from various terrestrial plants (Figure 1) are of interest due to their promising anti-tumoral and anti-infective activities [1].

We have previously developed a preparative method for the synthesis of compounds 1-5 and their homologues 6-8 [2]. Here we modified the structures of these compounds for further studying their biological properties. The thiomethylation of 2-hydroxynaphthoquinones 6-8 with 1,2,3,4-tetraacetyl-6-mercapto-6-deoxy-D-glucose 9 leads to acetylated conjugates 10-12, in which the carbohydrate moiety is separated from the quinoid core by a methylene spacer. The partial methylation of conjugates 10-11 with diazomethane leads to conjugates 13-14. The deacetylation of conjugates 10-14 of the related natural quinones 1-5 leads to conjugates 15-19 with a free fragment of glucose. The introduction of glucose fragment into a molecule increases water solubility and bioavailability of the substance. According to the Warburg effect based on increased glucose consumption by tumor cells it can also increase the cytotoxicity against tumor cells than normal ones [3].
Figure 1. The scheme of synthesis of quinone-carbohydrate conjugates.

References


Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project № 18–33-00460).
Currently, one of the promising areas of chemistry is the investigation of phosphorus compounds. This is an extensive group of substances containing P-C and P-O bonds, representatives of which are found in natural objects. Phosphonates are the subgroup of phosphorus compounds and correspond to organophosphorus compounds containing C−PO(OH)2 or C−PO(OR)2 groups (where R = alkyl, aryl). Phosphonates are of the greatest interest for science and technology as they can be used as plant growth regulators, drugs, antiviral treatments. That is why the creation of new phosphonate compounds with targeted properties is of great importance. In our research we deal with homemade member of the phosphonate family that is 6-methoxyphosphonate 3-amino-2-methyl-3H-thiazole [3,2-b] [1,2,4] triazole-7th (E151). Structural formula is presented in Fig 1.

![Figure 1. The structural formula of 6-methoxyphosphonate 3-amino-2-methyl-3H-thiazolo [3,2-b] [1,2,4] triazole-7-I.](image)

Based on non-experimental screening of biological activity using the PASS computer program, it can be assumed that this compound may have a wide spectrum of biological activity as a treatment for amyotrophic lateral sclerosis. The E151 investigations with absorption, Raman, FTIR spectroscopies and enzymatic method demonstrated possibility of laser-induced modification of physicochemical and functional properties of this substance. The difference between the irradiated and unirradiated sample was revealed, as well as the effect of laser radiation on the biological activity of the sample was also established.
ACCESS TO 5-ARYLPYRAZOLYL RECEPTORS ON A CALIXARENE SCAFFOLD THROUGH YNONE ROUTE

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At present, much attention is devoted to ketoacetylene molecules, which give access to diverse heterocycles. Such heterocycles often possess biological activity, such as antitumor, anti-inflammatory, antidiabetic, and many others. Assembly of such heterocyclic units on a calixarene scaffold is particularly attractive because of low toxicity of this macrocycle and a possible synergetic effect of the heterocycles on this macrocycle. This work is aimed at the synthesis of alkylnyl, alkynone, and 5-ary lp yrazolyl derivatives of calix[4]arene (Scheme 1).

\textbf{Scheme 1.}

In this work, a number of phenylpyrazolyl receptors on a calixarene scaffold in \textit{partial cone} and \textit{1,3-alternate} stereoisomeric forms (1 and 2) have been synthesized through alkyne–alkynone–arylp yrazole route and characterized using NMR and MALDI mass spectrometry. This approach proved effective in the synthesis of calixarenes containing tert-butyl (1) and hydrogen atoms on the upper rim (2).

This work was supported by the Russian Foundation for Basic Research (project nos. 17-53-10016-KO-A and 17-03-00389-A).
NEW REARRANGEMENT OF 1,2-DIHYDROPYRIMIDINES

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Compounds containing dihydropyrimidine-5-carboxylate moiety exhibit various biological activities, and could serve as scaffolds in the development of effective vasodilative and hypotensive drugs. Trifluoromethyl-substituted analogues in this regard are of especial interest. However the introduction of CF₃ group into the 1,2-dihydropyrimidine ring is quite complicated task, and these derivatives remain hardly accessible compounds.

In this work a three-step synthesis of 2-CF₃-substituted 1,2-dihydropyrimidine-5-carboxylates 5 from azirine-2-carbaldehydes 1, amines and ethyl 2-diazo-3,3,3-trifluoropropionate 3 is developed. The latter serves as a source both of the CF₃ group at the C2 and the ester group at the C5 of the final dihydropyrimidine. Azirincarbaldimine 2, quantitatively formed in the first step, is subjected to three-atom ring expansion to dihydropyrimidine 4 in the second step under the action of diazo compound 3 under rhodium(II) catalysis. The key stage of the synthesis is unusual thermal “1,2-dihydropyrimidine – 1,2-dihydropyrimidine” isomerization, which affords the targeted 1,2-dihydropyrimidines in good yields. The mechanism of this new rearrangement was investigated by DFT method.

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NEW FUNCTIONALLY SUBSTITUTED QUINAZOLINES: SINGLE CRYSTAL AND PXRD ANALYSIS

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Quinazoline derivatives are broadly used as anti-tumor agents (afatinib, gefitinib and erlotinib drugs), as radioligand, when labeled with $^{18}$F, in positron emission tomography and neuroimaging (altaserin), and in another areas of medicine, for example, prazosin is used to treat high blood pressure¹,². Thus, their practical importance in pharmacology and biology is great.

Wide range of new quinazoline derivatives has synthesized during our investigations, part of them has obtained in the form of a single crystals and their structures has been determined by the single X-ray analysis. Compound 1 (Ar=o-F-Ph) forms monoclinic crystals with one independent molecule in the unit cells, while the compound 2 (Ar=p-Br-Ph) crystallizes with a dimethyl sulfoxide molecule in the ratio 1:1. The geometry of molecules, intermolecular interactions and packing in the crystals will be discussed in the report. It is interesting to note that when the solvent leaves, compound 2 loses its crystallinity and becomes amorphous. The peculiarities of behavior and reversibility of this process are studied by powder diffraction and are discussed in the report. Other derivatives are characterized by powder diffraction method.

References

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FLUORESCENT LABELING OF C-PEPTIDE MOLECULAR TARGETS ON LIVE CELLS VIA ALKYNE-AZIDE CLICK CHEMISTRY

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C-peptide is a short peptide produced during processing of insulin from proinsulin. C-peptide is stored in pancreatic β-cells secretory granules and released into bloodstream in equimolar ratio with insulin in response to blood glucose stimuli. In 1990s it was reported that compensation of C-peptide levels in laboratory animals and type I diabetes patients improved diabetes-induced abnormalities in some peripheral tissues. These observations on C-peptide functions encouraged the searching of novel methods for diabetes treatment. Although our understanding of C-peptide role in biochemical processes increased, there remains uncertainty regarding exact cellular targets of C-peptide. In order to identify those targets we proposed an approach based on fluorescent visualization of C-peptide binding sites in cells. The visualization is facilitated by click-reaction termed as azide-alkyne cycloaddition.

For this purpose, C-peptide was covalently modified via N-acylation at N-terminus via introduction of an alkyne moiety to allow peptide interaction with N₃-finctionality of fluorescent dye. The latter was introduced after peptide binding to its targets. Therefore, we attempted minimal modifications of C-peptide molecule to preserve its biological activity and remove artifacts related to impact of fluorescent dye on the specificity of C-peptide binding.

As has been previously reported, HEK-293 cell line responded to C-peptide treatment, therefore this cell line was utilized in our study. TAMRA-azide was chosen for fluorescent labeling. Cells were incubated with modified peptide and then the fluorescent dye was introduced. Then the catalyst promoting click-reaction between binded peptide and dye was added. In order to produce contrast, cell’s nuclei and membranes were stained with bisbenzimide (Hoechst 33342, blue) and CellMask™ (green), respectively. After removal of excessive dyes, the cells were studied by fluorescent microscopy. The same manipulations were carried out with human insulin, which served as a control to verify of proposed experimental approach. Thus, we developed a method for C-peptide covalent modification for fluorescent labeling. The labeling on HEK-293 cell line was carried out to gain images illustrating targets and distribution of the C-peptide in cells without impact of fluorescent probe on C-peptide specificity of binding.
The need for nonsteroidal anti-inflammatory drugs (NSAID) remains high. Despite the positive effect of NSAIDs, it has some serious side effects, such as gastrotoxicity [1]. The side effect can be eliminated by masking carboxyl group, such as was done in the case of ibuprofen glycoside [1]. The objects of the study were selected amino acid derivatives of 4-(1-adamantyl) benzoic acid, which reliably exhibit anti-inflammatory and analgesic activity[2,3]. These compounds were administered in O-glycosylation reaction using respectively acetobromoglucose 2, acetochloroglucose 3 and tetraacetylglucose 4. The effect of reaction conditions on the yield and purity of desired products.

Figure 1. Reaction.

For each compound obtained anomeric composition analysis conducted using $^1$H NMR spectroscopy.

[Bu₄N]₂[MoO(mnt)₂] (1) can act as a synthetic analog of molybdenum oxotransferases [1]. The thermodynamic characterization of the oxotransfer processes involving complex 1 is important to understand the basic function principles of molybdenum oxotransferases.

Our work included two stages: synthesis of the complex 1 and the thermodynamic study of the oxidation process. The complex was synthesized by the following reaction [2]:

$$\text{H}_2\text{MoO}_4 + 2\text{Na}_2\text{mnt} + 2\text{Bu}_4\text{NBr} + \text{NaHSO}_3 \rightarrow [\text{Bu}_4\text{N}]_2[\text{MoO(mnt)₂}] + 2\text{NaBr} + \text{H}_2\text{O} + \text{NaOH} + \text{Na}_2\text{SO}_4$$

The structure of the complex was determined by the X-ray diffraction structure analysis. The enthalpy of the oxotransfer was determined in an acetonitrile solution using a calorimeter of the Calvé type using following reaction:

$$\text{Me}_3\text{NO} + [\text{Bu}_4\text{N}]_2[\text{Mo}^{IV}\text{O(mnt)₂}] \rightarrow \text{Me}_3\text{N} + [\text{Bu}_4\text{N}]_2[\text{Mo}^{VI}\text{O}_2\text{(mnt)₂}]$$

The calorimetric curve shows: the first endothermic peak corresponds to the dissolution of 1, the value of dissolution enthalpy is -206.8 kJ/mol. The second step corresponds to the molybdenum oxidation. The enthalpy of oxotransfer was calculated as a difference between the total reaction enthalpy and the enthalpy of dissolution: -206.8 kJ/mol.

Two steps of the oxidation process can be seen on the calorimetric curve, which is in good accordance to the proposed reaction mechanism [1].

References

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C,N-CHELATED DIAMINOCARBENE COMPLEXES OF Pt(II) AS NOVEL CATALYSTS FOR HYDROSILYLATION OF UNSATURATED COMPOUNDS

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Metal complexes with acyclic diaminocarbenes (ADCs) over the last few decades have been widely used in a broad range of catalytic reactions [1]. Diaminocarbene complexes of Pt(II) can be used as efficient catalysts for hydrosilylation reaction of unsaturated compounds [2].

Owing to the reactions of coordinated isocyanides with N-nucleophiles, the acyclic diaminocarbene complexes can be easily generated. We studied the interaction between 3,4-diaryl-1H-pyrrol-2,5-diimine and cis-[PtCl₂(CNR)₂]. The reactions are depicted in the scheme below.

Figure 1. Synthesis of C,N-chelated diaminocarbene platinum(II) complexes.

Unsaturated compounds undergo the platinum complexes catalyzed hydrosilylation, affording the corresponding silanes in high yields. The regio- and stereoselectivity of hydrosilylation will be discussed.

References

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SYNTHESIS OF STABLE, INDUSTRIALLY SCALABLE, EFFICIENT METATHESIS HOVEYDA-GRUBBS CATALYSTS WITH AN \( \text{N} \rightarrow \text{RU} \) OR \( \text{N} \rightarrow \text{S} \) COORDINATE BOND IN A SIX-MEMBERED RING

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The widespread application of various catalysts is required to achieve the best results in each of the many directions of metathesis reactions. This fact motivates the investigations into the development of new, efficient, stable, and highly selective catalytic system.

In this work the multigram synthesis of ruthenium catalysts was carried out using methods based on the interaction of the well known complex \( \text{1} \) with styrenes \( \text{2-4} \) that gave target Hoveyda-Grubbs type catalysts \( \text{5-7} \) in good yields [1, 2].

The synthesized catalysts demonstrated prominent stability in air at room temperature for at least 5 years. The catalysts have good solubility in \( \text{CH}_2\text{Cl}_2 \), \( \text{CHCl}_3 \) and hence, their can be used in any types of metathesis reactions.

Catalytic properties of metallo-complexes \( \text{5-7} \) were demonstrated in “standard” cross metathesis (CM), ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) reactions [1].
References


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SYNTHESIS OF A NOVEL NICKEL(II) COMPLEX AND ITS ANTIBACTERIAL ACTIVITY

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Infectious diseases are the major causes of death especially in developing countries. These diseases kill about 15 million people every year, which corresponds to about one-third of the number of deaths. The development of antimicrobial drugs, particularly antibiotics, has long been touted as one of the great medical success stories of the twentieth century. Although several classes of antimicrobial compounds are presently available, microorganism’s resistance to these drugs constantly emerges. In the search for new drugs against resistant infectious diseases, the modification of existing drugs or organic molecules by coordination to a metal center has attracted considerable attention [1]. Substituted thioureas are interesting as reagents for the separation of metal ions, as antibacterial, antiviral, or antifungal agents [1]. Herein, we report about synthesis of a novel nickel(II) complex (Scheme 1).


The obtained complex was characterized and its in vitro antibacterial activity against S. aureus and E. coli was also studied.

References

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PHOTOCATALYTIC ACTIVITY SOLUBILIZING PLURONIC F-127
STEROID BIOCONJUGATION of PYROPHEOPHORBIDE A

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In recent years, targeted delivery of photosensitizers (PS) to tumor cell receptors has been used. It is minimize the side effect and increase the effectiveness of photodynamic therapy (PDT) of malignant tumors [1]. In this work, we studied the photosensitizing activity of hydrophobic PS - steroid conjugates of pyropheophorbide a (PPa) in the generation of singlet oxygen 1O2 (playing the role of an active agent in PDT). Our PS were containing testosterone (PPT) and dihydrotestosterone (PDfT), isomers of PPT with a hexadecylamine (PPTH I,II). These compounds have been solubilized by non-toxic amphiphilic polymer - pluronic F-127. The photoactivity of PS was studied in the model photooxidation reactions of tryptophan in water and anthracene in chloroform [2]. It has been shown that PSs modified with steroid molecules have affinity for androgen-dependent cancer cells — prostate carcinoma cells [3]. It was shown that the pluronic F-127 practically didn’t affect the value of the effective rate constant keff for all bioconjugates pyropheophorbides a (PPa), in the reaction of photooxidation anthracene in chloroform. This is due to the fact that in chloroform the pluronic didn’t form micellar structures and didn’t interact with the substrate. In this case, the value of keff photooxidation tryptophan in water in the presence of solubilized substituted PPa increased with the concentration of F-127. The observed effects are associated with the disaggregation of PS molecules due to the formation of complex a pluronic-conjugates PS. The obtained dependencies of keff changes were confirmed by the data of electron and fluorescence spectroscopy. Thus, the fluorescence intensity of solubilizing pyropheophorbide PS was increased with increasing concentration of F-127, and indicating of process disaggregation. Thus, F-127 solubilization allows to obtain of water-soluble forms of PS, which are active in the processes of photocatalytic oxidation.

References

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DESIGN OF CRystalline FORMS OF CYCLOMETALATED PLATINUM(II) COMPLEXES

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Halogen bonding has found applications in organic and metal-organic synthesis, and the obtaining crystalline or liquid-crystalline materials in which halogen bonding involving molecular building blocks with interesting optical or emissive properties has been employed to generate materials exhibiting novel or improved optical properties. Halogen bond-based cocrystallization of platinum(II) complexes is an effective strategy for tuning the solid-state luminescence of crystals. In particular, heteroleptic square planar platinum(II) complexes with different kinds of ancillary ligands show significant scope for tuning their emissive properties over the entire visible spectra by modification of the cyclometalated and/or the ancillary ligands. [1].

In the course of our study of luminescent materials based on cyclometalated complexes platinum(II) with multifunctional isocyanide ligand was synthesized complex [Pt(ppy){C≡NC₆H₅}Cl] (ppy – phenylpyridine) and halogen-bonding cocrystallized with I-, o-Br,Br and p-Br,Br- PFB (PFB – perfluorobenzene).

Figure 1. Cocrystallizates of [Pt(ppy){C≡NC₆H₅}Cl]

References

This work was supported by grant of the President of the Russian Federation, project MK-1476.2019.3. Physicochemical studies were performed at the Center for Magnetic Resonance, X-ray Diffraction Center and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).
Fluorescence imaging has emerged as a very powerful technique to carry out a research into chemical and biochemical processes. Due to considerable significance of metal ions’ detection in biological systems and environment, increased attention has been focused on design of rapid and highly selective fluorescent chemosensors on metal ions.

Recently in our research group was developed a general approach towards cyclic $N$-hydroxytetrahydroquinolonic acids, which are representative of cyclic hydroxamic acids (CHA), via Castagnoli-Cushman reaction of homoptalic anhydride and oximes [1]. Synthesized CHA showed high ability to chelate ions Fe$^{3+}$ with strong complexes formation. Attaching fluorophores such as porphyrins derivatives to CHA may afford to obtain new fluorescent chemosensors for effective monitoring the concentration of metal ions.

In the present work we designed and synthesized a series of fluorescent dyes applying 5-(4-aminophenyl)-10,15,20-triphenylporphyrin as fluorophore and CHA with various substitutes as metal binding receptor. Synthesized compounds were investigated via UV/Vis absorption and fluorescence emission spectra and showed promising photo-physical properties.
INTERACTIONS OF DIAZIRIDINES WITH ISOCYANATES AND ISOTHIOCYANATES

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Reactivity of diazaridines, three-membered ring, containing two nitrogen atoms, cause increased interesting, because on the one hand they can undergo opening of three-membered cycle on C-N bond, with generation of 1,3-dipole – azomethine imine [1], on the other hand, due to presence of lonely electron pairs in two nitrogen atoms, in some cases diazaridines act as nucleophiles [2]. The aim of our research is to investigate interaction 1,5-diaza[bicyclo[3.1.0]hexane with arylisocyanates and arylisothiocyanates under different conditions.

![Figure 1. Interaction 1,5-diaza[bicyclo[3.1.0]hexane with arylisocyanates and arylisothiocyanates.](image)

It would be determine, that interaction non-substituted in 6 position 1,5-diaza[bicyclo[3.1.0]hexane 1 with isocyanates results in products 2, which is result of interaction of three equivalents isocyanates with one equivalents diazaridines. At the same time reaction 1 with isothiocyanates, giving products 3 attachment two equivalents isothiocyanates.

References

Acknowledgments. NMR, HRMS and XRD studies were performed at the Saint Petersburg State University Center for Magnetic Resonance, Center for Chemical analysis and materials research and X-Ray Diffraction Center, respectively.
3-methyl-1,2-butadienyl phosphine oxides \([X_2(O=)P–CR=C=CM\text{e}2, \ X = \text{Cl}, \ \text{OMe}, \ \text{NR}_2, \ \text{or} \ \text{SAr}]\) have undergone intramolecular cyclization into the stable 1,2-oxaphospholium ions in Brønsted superacid TfOH. These cations have been thoroughly studied by means of NMR. Solvolysis of superacidic solutions of these species has afforded cyclic phosphonic acid derivatives.

Contrary to that, P,P-dichloro-3-methylbuta-1,2-dienyl phosphine oxide \([\text{Cl}_2(O=)P–\text{HC}=\text{C}=\text{CM}\text{e}2]\) has reacted with Lewis acid AlCl\(_3\) in an intermolecular way forming non-cyclic intermediates, which have been investigated by NMR and DFT calculations. These intermediates react with arenes giving to products of hydroarylation of the allene system, phosphoryl substituted alkenes and/or indanes. Strong coordination of the oxygen of the P=O group with AlCl\(_3\) has prevented the formation of cyclic 1,2-oxaphospholium ions and played a crucial role in different reactivity of such allenes under the action of Brønsted or Lewis acids.

This is the first example of Lewis acid-promoted intermolecular hydroarylation of allenes bearing electron-withdrawing substituent.

**Figure 1.** Reaction of P,P-dicloro-3-methylbuta-1,2-dienyl phosphine oxide with TfOH or AlCl\(_3\).
1,3-DIPOLAR CYCLOADDITION OF ADAMANTANE DERIVED NITRONES WITH MALEIMIDES

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Adamantane derivatives have a wide range of pharmacological properties and are of increased interest for the search of new medicine [1-2]. It is known that the 1,3-dipolar cycloaddition of nitrones to olefins is the most simple and effective method for the synthesis of isoxazolidines. Nevertheless, the reactions of adamantane derived nitrones are insufficiently explored.

The aim of this work is to investigate 1,3-dipolar cycloaddition of adamantane derived 1 and 4 with N-substituted maleimides 2.

It has been established that 1,3-dipolar cycloaddition of considered nitrones proceeds giving from moderate to good yields of corresponding isoxazolidines.

References

Acknowledgments. NMR and HRMS studies were performed at the Saint Petersburg State University Center for Magnetic Resonance and Center for Chemical analysis and materials research, respectively.
NEW DIRECTION OF THE KNOEVENAGEL CONDENSATION OF OXINDOLES IN THE PRESENCE OF METAL ALKOXIDES

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The problem of low reactivity of benzophenones in the Knoevenagel reaction often causes difficulties during synthesis of biologically active compounds. When synthesizing AMPK activators of the benzylidene oxindole series using the convergent scheme, we proposed aluminum isopropoxide to carry out the first stage of the synthesis, consisting in the Knoevenagel condensation of N-unsubstituted oxindoles with various benzophenones [1]. Detailed study showed the possibility of alternative condensation pathway under these conditions (Figure 1).

![Possible pathways of condensation reaction](image)

In the present study, we consider the factors that influence the direction and yield of the condensation in the presence of aluminum isopropoxide and evaluate the aluminum isopropoxide activity in the target and alternative reaction directions.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-13-10358).
REACTIONS OF CYCLIC ALLENS WITH NITRONES

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Reactions of 1,3-dipolar cycloaddition are one of the most effective and modern methods of creation five-membered heterocycles demanded in pharmacology. The selectivity of cycloaddition in the case of cumulated diene varies considerably depending on the nature of the 1,3-dipole and substituents in the allen. Reactions of cyclic allens with nitrones insufficiently explored. Condensed polycyclic compounds containing the isoxazolidine cycle in the structure are used as pesticides [1] and cancer cell inhibitors [2].

The purpose of this work is to study the reactions of cyclic alleles 1 with medium-size cycles with keto- 2 and aldonitrons 3. The study of the regio- and stereoselectivity of cycloaddition.

![Figure 1. Reaction of 1,3-dipolar cycloaddition of cyclic allens with nitrones](image)

The 1,3-dipolar cycloaddition of ketonitrons with cyclic alleles proceeds with the formation of adduct 4 containing a double bond at the C₄ atom of the isoxazolidine cycle, and benzazepinone 5. The interaction of aldonitrons with cyclic alleles proceeds regio-and stereoselectively to form a mixture of diastereomeric isoxazolidines 6 и 7, with predominance of the isomer with the *cis*-position of substituents on the atoms C³ and C⁵ of the isoxazolidine cycle.

References
FOLIC ACID BASED RADIOPHARMACEUTICALS FOR PET-DIAGNOSTICS

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Folate receptors are considered to be a new promising target for radiopharmaceuticals. Currently, a number of radiopharmaceuticals for SPECT, PET and RNT (with ⁹⁹ᵐTc, ¹¹¹In, ¹⁸F, ¹⁷⁷Lu) have been developed. The purpose of this work is to study new folic acid based molecules labeled with the PET radionuclide ⁶⁸Ga.

In the course of this work two new compounds were synthesized. A procedure for labeling I and II with ⁶⁸Ga was developed. It allows obtaining target complexes with a yield of at least 95%.

Both compounds contain NODAGA chelating group for ⁶⁸Ga binding. First compound studied (I) is the closest analogue of folic acid based radiopharmaceuticals reported in the literature [1].

The biodistribution was studied using animal model (nude mice with KB tumor cell line xenograft). The biodistribution of ⁶⁸Ga-I is very similar to that of other folic acid based labeled compounds [1]. However an interesting finding occurred in the course of this experiment. One of male animals developed a spontaneous neoplasma located in the scrotum. Histological study determined it as a cyst. ⁶⁸Ga-I showed high accumulation in the neoplasma. Finding like this were never described before.

According to previously reported data this type of labeled compounds tends to be accumulated in the kidneys. That is why a His-Glu-His-Glu fragment was introduced into the second molecule (II) and the effect of this modification on the biodistribution was studied.

Data on the labeling process as well as the comparison of biodistribution of ⁶⁸Ga-I and ⁶⁸Ga-II in animal models with aseptic and septic inflammation foci will be presented.

References

Acknowledgements. The reported study was funded by RFBR (project No 19-33-70048).
SYNTHESIS OF NOVEL BIS(INDAZOLYL)ALKANES

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Bis(azolyl)alkanes and their derivatives act as both mono- and bidentate ligands forming coordination compounds with transition and main group metals [1]. We have developed novel approaches to synthesis of this type of ligands based on indazole. The first method is the double alkylation of indazole by dichloro- or dibromoalkanes in superbasic medium KOH-DMSO.

![Figure 1. Double alkylation of indazole in superbasic medium.](image)

The second approach is the addition of indazole to glyoxal leading to 1,2-bis(indazol-1-yl)-1,2-ethanediol, which can be converted to 1,2-bis(indazol-1-yl)-1,2-dichloroethane by the reaction with thionyl chloride. Such dichloroethanes are of interest as precursors to obtain bis(azolyl)alkenes and symmetrical and asymmetrical tetra- and tris(azolyl)alkanes.

![Figure 2. Synthesis of bis(indazol-1-yl)-1,2-ethanediol and 1,2-bis(indazol-1-yl)-1,2-dichloroethane](image)

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-33-50034). Physicochemical studies were performed at the Research park of Saint Petersburg State University.
New practical approach to the preparation of methyl naphthoxazole-2-carboxylates for lanthanides chelation was developed [1]. This coumarin ring contraction-based method utilized cheap reagents, simple purification and can be used in multigram scale (Fig. 1). Isomeric oxazole-based chelators show very good IR photoluminescence with ytterbium cations (Fig. 2).

Figure 1. Synthesis of methyl naphthoxazole-2-carboxylates.

Figure 2. Benzoxazole-based ytterbium-chelating ligand.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-00250 and 18-33-20210).
ACETYLEN-FUNCTIONALIZED PALLADIUM(II) ACYCLIC DIAMINOCARBENE COMPLEXES: SYNTHESIS AND STABILITY.

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Modern research is concerned to the design of N-heterocyclic carbene palladium complexes (Pd-NHCs), since studies [1-2] showed their high anti-proliferative activity. However, obtaining these compounds is often multistage. Acyclic diaminocarbene palladium complexes (Pd-ADCs) are an alternative to NHCs complexes. They can be generated by a simpler method and these complexes have a number of special advantages.

The metal-mediated nucleophilic addition of propargyl functionalized secondary amines to isocyanide palladium(II) complexes was performed to give alkyne bearing ADCs-Pd (Figure 1).

Figure 1. Synthesis of Pd-ADCs.

Complex 5 was not obtained under these conditions, mainly due to the steric effects of the benzhydrylamine substituent. $^1$H NMR spectroscopy monitoring of the reaction of PdCl$_2$(CN-$t$-Bu)$_2$ with propargylamine confirmed the formation of product 3, but this complex was not isolated because of rapid decomposition. Complexes 1, 2, 4 can be easily isolated with yields from moderate to high (44-95%). The products were stable in the solid state under air. The resulting complexes can be used for subsequent functionalization by the CuAAC reaction. The synthesized complexes are unstable in solution, and a possible mechanism of their destruction involves the carbopalladation stage. The mechanistic details of the decomposition of the complexes will be covered in a poster presentation.

References:


Acknowledgements: Scientific measurements were performed in the Research Park of the Saint Petersburg State University Magnetic Resonance Research Centre.
DOMINO-REACTION IN ONE-POT SYNTHESIS OF THE 3,4-DIHYDRO-2H-THIOPYRANS

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There are two types of domino-reactions leading to the formation of the 3,4-dihydro-2H-thiopyran derivatives. The first is a three-component domino-Knevenagel – hetero-Diels-Alder reaction of dithioester containing active methylene group via formation of thiabutadiene as intermediate. Another type, the intramolecular domino thionation – hetero-Diels-Alder reaction, is presented as the only example interaction of α, β-unsaturated ketones with 1,2,3-triazole fragments methyl acrylate and phosphorus pentasulfide as a thionation agent.

Previously, we have developed a one-pot method of synthesis of 3,4-dihydro-2H-thiopyran derivatives by Diels-Alder reaction between in situ generated sulfur-containing α, β-unsaturated dienes and various dienophiles. Following the example of the dibenzalacetone and other compounds with 1,4-pentadien-3-one moiety interaction with derivatives of vicinal dicarboxylic acids, we have demonstrated the first example of a three-step domino reaction, including the steps of thionation, hetero-Diels-Alder, and repeated [4+2] cycloadditions with high yields. As an example, the domino-reaction product of the dibenzalacetone with maleic anhydride shown below:

References
New materials with improved properties and sustainable manufacturing are in demand in industry and materials science. Terpenols have a great potential as initial substrates due to wide abundance in essential oils and resins. Some of them can be directly isolated or synthesized from renewable raw materials by simple methods. Modification of natural compounds requires enough amounts of a co-reagent (modifier). Calcium carbide, a known inexpensive vinylating agent, is also mined in large quantities in sustainable manner. Transformation of a hydroxyl group in terpenols into a vinyl group, using CaC₂, and subsequent polymerization of ethers provides the pathway to new materials [1].

We carried out the vinylation of several terpenols using calcium carbide according to the literature procedure [2]. Isolated monomers were purified and polymerized under cationic conditions (standard procedure without optimization, Scheme 1). Corresponding polymers were isolated, purified and studied.

The synthesized monomers were characterized by NMR-and ESI-spectroscopy. Size exclusion chromatography, the average molar mass and molar mass distribution values were determined for all the synthesized polymers. The presented method is convenient, safe and allows to obtain new materials from
inexpensive natural sources. Further investigations for biodegradability of terpenol-based polymers are in progress in our group.

References
SYNTHESIS AND STRUCTURE OF TRIS(5-ARYL-1H-TERAZOL-1-YL)METHANES

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A series of tris(5-aryl-1H-terazol-1-yl)methanes were synthesized by reaction of 5-aryl-NH-tetrazoles with trichloromethane in strong aqueous basic condition. The compounds obtained were fully characterized by means of HRESI MS, \(^1\)H, \(^13\)C{\(^1\)H}, and \(^19\)F NMR spectroscopies, DSC/TG analysis, as well as by X-ray diffraction analysis. Specific features of the crystal structure of tris(5-aryl-1H-terazol-1-yl)methanes were determined. In the crystals \((\pi \cdots \pi)\) and \((C-N \cdots \pi)\) interactions between a lonely pair of nitrogen with a positively charged carbon region of the heterocycle, where a \(\pi^*\)-orbital orbital is located, were found.

Figure 1. Noncovalent interactions involving tetrazole moieties \(\pi-\pi\) interactions (blue); \(\pi(C)\cdots\text{lp}(N)\) interactions (red).

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-13-01124)
The search for factors determining the spatial structure of proteins is traditionally one of the main tasks of biochemistry and organic chemistry [1]. Recently it was found that NH…π type hydrogen bonds make a significant contribution to the protein molecules conformation, in which, for example, the amide nitrogen atom can participate as an unexpected proton acceptor, that was showed by Lectka [2]. Thus the X-ray diffraction analysis of “amide proton sponge” for the first time allowed to fix the NH…π interaction with the sp²-hybrid amide nitrogen atom (Fig. 1). However, a detailed review of the evidence presented in the original work, as well as our study of the X-ray structures of other similar amides, raised some doubts about the correctness of the assumption put forward. In addition to X-rays, chemical shifts of acidic NH protons in ¹H NMR spectra, the values of the acidity constants pKₐ, as well as quantum chemical calculations of the hydrogen bond energy and proton transfer, indicate the illusory nature of this interaction. Understanding the energy of such weak non-valent interactions is of particular importance for insight into the acid and enzymatic hydrolysis of the amide bond.

![Figure 1. Structures of amides 1 and 2.](image)

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project № 18-33-00259).
A NEW APPROACH TO THE SYNTHESIS OF DONOR-ACCEPTOR CHROMOPHORES CONTAINING 2-(2-OXOPYRROL-3-YLIDENE)MALONONITRILE FRAGMENT


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Investigations in the field of creation of novel groups of donor-acceptor chromophores with a cyano-substituted acceptor in the structure are urgent nowadays due to a wide possibility for the practical use of these compounds in various areas.

Herein, an approach to novel group of donor-acceptor chromophores containing an electron-withdrawing 2-(2-oxopyrrol-3-ylidene)malononitrile fragment 1 is reported. Previously, it had been shown that compounds 1 could be synthesized from 4-oxoalkane-1,1,2,2-tetracarbonitriles by the action of bases [1]. Firstly, tetracarbonitrile 2 was directly synthesized from tetracyanoethylene and 4-fluoropropiophenone to introduce an electron-donating moiety into structure 1.

Then compound 2 was heterocyclized into pyrrole 3 by the action of morpholine. The presence of a fluorine atom in the compound 3 allowed us to carry out a nucleophilic substitution reaction by the action of secondary amines leading to the formation of chromophores 4a–c.

It was found that an introduction of the electron-donating group in structure 1 significantly shifts the absorption band in the visible region in comparison with a fluorine-substituted pyrrole 3. Thus, compound 3a in ethanol has an absorption maximum at 530 nm whereas chromophore 4a has a band with maximum at 603 nm.

References

Acknowledgements
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SYNTHESIS OF ZIDOVUDINE USING CONTINUOUS FLOW SYSTEMS

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The HIV/AIDS pandemic is a major health concern worldwide and Sub-Saharan Africa is the most affected region than any other part of the world and this marks a severe development crisis in these countries. As the number of people on treatment continues to increase so will the demand for antiretroviral therapy (ARV) continue to increase. With virtual no local production of Active Pharmaceutical Ingredients (APIs) used in the formulation of ARV drugs, most countries rely on imports and this increases the cost of medication. To develop production capacity of APIs in Africa, we envisage the use of continuous flow technology to meet local demand, treat HIV. The technology offers many advantages compare to batch technology such as, lower costs, reduced waste, higher yields, while solvent and energy waste is reduced.1 In this study we synthesized Zidovudine (AZT) using batch process (Figure 1) as a benchmark followed by the transfer into continuous flow process to develop a better and reproducible process. All the synthetic steps are optimized in continuous flow systems with the aim of developing a continuous synthesis process.

Figure 1. Synthetic process of zidovudine.

References


Acknowledgements. This work was supported by the National Research Foundation (NRF) and Postgraduate Research Scholarship (PGRS).
Different BODIPY-type dyes found extensive use in modern science and technology, especially in biotechnology. However, the main challenge of their application is a luminescence in the red region, which is needed for imaging of biological objects. This problem can be solved by conjugation of BODIPY core with aromatic fragments. Generally, it is possible to make BODIPY-dyes with 3 types of conjugated benzyl ring (A–C, presented on Fig. 1). Structures A [1] and B [2] are well known, however, structure C was not studied before. This is likely related to the low stability of corresponding anion D.

Figure 1. Types of aromatic-conjugated BODIPY-dyes.

To obtain the target structure C we decided to use 3-hetarylpyrroles F, which give stable betaines [3]. Retrosynthetic scheme of the target BODIPY-dye E is presented on Fig. 2. Luminescent properties of the target compounds were studied in details.

Figure 2. Retrosynthetic scheme of the target structure.

References

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TARGETING ANTITUMOUR METAL-BASED COMPOUNDS.

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The discovery of anticancer properties of platinum based complexes became a significant breakthrough in cancer treatment. Currently cisplatin, carboplatin and oxaliplatin remain major drugs for the first line treatment (alone and in combinations) for a variety of malignancies including head and neck, testicular, breast and ovarian tumors. However, despite the success of platinum containing drugs the intrinsic or acquired resistance, general toxicity and other severe side effects are clinically unfavorable. To overcome these problems novel strategies for the search of active antitumor compounds are being developed.

One of the strategies in the modern medicinal chemistry of anticancer drugs is the design of multifunctional targeting compounds able to bind to more than one molecular target. The activity and specificity of metal-based anticancer compounds can be modulated by ligand environment. Attachment of Pt or Ru moiety can create dual action compounds that upon reduction in the cell environment generate two or more active components with the define molecular targets, increase anticancer properties and provide a multitargeting mode of action.

This presentation will focus on the hybrid complexes of Pt(IV), Ru(II) and Ru(III) bearing targeting moiety. Several compounds found to be highly cytotoxic against several human cancer cell lines with excellent selectivity towards cancer cells.

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The rapid development of various industries in the modern world leads to an increase of waste materials. Particular attention in the past few decades, given to purification of wastewater from heavy metal, which in large quantities is released into the environment. Heavy metals are not biodegradable unlike organic waste, besides one of the most dangerous properties of heavy metals is their accumulation in living organisms for which they are toxic. In this regard, the identification of residues of heavy metals is of paramount importance. The application of metacyclophanes (calix[n]arenes and thiacalix[n]arenes, cucurbit[n]urils, cyclodextrins) is currently shown in separation and extraction of heavy metals. Unlike metacyclophanes classical paracyclophanes are scaffold structures that are rather difficult to further functionalize. However, in the last decade, a macrocyclic platform, namely pillar[n]arenes, synthesized by the Ogoshi group, has become widespread. With the advent of the pillararenes it was appear the opportunity to fully reveal and show the interesting properties of paracyclophane, which can be functionalized due to the presence of free phenolic groups.

Under this research work, a number of new monofunctionalized pillar[5]arenes containing 1-aminophosphonate and phosphonate fragment were obtained, as well as their binding ability to metal cations were studied. The structure of the new synthesized derivatives was fully proved by NMR $^1$H, $^{31}$P, $^{13}$C, IR spectroscopy, mass spectrometry (MALDI-TOF) and elemental analysis.

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ANTIOXIDANT ACTIVITY OF PYRIDINES WITH 2,6-DI-TERT-BUTYLPHENOL MOIETIES

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Oxidative stress participates in a pathogenesis of many diseases. 2,6-Di-alkylphenols are widely used as antioxidants and stabilizers of cellular membranes. On the other hand, pyridines are engaged in structures of many biologically active compounds.

New substituted picolylamines with 2,6-di-tert-butyl-4-hydroxyphenyl groups were synthesized and characterized by IR, NMR, X-ray and elemental analysis.

Antioxidant potential of compounds was studied as an inhibition of lipid peroxidation (LP) in rat liver homogenates. To elucidate the possible mechanisms of antioxidant activity the radical scavenging activity (in DPPH-test), superoxide radical anion O₂⁻ scavenging activity (xanthine-xanthine oxidase assay), reducing ability (CUPRAC-test) and inhibition of lipoxygenase (LOX 1-B) were evaluated.

All the compounds showed high antioxidant activity depending on the length of the linker and the position of nitrogen atom in the pyridine ring (Table 1). Moreover, compounds possess moderate superoxide radical anion scavenging activity and act as mild inhibitors of lipoxygenase. Thus, studied compounds can be considered as potential antioxidants and cytoprotectors.

Table 1. Antioxidant activity of compounds 1-6.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>TEAC (CUPRAC)</th>
<th>% of reduced DPPH, 20 h</th>
<th>IC₅₀, µM (BHP-induced LP)</th>
<th>IC₅₀, µM (Fe³⁺-induced LP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.89 ± 0.03</td>
<td>24.2 ± 1.2</td>
<td>11.0 ± 3.9</td>
<td>22.8 ± 6.4</td>
</tr>
<tr>
<td>2</td>
<td>0.29 ± 0.01</td>
<td>3.0 ± 0.1</td>
<td>5.3 ± 1.0</td>
<td>14 ± 2.8</td>
</tr>
<tr>
<td>3</td>
<td>0.35 ± 0.01</td>
<td>n/a</td>
<td>24.1 ± 6.4</td>
<td>4.47 ± 0.47</td>
</tr>
<tr>
<td>4</td>
<td>1.71 ± 0.05</td>
<td>85.2 ± 3.3</td>
<td>0.9 ± 0.2</td>
<td>3.4 ± 0.8</td>
</tr>
<tr>
<td>5</td>
<td>1.00 ± 0.03</td>
<td>87.3 ± 3.4</td>
<td>0.45 ± 0.11</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>6</td>
<td>1.10 ± 0.03</td>
<td>89.1 ± 3.4</td>
<td>0.82 ± 0.17</td>
<td>3.9 ± 1</td>
</tr>
</tbody>
</table>

Acknowledgement: The financial support of RFBR (17-03-01070, 18-03-00203) is gratefully acknowledged.
SYNTHESIS AND BIOLOGICAL ACTIVITY EVALUATION FOR ISOMER SERIES OF PYRROLIDIN-2-ONE DERIVATIVES


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A series of Castagnoli-Cushman acid derivatives of the pyrrolidin-2-one chemotype with high proapoptotic activity was identified by virtual screening of a combinatorial library of compounds consisting of more than a million structures and the subsequent biological evaluation of hit compounds [1]. The presence of cis-/trans- and optical isomerism is a feature of the newly identified MDM2 inhibitors. During the synthesis of the target structures, four possible isomers are formed (Figure 1). In the study, we developed the methods of synthesis and isolation of a series of individual isomers and evaluated their activity within the used pharmacophore hypothesis. The target activity of the obtained compounds was studied in different cell models.

Figure 1. Synthesis of individual isomers of active compounds

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-13-10358).
SYNTESIS AND STUDY OF 4-OXO-1,4-DIHYDROCINOLINE DERIVATIVES - PROMISING INHIBITORS OF PROTEIN PHOSPHOTYROSINE PHOSPHATASE 1B

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The enzyme protein phosphotyrosine phosphatase 1B (PTP1B) is the most important negative regulator of the insulin and leptin systems functioning through the activation of a cascade of tyrosine phosphorylation. The increased activity of PTP1B leads to the insulin (IR) and leptin resistances (LR) and is the cause of obesity, diabetes mellitus and other socially significant metabolic disorders [1]. In this regard, an actual problem of modern medicine are deciphering the mechanisms of action of PTP1B and developing its selective inhibitors, which will allow to treat the metabolic disorders associated with IR and LR. [2]. In present work we proposed a structure of PTP1B inhibitors based on the 4-oxo-1,4-dihydrocinnoline scaffold. The Sonogashira reaction to obtain ortho-ethynyl substituted anilines and the Richter reaction to generate the cinnoline core were used to synthesize several PTP1B inhibitors (Scheme 1).

Scheme 1.
We have shown that synthesized 4-oxo-1,4-dihydrocinnoline derivatives stimulate the insulin and leptin signaling pathways and normalize the metabolic parameters in obese rats. Details of the synthesis and biological tests will be presented in the report.

References:

Acknowledgements. This work was supported by the Russian Science Foundation (project No 119-73-00228).
Today palladium catalysts and cross-coupling reactions are used for the synthesis of a variety of substances (drugs, new materials, natural compounds). Plastics, pharmaceuticals, materials for the electronics industry and many other substances can be synthesized using cross-coupling reactions [1].

The new versatile synthetic approaches for the synthesis of modern drugs as heterocyclic compounds have been developed [2]. Within the framework of this research project, the task was to work out a strategy for the synthesis of potential inhibitors of protein tyrosine phosphatase 1B (PTP1B). The target biological activity of the studied compounds is aimed at the treatment of type 2 diabetes mellitus (DM2) [3]. We have been developed the synthetic approach specially selected sequence of Sonogashira reactions and subsequent Richter cyclization (Scheme 1).

Scheme 1. Synthesis of 6-bromo-3-(hydroxyalkyl)cinnolin-4(1H)-one

We have carried out a study of influence of the hydrocarbon chain length in the starting hydroxyalkynes for Sonogashira coupling and Richter cyclization. The possibilities and limitations of the applicability of this method are shown.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 119-73-00228).
Attempted use of glutamine in the Ugi reaction with aldehydes or ketones and isocyanides for the synthesis of substituted glutarimide via Ugi-5C-4CR resulted in an unexpected formation of iminopyrrolidine-2-carboxylic acids. We optimized the transformation to a useful synthetic procedure by synthesizing more than 15 derivatives, exploring scope and limitations. The reaction is accelerated in water and involves an Ugi reaction followed by an intramolecular condensation (Figure 1). The reactions proceed under mild and green conditions and lead to a biologically relevant iminopyrrolidine scaffold otherwise inaccessible via conventional synthetic methodologies.

![Chemical structure](image)

**Figure 1.** A reported strategy to the iminopyrrolidine-2-carboxylic acid core and our new methodology

The structure of compounds was unambiguously confirmed by NMR, HRMS, IR, and single-crystal X-ray diffraction study. The resulting compounds can be applied for further functionalization or subsequent post condensational modification and are of interest as scaffolds for drug design.

References

Acknowledgments. This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 754425.
Since its discovery in 1999 [1], the tandem Ugi/Diels-Alder reaction has proven to be a convenient tool for the construction of densely substituted tricyclic compounds 1 in a high-yielding and stereocontrolled fashion. Moreover, these compounds can undergo numerous transformations providing access to a wide range of nitrogen heterocycles [2]. However, in most cases the isocyanide scope remains somewhat limited due to instability and revolting odor of isocyanides. In situ dehydration of formamides to generate isocyanides first reported by Dömling in 2015 [3] provides a solution for both of the aforementioned limitations; thus, we investigated the Ugi/IMDA reaction under “isocyanide-less” conditions attempting to broaden the scope of accessible products.

We successfully applied the “isocyanide-less” protocol to the Ugi/IMDA sequence and obtained compounds 1 in moderate yields as single isomers [4].

References

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF ISOALANTOLACTONE-FUROPYRIMIDINE HYBRIDS

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Synthesis of hybrid structures containing a fragment of sesquiterpene lactone and N-containing heterocyclic fragment has great interest for the creation of biologically active agents [1]. We proposed an effective method for the synthesis of isoalantolactone-furopyrimidine hybrids 5 based on the Sonogashira-coupling of iodide 2 with acetylene 3 and subsequent Ag-catalyzed cyclization of 4. Antimicrobial and antiviral activity of 5a-f compounds is discussed.

![Synthesis of furopyrimidine derivatives of isoalantolactone and the molecular structure of compound 3c](image)

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research and the Government of the Novosibirsk Region (project No 19-43-543042).
The compounds bearing 4-oxo-1,4-dihydrocinnoline fragment have been reported as the protein tyrosine phosphatase 1B inhibitors (PTP1B) [1]. PTP1B is a negative regulator of leptin system which plays an important role in many physiological processes. Direct modification of these compounds using click-reagents would be useful for pharmacodynamic studies and bioimaging.

CuAAC reaction is an effective way to obtain 1,2,3-triazoles regioselectively, which can be carried out with the use of copper complexes (N-heterocyclic carbene) halide [(NHC)CuX] in mild conditions giving the target triazoles in high yields. These copper complexes have unique properties in homogeneous catalysis and showed excellent activity in the azide-alkyne cycloaddition[2,3]. Present work is devoted to the development of the conditions for the propargylation of 4-oxo-1,4-dihydrocinnoline substrates and for the click reaction. Some NHC-CuX complexes showed excellent activity in the CuAAC modification. The developed method provides an extremely simple path to modification of propargyl-functionalized 4-oxo-1,4-dihydrocinnoline derivatives, and makes it possible to vary azide radical (R²), which can be a phosphor, labeled or possess new biological properties. Details of the synthesis and the study of the catalytic activity will be reported in the poster session.

References

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SYNTHESIS OF ADAMANTYL DERIVATIVES
OF VARIOUS NAPHTHALENEDIOLS

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The naphthalene core exists extensively in natural products and bioactive molecules. [1] A wide application of adamantane derivatives allows to suggest that containing in its structure various naphthalenediols are of definite practical interest. [2]

The interaction of adamantane with ten derivatives of naphthalenediols (1,2-; 1,3-; 1,4-; 1,5-; 1,6-; 1,7-; 1,8-; 2,3-; 2,6- and 2,7-) has not been studied systematically before. We have shown that the interaction of 1-adamantanol (1-AdOH) with naphthalenediols in such acid media as CF₃COOH or CH₃COOH:H₃PO₄ are convenient method of C-alkylation of these compounds with formation mono- and di-adamantyl substituted derivatives. Moreover, we developed environmentally friendly solvent free and metal catalyst free method (1-AdOH with 1-bromoadamantane (1-AdBr) as an alkylation agent in a sealed tube at 200 °C) for the preparation of diadamantyl-substituted naphthalenediols.

Figure 1. Schemes for synthesis of adamantyl derivatives of naphthalenediols.

Thereby, series of fifteen mono- and di-adamantyl-substituted naphthalenediols were synthesized and characterized by 1D and 2D NMR spectroscopy (Bruker Avance III 600, Krasnoyarsk regional research equipment centre of Siberian branch Russian academy of science). [3]

References
HPLC-MS/MS METHODS FOR METHIONINE, INOSINE, NICOTINAMIDE, AND SUCCINIC ACID DETERMINATION IN RABBIT AND HUMAN PLASMA: APPLICATION TO PRECLINICAL STUDY

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Developing and registration process of a new drugs requires to conduct a pharmacokinetic and pharmacodynamic studies in the framework of preclinical and clinical trials. To determine the active pharmaceutical ingredients and biomarkers in physiological fluids and tissues a bioanalytical method is developed and validated in accordance with the European Medicines Agency (EMA) requirements. A special approach is needed for the analysis of endogenous compounds.

The aim of our study was a quantification of four active substances (Figure 1): methionine (MTN), inosine (INO), nicotinamide (NAM), and succinic acid (SuA) in blood plasma. These analytes are endogenous compounds and present in biological matrix in a normal diet.

Figure 1. Chemical structures of MTN, INO, NAM and SuA

Two HPLC-MS/MS methods have been developed and validated for analytes determination in biological samples: the first one for simultaneous analysis of MTN, INO, and NAM, and individual method for SuA analysis.

There are several challenges for these tasks: low sample volume; absence of analyte-free matrix; stability of analytes in whole blood plasma and during sample preparation and analysis; selection of low limit of quantification (LLOQ) according to endogenous level and circadian rhythm.
For the analysis of MTN, INO, and NAM the chromatographic separation was achieved on YMC Triart PFP column (100 ×2.1 mm, 5 μm) in gradient elution mode, the retention times were 0.91; 1.44 and 2.94 min for INO, NAM and MTN respectively. For SuA the YMC Pack-SIL column (100 ×2.1 mm, 5 μm) was used in isocratic mode, retention time was 1.16 min. Mass-spectrometric detection was implemented on API 4000 Sciex triple quadrupole tandem mass spectrometer with atmospheric pressure ionization source. Ions were monitored in a positive (MTN, INO, and NAM) and negative (SuA) modes with transitions: m/z 150.0→104.1 for MTN, m/z 269.1→137.1 for INO, m/z 123.0→80.0 for NAM, and m/z 116.9→72.9 for SuA.

Protein precipitation technique using acetonitrile was employed for both methods. Calibration curves showed linearity in following concentration ranges: 3-100 mkg/mL for MTN, 0.1-50 mkg/mL for INO, 0.2-6 mkg/mL for NAM and 0.3-30 mkg/mL for SuA. The methods allow analyzing small aliquot of biosample: 50 mkl for MTN, INO, and NAM determination; 100 mkl for SuA. Due to absence of analyte-free matrix working solutions and calibration standards were prepared in plasma diluted with water. Quality control samples must be prepared in non-diluted plasma, as a result plasma pool with known endogenous level was spiked with working solution.

MTN, INO and NAM in plasma were found to be stabled up to only 4 hours at 4 ± 2°C. Therefore, the sample preparation, thawing (for three freeze–thaw cycles) for these analytes was carried out at temperature about 4°C. Autosampler stability of MTN, INO, NAM was found for 20 hours at 4 ± 2°C. Stabilities of SuA in plasma at room temperature, in autosampler at 15°C, three freeze–thaw cycles (thawing at room temperature) were examined.

The overall recoveries were 48±9 %, 68±13 %, 63±11 % for MTN, INO, and NAM, respectively, and 100±4 % for SuA. Average endogenous level for each analytes were measured in rabbit plasma, concentration of MTN, INO, NAM, SuA were 5.1-11.8 mkg/mL, 0-3.4 mkg/mL, 0.3-0.6 mkg/mL, and 1.4-3.5 mkg/mL, respectively.

The methods were successfully validated on rabbit and human plasma according EMA and local requirements, applied to preclinical study and could be applied to clinical trials within a Phase I study.
NEW N-SUBSTITUTED DERIVATIVES OF INDOLE-3-CARBOXYL ACID: DESIGN AND SYNTHESIS

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The indole moiety represents certainly an important structural subunit for a large number of natural products and pharmaceuticals [1]. This research presents new N-acyl- and N-sulfonylsubstituted indole-3-carboxylic acid derivatives obtained (received) from commercially available 2-iodoaniline. Palladium (II) phthalocyanine complex was used as a Sonogashira reaction catalyst for the first time at second stage [2].

Scheme 1. Synthesis of N-substituted derivatives of indole-3-carboxyl acid.

The compounds obtained were characterized by physicochemical methods: FTIR, 1H, 13C NMR spectroscopy, HRMS, and thermogravimetry.

References

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SYNTHESIS OF ETHYNYLPYRIDINE DERIVATIVES

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We have developed a new method for the synthesis of 2-amino-5-aryl-6-(trimethylsilylethynyl) nicotinic acid esters by the reaction of 2-aryl-5-trimethylsilyl-1-ethoxypent-1-en-4-in-3-ones with endiamine hydrochlorides.

\[
\text{Ar} = \text{Ph}, 4-\text{ClC}_6\text{H}_4, 4-\text{O}_2\text{NC}_6\text{H}_4; \text{R} = \text{H}, \text{Me} 
\]

Figure 1. Reaction of Enynones and Endiamines

The reaction proceeds regioselectively with high yields of the corresponding products, and some compounds have noticeable fluorescent properties. It turned out that the best results are achieved at a lower temperature (cf. [1-4]), but, despite the high activity of endiamines, the trimethylsilyl group is retained in the reaction products.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-73-00089).
THE SYNTHESIS OF BENZO[4,5]THIENO[2,3-f]ISOINDOLE-CARBOXYLIC ACIDS BY IMDAV REACTION

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The broad implementation of the [4+2] cycloaddition reactions in advanced organic chemistry paved the way for easily approachable syntheses of heterocyclic scaffolds. The reaction of vinylthiophenes with unsaturated carboxylic acids anhydrides yields thienoisindole derivatives, a class of compounds that are expected to exhibit biological activity [1].

The recent researches indicate the formation of thieno[2,3-f]isoindole-4-carboxylic acids by interaction of 3-(thien-2-yl)allylamines with maleic anhydride. The initial N-acylation of allylamines is supervened by cyclization of intermediate maleinamides through the step of intramolecular Diels-Alder vinylthiophene (IMDAV) reaction [2].

We successfully managed to expand the described approach to benzothiophene derivatives. 3-(Benzo[b]thiophen-2-yl)allylanilines were made to react with maleic anhydrides, a number of benzo[4,5]thieno[2,3-f]isoindole-10-carboxylic acids were obtained in different yields.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant No. 17-53-45016).
Electrophile-promoted cyclization of unsaturated compounds is one of the most effective transformation for the synthesis of heterocyclic compounds [1]. Nevertheless, iodoalkynes have hardly been studied as starting materials for the electrophile-promoted cyclization. Pursuing the goal of using diiodoheterocycles in the synthesis of enediynes fused to a heterocyclic core [2], iodine-promoted cyclization of ortho-functionalized iodoethynylarenes could be thought as a convenient synthetic tool towards diiodoheterocycles.

Starting iodoalkynes were prepared by a three-step protocol: the Sonogashira reaction, desilylation and iodination of terminal alkynes. The cyclization study revealed the significant influence of a nucleophilic group nature on the regioselectivity of cyclization. Thus, iodine-promoted cyclization of thioanisole and aniline derivatives was found to be a facile approach for the synthesis of diiodobenzo[b]thiophene and diiodoindole through the 5-endo-dig ring closure, meanwhile 5-exo-dig is a predominant process for “biatomic” nucleophilic functions. Subsequent Sonogashira reaction of 2,3-diiodoheteroindenes proceeded regioselectively affording 2-ethynyl-3-iodoheteroindenes. Extension of this approach is in progress.

References

Acknowledgements. The research was carried out by using the equipment of the SPbSU Resource Centres: Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for X-ray Diffraction Studies.
In recent decades, transition metal complexes with aminocarbene ligands (NHC - N-heterocyclic carbenes, ADC - acyclic diaminocarbenes) have taken a special place in coordination chemistry due to their wide application in catalysis, material design and medical chemistry. One of the promising and easy in processing methods for generating complexes with various types of aminocarbene ligands is metal-mediated addition of nucleophiles to coordinated isocyanides.

Recently in our research group it was found that the reaction of Pd$^\text{II}$ isocyanide complexes with ambident nucleophiles such as aminazole leads to C,N-chelate carbene complexes, which themselves can act as nucleophiles and react with another moiety of the isocyanide complex, yielding binuclear products [1,2]. In the present work, we have studied the coupling of bis(xylyisocyanide) Pd$^\text{II}$ and Pt$^\text{II}$ complexes (1) with the another type of ambident nucleophiles – mercaptoazoles 2–6 (Figure 1), which leading to C,S-chelate carbene complexes.

![Figure 1. Reaction. Coupling of bis-(xylylsocyanide) Pd$^\text{II}$ and Pt$^\text{II}$ complex with mercaptoazoles.](image)

References

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MACROCYCLIC BETAINES DERIVATIVES: DESIGN AND BIOLOGICAL ACTIVITY


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The development of approaches to the design and synthesis of compounds with the ability to molecular recognition is one of the promising directions in modern supramolecular chemistry. Interest in the directed synthesis of multivalent macrocyclic structures is due both to the prospects of practical use and importance for the development of basic science. The tendency to self-assembly and self-association of various cyclophane due to specific and non-specific interactions allows to create synthetic receptor systems that are comparable with natural analogues or have superior properties. The basis for the creation of such multifunctional "hosts" are calix[4]arenes. The main obstacle for the practical application of calixarenes, as well as other numerous cyclophane structures, is their low solubility in water. The introduction of betaine fragments into the structure of macrocycles opens new possibilities for their use due to an increase in water solubility.

The aim is the synthesis, study of the structure and aggregation properties of p-tert-butylthiacalix[4]arenes containing betaine fragments at the lower rim of the macrocycle in cone and 1,3-alternate conformation and the study of their biological activity.

The aggregation in water of the obtained betaine derivatives of p-tert-butylthiacalix[4]arene in cone and 1,3-alternate conformation was studied by dynamic light scattering. Ability of the resulting systems to inhibit acetylcholinesterase and butyrylcholinesterase was studied. Acute toxicity in mice of the synthesized compounds was also evaluated.

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SYNTHESIS OF POLYCONDENSED HETEROCYCLES THROUGH REACTIONS OF PARTIALLY HYDROGENATED 2-AMINO[1,2,4]TRIAZO-LO[1,5-a]PYRIMIDINES WITH BIELECTROPHILES

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1,2,4-Triazolo[1,5-a]pyrimidines (TP) are purine analogues that are important in agricultural chemistry and medicine [1]. In this report, we describe a new methodology for the synthesis of polycondenced heterocycles based on reactions of partially hydrogenated 2-aminoTP with carbonyl-containing bielectrophiles and discusses its features [2-4].

Figure 1. Synthesis of various polycondensed heterocycles from 2-aminoTP and carbonyl-containing bielectrophiles.

References

This work was supported by the Russian Science Foundation (project No 14-23-00078) and Russian Foundation for Basic Research (project No 13-03-00253).
The classic Castagnoli-Cushman reaction (CCR) represents a lactam synthesis, based on interaction of succinic or glutaric anhydride and imines. In this study six novel spiroannelated analogs of glutaric anhydride (1-6) were synthesized and tested in reaction with imines (7) to give a series of novel lactams (8-13). Comparing the obtained results with corresponding carboanalogs (n=1, X=Y=CH₂), it was demonstrated that heteroatoms (X,Y=O,S) and ring size of spirocyclic system dramatically affect the yield and scope of applicable imines for CCR. In this case novel compounds with sulfur and oxygen atoms showed significantly higher reactivity in the Castagnoli-Cushman reaction. All products were fully characterized and their trans-configuration was supported by X-ray analysis data.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-20194).
Fluorine-bearing compounds have a wide range of applications in the pharmaceutical industry, agrochemistry, and materials science due to unique properties provided by fluorine presence. Among such type of compounds the trifluoromethylated derivatives (including halogenated CF$_3$-ketones) have received a great attention [1]. The conjugate nucleophilic addition to functionalized enones is a straightforward method for the carbon–carbon or carbon–heteroatom bond formation.

In this context, we studied the reaction of fluorinated α-bromoenones 1 with carbon-centered nucleophiles. Malonate derivatives 2 react with enones 1 to give corresponding cyclopropane derivatives 3 in good yields (Figure 1, direction A). In all cases cis-stereoisomer was isolated as a sole product.

Organomagnesium bromides in the reaction with the same enones 1 undergo either 1,4- or 1,2-addition (Figure 1, direction B). The regioselectivity of reaction depends strongly on the nature of the Grignard reagent [2]. Thus, arylmagnesium bromides 4d-f give 1,4-adduct as a dominant product while in the case of alkyl-, alkenyl-, and alkynylmagnesium bromides 4a-c the ratio is shifted towards 1,2-adduct. The stereo- and regioselectivity as well as mechanisms of reactions are discussed.

![Figure 1. Reaction of CF$_3$-α-bromoenones 1 with C-nucleophiles.](image)

2: $R^1 = R^2 = \text{CO}_2\text{Et}$ (a), $R^1 = R^2 = \text{COMe}$ (b), $R^1 = \text{CO}_2\text{Et}$, $R^2 = \text{COMe}$.
4: $R^3 = \text{Et}$ (a), vinyl (b), 1-propynyl (c), Ph (d), 4-MeOC$_6$H$_4$ (e), 4-FC$_6$H$_4$ (f).

References


Acknowledgements. This work was supported by the Russian Foundation for Basic Research (projects No 18-33-00119 and 19-03-00206).
Bis(imino)acenaphthenes (BIANs) are highly conjugated, redox active, and sterically bulky α-diimines that have been used widely as bidentate ligands in coordination chemistry and catalysis. The key characteristic of BIANs as strong π-acceptor molecules is their ability to reversibly accept up to four electrons and reversibly exchange them with the coordinated metal, that can facilitate redox based chemical processes [1]. Indeed, BIANs have been shown to be active in many catalytic transformations. In addition, a reversible intermolecular metal-to-ligand electron transfer (redox isomerism) has been established in such metal complexes [2].

In this work, the octahedral complex $[\text{Rh}^{\text{III}}(\text{dpp-bian})(\text{H}_2\text{O})\text{Cl}_3]$ (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and the square pyramidal complex $[\text{Rh}^{\text{I}}(\text{cod})(\text{dpp-bian})\text{Cl}]$ (cod = 1,5-cyclooctadiene) have been synthesized from rhodium trichloride and bis(1,5-cyclooctadiene)dirhodium(I) dichloride, respectively. Heteroleptic complexes $[\text{Pd}(\text{dpp-bian})(\text{dmit})]$ and $[\text{Pd}(\text{dpp-bian})(\text{dsit})]$ have been obtained by the reaction of $[\text{Pd}(\text{dpp-bian})\text{Cl}_2]$ with $(\text{TBA})_2[\text{Zn}(\text{dmit})_2]$ or $(\text{TBA})_2[\text{Zn}(\text{dsit})_2]$. The complexes have been characterized by IR, UV/vis and NMR spectroscopies, ESI-MS, elemental analysis and cyclic voltammetry (CV). Their molecular structure has been determined by single-crystal X-ray analysis. The CV of all complexes show reversible redox events assigned to reduction of the dpp-bian ligand. DFT calculations have been performed to interpret redox behavior of the complexes in solution. The complex $[\text{Rh}^{\text{III}}(\text{dpp-bian})(\text{H}_2\text{O})\text{Cl}_3]$ shows catalytic activity in electrochemical reduction of CO$_2$. 
Figure 1. Molecular structures of $[\text{Rh}^\text{III}(\text{dpp-bian})(\text{H}_2\text{O})\text{Cl}_3]$ and $[\text{Pd}(\text{dpp-bian})(\text{dmit})]$.

References

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NOVEL SYNTHESIS OF 2-HALO-2H-AZIRINES AND THEIR APPLICATION IN SYNTHESIS OF AZIRINE DERIVATIVES


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2H-Azirines are valuable synthetic intermediates widely used in the preparation of various nitrogen-containing compounds [1]. In this work, a convenient and efficient synthesis of 2-halo-2H-azirine-2-carboxylic acid derivatives via catalytic isomerization of readily available 5-heteroatom-substituted isoxazoles has been developed. The reaction makes use of cheap Fe(II) salts as catalysts and can be conducted on a gram scale.

We also studied the reactivity of obtained 2-halo-2H-azirines in nucleophilic substitution reactions. Using appropriate nucleophiles, 2-acyloxy, 2-azolyl, 2-sulfonyl, 2-fluoro-2H-azirines were synthesized in good yields. According to the DFT calculations, the formal substitution of the halogen in these reactions proceeds via an unusual SN2'-SN2' cascade mechanism.

References

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RADICAL-MEDIATED DEAROMATIZATION OF INDOLES WITH SULFINATE REAGENTS AND PHOSPHITES FOR THE SYNTHESIS OF FLUORINATED AND PHOSPHONATED SPIROCYCLIC INDOLINES.

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The spirooxindole scaffold is frequently found in natural products and biologically active compounds[1]. Some pharmaceuticals containing spirooxindole motif were also reported, stimulating a great interest in construction and modification of this skeleton[2]. However only few works were done to replace the carbonyl in position 2 by another valuable functional group[3].

Considering the importance of CF₃, CF₂H and PO(OR)₂ groups in therapeutic and radical chemistry, we believe that the diastereoselective introduction of these functional groups into the structure of spiroindolines can lead to compounds of biological interest. Based on the recognized expertise of our group in the creation of spiroindoline compounds using the umpolung of indole, we developed a simple and efficient diastereoselective method for the synthesis of fluorinated and phosphonated spirocyclic indoline using respectively sulfinate reagents and CAN* as oxidant [4] or phosphites and Mn(OAc)₃ [5].

![Chemical Diagram]


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SUPRAMOLECULAR STRUCTURE OF NEW PHOSPHORYLATED 1,2,4-TRIAZOLES

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1,2,4-triazole-3-thions possess a rich spectrum of biological activity [1,2], which makes the synthesis of new structures, in particular, containing the pharmacophoric phosphoryl group, the advanced direction. According to previously published synthesis [3], a number of new 1,2,4-triazoles derivatives was obtained by the heterocyclisation of phosphorylated thiosemicarbazides.

Here we present the results of X-ray analysis of new phosphorylated 1,2,4-triazole with the functionalization on N- and S-atoms. The interesting feature of the crystals of these compounds is the formation of hydrophobic and hydrophilic areas due to the presence of a bulky diphenylphosphoryl fragment in the molecules. The geometry of molecules, intermolecular interactions and packing in the crystals of various forms will be discussed in the report.

References

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2H-AZIRINES IN A NOVEL SYNTHESIS OF 5-AMINOBUTENOLIDES

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A butenolide (2-furanone) ring is often found in a variety of pharmaceuticals and naturals products, including vitamin C, lanthellidone G, lanthellidone H, rofecoxib, PD 156707, butyrolactone I. Besides, butenolides due to high reactivity of the lactone ring serve as important synthetic building blocks in organic synthesis.

5-Aminobutenolides being hardly accessible compounds are of particular interest as scaffolds in diversity-oriented synthesis and compounds with useful biological properties.

In this work an effective synthetic scheme for the preparation of fully substituted 5-aminobutenolides based on the new reaction of 2H-azirines is described. The method uses commercially available starting materials and provides high yields of the products at each step of the synthesis. The key step of the scheme is the base-promoted cyclocondensation of the 2-bromo-2H-azirine-2-carboxylates with functionally substituted carboxylic acids. The scope and limitations of this domino reaction as well as its mechanism are discussed.

Acknowledgements. We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (Grant No 18-33-00699). This research used resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies, and Chemistry Educational Centre of the Research Park of St. Petersburg State University.
UNUSUAL PSEUDOPOLYMORPHIC BEHAVIOR OF THE PHENYL-SUBSTITUTED THIOSEMICARBAZIDE DERIVATIVE

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By the modification of diphenylphosphoryl acetic acid hydrazide (fosenazid, active pharmaceutical ingredient) with thiosemicarbazide fragment a series of new phosphorylated thiosemicarbazide derivatives was synthesized [1]. Establishing of the molecules geometry and the crystal structure of compounds with potential pharmacological properties, the study of solid state phase behavior is important and is one of the directions in the development of new polyfunctional biologically active compounds.

It was established that, by varying the nature of the solvent, it is possible to purposefully obtain various crystalline modifications, both in individual form (polymorphs) and in crystal solvates (with acetone, methanol and two different types with DMSO). The structures of individual forms and its various solvates were determined by the method of a single X-ray analysis. The geometry of molecules, intermolecular interactions and packing in the crystals of various forms will be discussed in the report. To study the possible solid-phase phase transitions, all modifications were investigated by DSC and powder X-ray diffraction, the results of which will be presented in a report.

References

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SYNTHESIS OF N-(SILYL METHYL)BENZENESULFONAMIDES

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N-(Silylmethyl)-4-chlorobenzenesulfonamides 1-5 were obtained by interaction of 4-chlorobenzenesulfonic acid chloride with N-(silylmethyl)amines (Scheme 1). The reaction proceeds in benzene solution at room temperature with using an excess of triethylamine as an acceptor of hydrogen chloride. N-(Silatranylmethyl)-4-chlorobenzenesulfonamide 6 was prepared as result of the treatment of N-[(trimethoxysilyl)methyl]-4-chlorobenzenesulfonamide by tris(2-hydroxyethyl)amines. The interaction of N-methyl-N-(trimethylsilylmethyl)amide of 4-chlorobenzenesulfonic acid with amines lead to form the corresponding N-methyl-N-(trimethylsilylmethyl)amides of 4-aminobenzenesulfonic acids 7-10. The structure of the synthesized compounds was confirmed by NMR and IR spectroscopy.

Scheme 1. Synthesis of N-(silylmethyl)benzenesulfonamides

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-00368).
SYNTHESIS OF 2-(ARYLAMINO)ACETOHYDRAZIDE DERIVATIVES AND PRELIMINARY ASSESSMENT OF THEIR BIOPROPRTIES

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Acyl hydrazines have high phytotoxicity and have been proposed for use as herbicides [1], and among 1,3,4-oxadiazole derivatives a number of biologically active compounds have been found, which are used not only in medicinal practice, but also in agriculture [1-5].

For the purpose to synthesize new biologically active compounds, the functionalization of 2-(arylamino)acetohydrazides were carried out, and the corresponding acyclic N'-benzylidene-2-(phenylamino)acetohydrazides and N'- (4-oxopentan-2-ylidene)-2-(phenylamino)acetohydrazides were obtained. Heterocyclization of the same hydrazides afforded 5-((phenylamino)methyl)-1,3,4-oxadiazole-2(3H)-thiones, and the alkylation of latter led to S-alkyl substituted derivatives.

The synthesized compounds demonstrated a stimulating effect on plant growth. The substances with the activity higher than 80% (compared to heteroauxin) were selected for deeper study and further field trials.

References

Available at http://www.alanwood.net/pesticides/class_pesticides.html.
COLCHICINE-BASED LIPID PRODRUGS AS EFFECTIVE ANTICANCER AGENTS

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Two examples of heterocyclic colchicinoid-based lipid prodrug were synthesized. The corresponding prodrugs were incorporated into enzyme-responsive liposomal nanocarriers. The lipid forms were designed to address important issues: to be hydrolyzable with PLA2 – enzyme, accompanying inflammation and cancerogenesis process, and to release an active compound by action of unspecific esterases.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Structural design of a colchicinoid-containing phospholipid}
\end{figure}
Scheme. 1. Active colchicinoids and their lipid prodrugs.

References
During the two last decades, gold homogeneous catalysis of organic transformation has been developed into a highly useful tool for the construction of valuable synthetic building blocks [1]. Au-catalyzed oxidation procedures using N-O species as oxygen donors were established, which strongly enriched the field of oxidation chemistry [2]. Notable results were obtained by Hashmi and co-workers who developed an Au-catalyzed acid-supported approach to glyoxals via oxidation of terminal alkynes using pyridine N-oxide derivatives as convenient oxygen carriers [3]. Later, we expanded this strategy to obtain 1,2-diaryldiketones from internal alkynes [4]. A significant drawback of the last two approaches is the need to use stoichiometric quantities of strong acids (TfOH, Tf2NH), which limits the reaction scope.

We have developed an efficient acid-free gold(I)-catalyzed transformation of both terminal and internal alkynes to vicinal dicarbonyl compounds by 2,3-dichloropyridine N-oxide (Scheme). The advantages of this method include mild reaction conditions and high functional-group tolerance with good yields of target compounds at the same time.

References

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SYNTHESIS OF NEW DERIVATIVES OF 1,3,4-OXADIAZOLES

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Heterocyclic compounds, in particular oxadiazoles and their derivatives, are an important area of research attracting the interest of a large number of scientists. As is known, compounds containing an oxadiazole moiety in their composition have a wide range of a wide variety of biological active properties, including anti-inflammatory, antimicrobial, analgesic, anti-parkinsonian, anticonvulsant, antimalarial, hypotensive, antioxidant, anti-tuberculosis, sedative, etc. Oxadiazole derivatives are also used as bleaching agents, inhibitors, pesticides, etc. [1].

This paper presents the synthesis of a new compound, the ethylene derivative of 1,3,4-oxadiazole from commercially available 2-iodobenzoic acid (1) in three stages.

At the first stage, 2-iodobenzohydrazide was synthesized under one pot from 2-iodobenzoic acid with the help of thionyl chloride (SOCl₂) and hydrazine hydrate. At the next stage, we modified the literature method of synthesis 1,3,4-oxadiazoles, combining the stages of obtaining diarylhydrazines and their cyclization [2]. Also, by optimizing this reaction, the addition of solvent and base was excluded. In summary, benzoyl chloride was added with stirring to a solution of 2-iodobenzohydrazide in POCl₃, followed by keeping the mixture for 3 hours at 110 °C. As a result of oxidative cyclization, 2-(2-iodophenyl)-5-phenyl-1,3,4-oxadiazole (3) was obtained; the yield was 55%.

For the introduction of the vinyl fragment, we used the Heck reaction on a palladium catalyst in DMFA with 2- (2-iodophenyl)-5-phenyl-1,3,4-oxadiazole (4) and ethylene.
All synthesized compounds were characterized using modern methods of analysis.

References:

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The azines containing the C – P bond are increasingly used as effective ligands for metal complex catalysts, components of optoelectronics, and are widely used in organic synthesis. Phosphonate fragments are present in many biologically active compounds that exhibit antiviral, antibacterial and anti-cancer activity. However, traditional methods for the synthesis of phosphorylated azines are based on the use of halides and organometallic reagents, which is accompanied by the formation of difficult to dispose of wastes. One of the atom economy variations of cross-coupling, which does not require the use of halides and transition metal catalysis, is the aromatic nucleophilic substitution reaction of hydrogen (S$_N^H$) [1]. S$_N^H$ - reactions proceed through a stage of formation of an intermediate $\sigma^H$- adduct, which can be selectively oxidized to the desired product at the anode under the conditions of electrosynthesis [2].

In order to obtain quantitative data on anodic dehydroaromatization of azines, and to estimate effects of both electronic and steric factors on oxidation of these compounds, a series substituted dihydroazines have been synthesized. The compounds were studied in detail using physicochemical and electrochemical methods of analysis. This allowed us to develop a simple, convenient, selective method for electrochemical C – H phosphorylation.

References

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SYNTHESIS OF NEW HETEROMETALMIC CUBANE-TYPE CLUSTERS

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A large variety of heterometallic cubane-type clusters \{M₃S₄M’\} (M = Mo, W; M’ = transition metal) with relevance in bioinorganic chemistry and organic catalysis are known 1. These species are easily accessible by direct incorporation of a metal atom in low oxidation state (zero to two) into homometallic \{M₃S₄\} clusters (M = Mo, W) as represented at Figure 1.

In this work we report reactions of trinuclear complexes, [M₃S₄(dbppy)₃Cl]PF₆ and [M₃S₄(py)₃(acac)₃]PF₆ (M = Mo, W), previously prepared in our laboratory 3, with Pt(PPh₃)₄, Au(PPh₃)Cl and Ag(CF₃SO₃) as heterometal M’ sources. New heterometallic complexes of general formula [M₃S₄(M’PPh₃)(L₁)₃(L₂)₃]ⁿ⁺ (M’ = Pt, Au, Ag; L₁ = py, dbppy; L₂ = acac, Cl; n = 1-2) have been isolated and thoroughly characterized by X-ray single crystal analysis, multinuclear NMR and IR spectroscopies, ESI-MS, cyclic voltammetry and elemental CHN analysis.

The obtained complexes were tested as catalysts in C-H bond activation processes.

Figure 1. General scheme for preparation of \{M₃S₄M’\} clusters.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-20056).
Ru(II)-ARENE COMPLEXES WITH LONIDAMINE AND BEXAROTENE LIGANDS: STABILITY AND BIOLOGICAL ACTIVITY

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After platinum drugs widely used in the cancer chemotherapy, the most promising compounds are Ru(II)-arene complexes such as RAPTA-C. Earlier we reported analogues of RAPTA-C with biologically active targeting ligands [1] based on lonidamine and bexarotene (compounds with well-known tumor specific molecular targets). It was reported earlier that Ru(II)-arene complexes with heterocycle ligands may enter in ligand exchange reactions with coordinating solvents, for example, water or DMSO. To increase the stability of our complexes with bioactive targeting ligands we replaced chloride ligands with a ligand that can resist hydrolysis or fast ligand exchange.

For all Ru(II)-arene complexes cytotoxicity were studied by MTT-test using a small library of the human cancer cell lines, the lipophilicity of complexes with oxalate moiety 4-6, 13-15 was determined by HPLC. Stability of new compounds was investigated in DMSO containing solutions, it was shown that our complexes resistant for ligand exchange reactions.

References

This work was supported by Russian Science Foundation (19-13-00084)
Today 1,3-dipolar cycloaddition of nitrones to unsaturated compounds is one of the most universal and convenient methods of synthesis of N,O-containing heterocycle structures, including isoxazolidines [1]. The special interest is in research of new ways of synthetic application for this cycloadducts, which are supposed to be perspective substrates for obtaining of different classes of organic compounds, which were hard-accessible before [2].

The aim of this work is to investigate regio- and stereoselectivity of 1,3-dipolar cycloaddition of arylpropenones with nitrones and to study subsequent transformation of formed isoxazolidines.

It was found that the cycloaddition of nitrones with 1,3-diarylpropenones proceeds regio- and stereoselectively giving isoxazolidines as a single diastereomer. The reduction of the isoxazolidines was carried out with various reagents. It was shown that the reaction with NaBH₄ proceeds with the formation of bicyclic 6-oxoperhydrofuroisoxazoles. Upon reduction of isoxazolidines with zinc in acetic acid 1,3-amino alcohols are produced, further cyclization of which leads to formation of α-amino lactones.

References
SYNTHESIS AND BIOLOGICAL ACTIVITY OF ALKYL-2-DIARYLMETHYLENEHYDRAZONO-5,5-DIMETHYL-4-OXOHEXANOATES

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New alkyl-2-diarylmethylenehydrazono-5,5-dimethyl-4-oxohexanoates were obtained by the reaction of decyclization of various hydrazonofuranones under the action of alcohols (Figure 1). It was shown that compounds of similar structure possess various types of biological activity with low toxicity [1, 2]. The chemical properties and biological activity of hydrazonofuranone derivatives with an alkyl substituent in the fifth position of the cycle are not investigated.

![Chemical structure](image)

**Figure 4.** Decyclization of various hydrazonofuranones under the action of alcohols.

The structure of the synthesized compounds was confirmed by the data of IR, $^1$H NMR spectroscopy, and mass spectrometry. According to the spectral data, the obtained esters exist in enhydrazine (A) and hydrazone (B) forms in
solution. A pharmacological screening of the synthesized compounds was carried out.

References

SYNTHESIS OF PHOSPHINE LIGANDS FROM CALCIUM CARBIDE AND PHOSPHORUS COMPOUNDS

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In the contemporary period of science development phosphine ligands are very demanded substrates. Their gold (I) coordination complexes demonstrate antitumor activity and this is why they can be used for the mechanistic investigations [1]. Especially valuable are bidentate organophosphorus compounds due to a plethora of application ways. The most significant among them are extraction, creation of ion-selective electrodes and medical treatment [2], [3].

There is still no effective method for producing such compounds. Michaelis-Arbuzov reaction is at the core of already existing methods, which allow obtaining bidentate phosphorus ligands, but the yields of the products are below 70%. Therefore, new methodology of the synthesis has been developed. It requires available and cheap calcium carbide and phosphorus compounds and implies the incorporation of the acetylene fragment (fig.1). The yields are around 96% and the purity of the products is sufficient.

Reference


SYNTHESIS OF N-CYANOMETHYL SALTS OF α-PICOLINES AND THEIR INTERACTION WITH ENAMINONES

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Quaternary salts of pyridines are excellent substrates for the creation of various heterocyclic systems. We recently showed that the interaction of 4-substituted \(N\)-(cyanomethyl)pyridinium salts with vinamidium perchlorates or enaminones leads to the formation of pyrido\[2,3-b\]indolizine-10-carbonitriles - compounds with highly potent optical properties. We continued our research on the \(N\)-cyanomethyl salts of α-picoline.

Salts 1 were synthesized through alkylation of corresponding 2-methylpyridine with bromoacetonitrile.

![Scheme 1. Synthesis of \(N\)-(cyanomethyl)pyridinium salts 1.](image1)

The reaction of salts 1 with enaminones 2 in the presence of sodium acetate did not give the expected pyridoindolizine-10-carbonitriles 3 but proceeded with the formation of pyrido\[2,3-b\]indolizines 4.

![Scheme 2. Synthesis of pyrido\[2,3-b\]indolizines 4.](image2)

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-20101).
Heteroleptic C,N-cyclometallated platinum(II) complexes \([\text{Pt}(C^N)(L,L')]^Z\) have an ability to luminesce in the whole visible spectrum region. The wavelength of the emission are modulated by the variation of the cyclometallated (C^N) and auxiliary (L, L') ligands [1]. Addition of the strong σ-donor ligands – particularly, isocyanides – leads to an increase of energy difference between HUMO and LOMO, shows blue-shifted emission maximum and makes it possible to get highly phosphorescent emitters with emission maximum in the blue to red region.

In this work we have synthesized isocyanide cyclometallated platinum(II) complexes \([(\text{ppy})\text{Pt}(\text{CNCy})_2](\text{OTf})\) and \([(\text{ppy})\text{Pt}(\text{PPh}_3)(\text{CNCy})](\text{OTf})\) (Hppy = 2-phenylpyridine, yield 70–90%). The obtained compounds were characterized with ESI+−MS, IR, \(^1\text{H}, \text{^}{13}\text{C}\{^1\text{H}\} \text{ and ^}{195}\text{Pt}\{^1\text{H}\} \text{ NMR spectroscopies. The structures were confirmed with the X-ray diffraction method.}

Figure 5. Scheme of synthesis cyclometallated platinum(II) complexes with isocyanide ligands

References

Acknowledgements. The work was supported by the Russian Foundation for Basic Research (18-33-20073) and Grant Program of the President of Russian Federation (MK-4457.2018.3). Physicochemical studies were performed at the Center for Magnetic Resonance Research, Center for X-ray Diffraction Studies and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).
Compounds containing activated triple bond are widely used in the creation of new materials and in the total synthesis of natural compounds. A special place in the series of electrophilic-activated acetylenes is occupied by the derivatives of propargyl aldehyde – compounds containing in their structure a sterically available aldehyde group coupled with a triple bond. We have studied the interaction of aldehydes 1 with Meldrum acid 2, malononitrile 3, malonic 4 and barbituric 5 acids. These reactions occur in different conditions (catalysis with MeONa, the exposure with AcOH within a few days or without catalyst at all) and lead to the formation of enins with electron acceptor groups 7–10.

As a result of the interaction of aldehydes 1 with malonic acid 4 in the presence of substituted pyridines 6, previously indescribable betaines are formed 11.\(^1\) The resulting compounds can be subjected to further interaction on unsaturated bonds to obtain biologically active derivatives.

**References**

SYNTHESIS OF NOVEL PORPHYRIN-FULLERENE DYADS FROM AB₂C-TYPE PORPHYRIN PRECURSORS

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Investigation of porphyrin-fullerene dyads is an important direction in the field of solar energy conversion: materials based on such compounds can be used in photovoltaic devices and in photocatalysis [1]. The rates of photoinduced processes occurring in such molecules are described by Marcus electron transfer theory [2], they depend on the structural parameters of compounds such as distance between the chromophores and their electron interactions [3]. We propose new synthetic protocol for porphyrin-fullerene dyads with different chromophores separation distance which is provided by the variation of the spacer between donor and acceptor moieties.

Figure 1. Structure of the porphyrin-fullerene dyads.

The proposed approach allows modification of the electronic structure and nature of the intermolecular interactions of the target compounds by introducing various substituents either into the porphyrin or to the aziridine fragment, which makes it possible to expand the library of porphyrin-fullerene dyads for the further study of the electron transfer photodynamics dependence on the structure of molecules.

References

Acknowledgements. The studies were carried out using the equipment of resource centers of the Research Park of St. Petersburg State University "Magnetic Resonance Research Methods", "Substance Composition Analysis Methods", "Chemistry Education Resource Center"
The work is devoted to the investigation of the interaction of pyrazoles with rhodium(II) α-iminocarbenoids generated from 1-sulfonyl-1,2,3-triazoles. It was shown that the result of the reaction significantly depends on the nature of the substituent at the N1-position of pyrazole. In the case of N-arylpyrazoles, the reaction leads to the formation of 2,6,8-triazabicyclo[3.2.1]octa-3,6-diene derivatives in almost quantitative yield. For N-alkylpyrazoles, the reaction does not stop with the formation of the bicyclic product and proceeds further to yield imidazole derivatives in high yields.

Taking into account the availability of the starting compounds, the discovered reaction is a simple and reliable method for the synthesis of previously unknown 2,6,8-triazabicyclo[3.2.1]octa-3,6-dienes and 2-(2-aminovinyl)imidazole derivatives. The study also considers limitations of the methods with regard to the structure of pyrazole, as well as a detailed study of the product formation mechanism, including quantum-chemical calculations. In addition, it has been shown that some bicyclic products can be quantitatively converted to the corresponding imidazoles by heating in the presence of silica gel.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-13-01078). This research used resources of “Magnetic Resonance Research Centre”, “Chemical Analysis and Materials Research Centre”, “Centre for X-ray Diffraction Studies”, and “Computing Centre” of St. Petersburg State University.
A condensation of amidoximes with dicarboxylic acid anhydrides represents a general route to 1,2,4-oxadiazole-based acids [1]. Typically this reaction is carried out in “two-step, one-pot” fashion via O-acylamidoxime intermediate generation and subsequent thermal cyclodehydration to the 1,2,4-oxadiazole. A number of reagents have been developed for the room-temperature synthesis of 1,2,4-oxadiazoles: TBAF, TBAH [2] and MOH/DMSO [3]. A mild and efficient protocol for the synthesis of 1,2,4-oxadiazoles containing a carboxyl functionality from readily available starting materials such as amidoximes and dicarboxylic acid anhydrides is highly desirable [4].

In conclusion, an effective, convenient one-pot protocol for the synthesis of 1,2,4-oxadiazoles bearing carboxyl group from bifenyl dicarboxylic acid anhydrides and amidoximes has been developed. We hope that the simple work-up procedure, mild condition (particularly, the ambient temperature), inexpensive and readily available starting materials, and a low-toxicity solvent, will make this method a useful tool in medicinal and process chemistry.

References
SYNTHESIS AND TRANSFORMATIONS OF ADDUCTS OF ITACONIMIDES WITH NITRONES

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Isoxazolidines cause an increased interest due to a wide range of pharmacological properties [1], including antiviral, antibacterial and antitumor activities. 5-Spiroisoxazolidines have attracted enlarged interest in recent years [2]. High efficiency and selectivity of 1,3-dipolar cycloaddition of nitrones to exocyclic double bonds allows to create complex heterocyclic scaffolds possessing valuable biological properties. Another distinct advantage of isoxazolidines is the possibility of cleavage of N-O bond when acted upon by various reagents to form 1,3-amino alcohols, the subsequent intramolecular cyclization of which can lead to different classes of organic compounds.

The aim of this work is to investigate regio- and stereoselectivity of nitrone cycloaddition to N-arylitaconimides and transformations of obtained spiroisoxazolidines under zinc in acetic acid conditions.

Figure 1. Synthesis and transformations of cycloadducts.

It was found that the cycloaddition reaction proceeds regioselectively and with high diastereoselectivity to form isoxazolidines as a single 5-spiro regioisomer. Also it was found that the reduction of N-O bond gave α-amino lactones or 1,3-amino alcohols depending on the structure of the substrate.

References
SYNTHESIS OF PYRIMIDINES VIA Rh(II)-CATALYZED REACTION OF 1-SULFONYL-1,2,3-TRIAZOLES WITH ISOXAZOLES AND 2H-AZIRINES

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In recent years, the development of new methods for the synthesis of heterocyclic compounds using 1-sulfonyl-1,2,3-triazoles is an actively developing area of organic synthesis [1]. Earlier in our research group, it was shown that Rh(II)-catalyzed reaction of 2-acetyl substituted 2H-azirine 1 with triazole 3 leads to the formation of substituted pyrimidine 4. In this study, it was found that the use of 5-methylisoxazole 2, which is an isomer of azirine 1, as a substrate also leads to the formation of product 4 and gives higher yield of pyrimidine 4 (Fig. 1).

![Reaction scheme](image)

Figure 1. Reaction scheme.

The aim of this work is to develop a method for the synthesis of substituted pyrimidines 5 using above-mentioned reactions. During the study, the most effective catalyst was found and the reaction conditions were carefully optimized. From substituted 3,5-dimethylisoxazoles and 1-sulfonyl-1,2,3-triazoles, a wide range of pyrimidines was synthesized with yields of 40–90%. Much attention was paid to the study of reaction mechanism. The experimental results and the results of DFT calculations evidence in favor of the formation of 1,3-oxazine intermediate in course of the reaction.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-13-01078). This research used resources of “Magnetic Resonance Research Centre”, “Computing Centre”, and “Chemical Analysis and Materials Research Centre” of St. Petersburg State University.
Catalysis by copper complexes containing halides and N-donors as ligands is actual field in chemical redox catalytic processes. Besides that, design of supramolecular structures for catalysis is a rapidly developing area today, and copper complexes can serve as building units for these compounds. Therefore in this work, tetranuclear clusters Cu₄Cl₆O₄L₄ (L is NCNR₂) were chosen for further design of supramolecular structures and the study of their catalytic activity that is relevant in developing selective catalysts for biochemical processes [1, 2].

The synthetic procedure for tetranuclear complexes is presented on the Scheme 1.

\[
\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{NCNR}_2 \xrightarrow{\text{i)} RT, 24–48h} \xrightarrow{\text{ii)} \text{toluene, Me}_2\text{CO/EtOAc or Et}_2\text{O; RT, 48–75h}} \text{R = Me}
\]

Scheme 1. Scheme of tetranuclear cluster synthesis

The chemical compositions of the synthesized complexes, geometric parameters of crystal structures, the thermal stability of the products, the solvent effect on the composition and structure of products and reactivity of coordinated NCNR₂ will be under discussion.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-13-00013).
[n]Helicenes constitute a class of polycyclic aromatic molecules in which \( n \) ortho-condensed aromatic rings give rise to a helical structure with extended \( \pi \)-system. Initial research was concentrated on carbohelicenes, but recently more interesting physical properties have been observed for the heterohelicenes.\(^1\) However, examples of helicenes based on heterocyclic rings (except of pyridine, pyrrole and thiophene rings) are rare because of the lack of common methods for their preparation.

We developed a general synthetic approach to [4]-, [5]- and [6]helicenes annelated by azine rings (pyridine, pyrazine, quinoxaline) starting from commercially available ortho-dihaloazines (Scheme 1).\(^2\) The effectiveness of the above strategy was demonstrated by the example of the synthesis of pyrazine-fused helicenes.

Scheme 1. Synthesis of pyrazine-fused helicenes.

Physical properties of the azine-fused helicenes 1-4 (UV-vis spectra, cathodic and anodic electrochemistry, X-ray structures) were compared to the parent [n]helicenes to discern the effect of merging an azine moiety within a helical skeleton.

References


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LUMINESCENT DINUCLEAR COPPER(I) HALIDE COMPLEXES BEARING PYRIDYLPHOSPHOLANES

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Complexes Cu(I) based on P,N-ligands attract great interest of researchers due to their remarkable luminescent properties [1]. Recently, we obtained new pyridyl-containing cyclic phosphines - pyridylphospholanes and a number of their luminescent complexes with copper (I) iodide. [2]. This work presents the synthesis of new complexes of phospholanylpyridines with copper (I) halides (Cu(MeCN)$_4$BF$_4$, CuCl and CuBr) (Scheme 1).

Obtained complexes are charged dinuclear species formed by three molecules of ligands coordinated to two metal ions via both donor atoms. Depending on the crystallization these compounds could be crystallized in two isomeric forms: head-to-head or head-to-tail. In both cases the coordination geometry around each metal atom is different: one being three- and the other one is four-coordinated. All complexes exhibit distinct luminescence in the solid state at room temperature with emission maxima at the range 520-540 nm.

References

Acknowledgements. The reported study was funded by RFBR according to the research (project № 18-33-00190). Photophysical measurements were performed by SPSU Center for optical and laser materials research.
SYNTHETIC AND NATURAL 2-PYRIDONES AS SCAFFOLDS FOR ELABORATION OF ANTI-INFLUENZA AGENTS: FROM IN SILICO PREDICTION TO REAL INHIBITION OF VIRUS REPRODUCTION

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On the basis of data about anti-influenza activity of derivatives of quinolizidine alkaloid (-)-cytisine [1] a virtual library of potential influenza A virus (H1N1) neuraminidase (NA) inhibitors was obtained as a result of the procedure of ‘peripheral design’ (LeadIT software package, ReCore and SeeSAR) of 2-pyridone matrixes I-IV (Figure 1). Docking of all predicted NA ligands into the 4B7R active site of NA of A (H1N1) flu virus (reference ligand zanamivir) was carried out using the software package Schrödinger Suite 2018-4 (Schrödinger, LLC, New York, NY, 2018) in order to identify the molecules with best calculated properties

![Figure 1. Starting quinolizidine matrixes I-IV](image)

Synthetical approaches to the hit-compounds identified on the basis of the docking data have been developed, and potential NA inhibitors have been synthesized (Figure 2).

![Figure 2. Potential NA inhibitors – derivatives of 2-pyridone IV](image)

Obtained compounds were studied for their ability to inhibit reproduction of A (H1N1)pdm09 flu virus reproduction (reference drugs were zanamivir and ribavirin); the compounds with selectivity indexes more than 80 were found.

References

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SYNTHESIS OF ANTIMITOTIC DRUG CONJUGATES BASED ON PSMA LIGANDS WITH DOCETAXEL

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Methods of selective delivery of drugs and other agents directly to the tumor, including prostate, have been actively developing. A promising protein marker for the diagnosis and treatment of prostate cancer is the prostate-specific membrane antigen, PSMA. The high expression of PSMA in prostate cancer cells compared with normal cells and vascular tumors has made it very promising for study. Urea-based low molecular weight ligands are described, providing selective binding to PSMA, and used to create therapeutic and diagnostic conjugates [1].

The results of docking show that ligands containing dipeptide linkers, based on amino acids (phenylalanine and tyrosine), has good affinity to PSMA and show high selectivity. Also, the modifications of the urea-based vector-molecule with various benzaldehyde fragments has a positive effect on affinity to PSMA. The modifications of urea-based vector and the dipeptide linkers for urea-based ligands PSMA were synthesized and optimized in present work. In vitro series of 24 ligands demonstrates the highest selectivity (IC₅₀ = 22.5 nM and 9.7 nM for LNCaP) were selected, while urea-based ligand without modification has low selectivity (IC₅₀ = 2149 nM for LNCaP). Antimitotic conjugates with Docetaxel were synthesized with high selective ligands.

Docetaxel drug conjugates were obtained and characterized in vitro and in vivo tests. The results show good cytotoxicity (comparable to Docetaxel without modification) and will be presented on the report.

References

This work was done mainly in MSU and kindly supported by Ministry of Education and Science of the Russian Federation (03.G25.31.0219).
SOLID FORMS OF CIPROFLOXACIN SALICYLATE: POLYMORPHISM, FORMATION PATHWAYS, AND THERMODYNAMIC STABILITY

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The crystallization of ciprofloxacin - an antibacterial fluoroquinolone compound - with salicylic acid resulted in the isolation of five distinct solid forms of the drug, namely, an anhydrous salt, two polymorphic forms of the salt monohydrate, methanol and acetonitrile solvates, and the salt-cocrystal hydrate. The salicylate salts were investigated by different analytical techniques ranging from powder and single crystal X-ray diffractometry, differential scanning calorimetry, thermogravimetric analysis, variable temperature powder X-ray diffraction, dynamic vapor sorption analysis, dissolution, and solubility investigations. Real-time in situ Raman spectroscopy was used to investigate the mechanochemical formation pathways of the different solid polymorphs of ciprofloxacin salicylate. The mechanism of the phase transformation between the crystalline forms was evaluated under mechanochemical conditions. It was found that the formation pathway and kinetics of the grinding process depend on the form of the starting material and reaction conditions. The analysis of the solid-state thermal evolution of the hydrated salts revealed the two-step mechanism of dehydration process, which proceeds through a formation of the distinct intermediate crystalline products [1].

![Packing arrangement of [CIP+SA+H₂O] (1:1:1) (a) form I and (b) form II.](image)

References

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A NOVEL SYNTHESIS OF 1,2,4-TRIAZINES

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Earlier we have developed a new synthesis of 1,2,4-triazines by Zn-catalyzed hydroamination of propargylamides with BocNHNH$_2$ (Fig.1) [1].

![Figure 1. Hydroamination of propargylamides with Boc-NHNH$_2$ by Zn(CF$_3$SO$_3$)$_2$ catalysis [1]](image)

Based on these results we investigated the hydroamination reaction of a variety of propargylamides (1) with different phenylhydrazines by Zn(CF$_3$SO$_3$)$_2$ catalysis. To our surprise depending on the initial propargylamide the main products of the reaction was N-(phenyl)amino imidazoles (2) on the one hand, and 2-methyl-1$H$-indoles (3) on the other hand (Fig.2).

![Figure 2. Hydroamination of propargylamides with different phenylhydrazines by Zn(CF$_3$SO$_3$)$_2$ catalysis](image)

References
Cisplatin has expressive cytotoxic, bactericidal and mutagenic properties. The mechanism of action is similar to the action of other alkylating drugs and is a violation of the functions of DNA caused by chemical damage to the DNA bases. At the cellular level, cisplatin causes replication and transcription disruption, leading to cell cycle delay and apoptosis. In recent years, the world's leading medical institutions are trying to find bioactive drugs among other compounds of the platinum group, including palladium. Palladium compounds are significantly less toxic than platinum complexes. The literature also contains information about the high antitumor activity of palladium complexes with organic ligands. A large number of scientific articles are devoted to analogues of cisplatin, in which ammonia ligands are replaced by N-heterocyclic ligands and analogues of cisplatin, which contain heterocyclic ligands having unsaturated substituents, such as substituted vinyls, allyls, allenyls, etc. It is shown that such complexes have antitumor biological activity[1]. Therefore, we decided to synthesize palladium chloride complexes containing terpenyl benzimidazole ligand (Scheme). It is known that terpenyl substituents have the ability to pass through lipid cell membrane some organic molecules for targeted action at the cell biological target. Terpenyl benzimidazole ligand (I) was synthesized as described in the article [2].
Acknowledgements. This work was performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

References
Indoloquinolinones are very important in the fused indole family due to their wide occurrence in numerous bioactive natural products.[1] Isocyanide-based multicomponent reactions (IMCRs) have attracted a lot of attention, due to the fact that versatile functional groups can be introduced in the MCR adducts, which can undergo further condensations or cyclizations reactions leading to an array of structurally diverse scaffolds.[2]

References

Acknowledgements. This work was supported by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreements No 713482 and No 754425 and the China Scholarship Council.
MULTIFUNCTIONAL LIGANDS COMBINING 5-HT₆ RECEPTOR ANTAGONISM, INHIBITION OF CHOLINESTERASES AND BETA-AMYLOID AGGREGATION AS POTENTIAL DISEASE-MODIFYING AGENTS AGAINST ALZHEIMER’S DISEASE

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Alzheimer’s disease (AD) is a fatal neurodegenerative disorder caused by a set of pathological processes including impaired neurotransmission, aggregation of amyloid-β (Aβ) and inflammation [1]. Currently available anti-AD drugs, developed on the one-target one-drug paradigm, do not stop or reverse the progression of the disease. Complex diseases, like AD, require a multi-target approach for effective treatment. Selection of appropriate combination of biological targets to obtain multi-target (multifunctional) molecules able to interfere with several pathological processes at the same time is crucial for the effectiveness of the new therapies. Based on the results of preclinical and clinical trials, we have selected 5-HT₆ receptors, cholinesterases and Aβ as biological targets of key importance for AD [2]. Previously, we have developed the first series of multifunctional molecules combining activities against these three targets [3]. Although the compounds displayed unique pharmacological profile in vitro and in vivo, their physicochemical and pharmacokinetic properties needed improvement (compound I, Figure 1). Herein we present design, synthesis and biological evaluation of a new set of multifunctional compounds with improved drug-like properties promising for the development of new anti-AD therapeutics.

Figure 1. Design of new multifunctional ligands addressing disease-modifying and symptomatic targets

References

Acknowledgements. This work was supported by the National Science Centre Poland, grant No 2016/23/D/NZ7/01328.
NEW METHOD OF PRODUCING 5-DIALKYLAMINO-1,2,4-TRIAZOLES FROM ACYL HYDRAZIDES AND DIALKYLICYANAMIDES

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1,2,4-Triazole and its derivatives represent an important class of five-membered heterocycles. These heterocycles and their derivatives are widely used in materials chemistry (gas adsorbents and separators, components of OLEDs, proton conductive nanotubes), in medical chemistry (display broad spectrum of biological activities) and in synthetic chemistry as synthons for generation of other heterocyclic systems.

This work describes new highly efficient synthetic methodology to preparation of 5-dialkylamino-1,2,4-triazoles from acyl hydrazides and dialkylcyanamides in the presence ZnⅡ [1]. The protocol utilizes simple and readily available reagents and proceeds under mild conditions giving the triazoles in good to excellent yields (76–99%) (Scheme 1). The ZnⅡ-catalyzed reaction proceeds via initial generation of the \([\text{Zn}\{\text{RC(=O)NHNH}_2\}_3]\) complexes.

In this work, 17 new 5-dialkylamino-1,2,4-triazoles have been obtained and characterized by a set of physicochemical methods of analyses (HRESI+MS and IR, \(^1\)H, and \(^{13}\)C\{\(^1\)H\} NMR spectroscopies; five species were additionally characterized by single-crystal X-ray diffraction (XRD)).

Scheme 1. Zinc(II)-mediated benzoyl hydrazide–dimethylcyanamide coupling.
In order to estimate electronic effects of the substituents at the acyl hydrazide moiety, we performed a kinetic study with a series of para-substituted benzoyl hydrazides. We found that neither the nature of the solvent, nor the substituent electronic effects significantly influence the observed pseudo-first order rate constant $k$, which is ca. $10^{-3}$ s$^{-1}$ in all cases (Table 1.). Based upon the kinetic study it can be concluded that electronic effect of substituents in acyl hydrazide do not significantly affect the reaction rate and these data are useful for further control of the coupling.

Table 1. Observed pseudo-first order rate constant.

<table>
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<th>Nos</th>
<th>R</th>
<th>$k \times 10^{-3}$ (s$^{-1}$)</th>
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<th>(CD$_3$)$_2$SO</th>
</tr>
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<tr>
<td>3</td>
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<td>1.37(8)</td>
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<tr>
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<td>1.28(10)</td>
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</tr>
<tr>
<td>7</td>
<td>Br</td>
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<td>8</td>
<td>NO$_2$</td>
<td>(-^a)</td>
<td>1.09(5)</td>
<td></td>
</tr>
</tbody>
</table>

[1] Yunusova, S. N.; Bolotin, D. S.; Suslonov, V. V.; Vovk, M. A.; Tolstoy, P. M.; Kukushkin, V. Yu., ACS Omega, 2018, 3 (7), 7224-7234

This work was financially supported by the Russian Science Foundation (grant 17-73-20004). Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).
THE 5-(ARYLMETHYLIDENE)-2,4,6(1H,3H,5H)-TRIONES IN REACTION HETEROCYCLIZATION WITH N-OXIDE MORPHOLINE

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The reaction of 5-(arylmethylidene)-2,4,6(1H,3H,5H)-trions (1-3) with morpholine (4) in the presence of hydrogen peroxide and catalytic amounts Na₂WO₄ ends with the formation of cycloaddition products of substituted 2-aryltetrahydro-1'H,2H-spiro[isoxazole[3,2-c][1,4] oxazin-3,5'-pyrimidine]-2',4',6(3'H)-trions (5-7).

Ar=Ph (1,5); 4-MeOC₆H₄ (2,6); 4-Me₂NC₆H₄ (3,7)

It is likely that in the process of interaction of morpholine (4) with hydrogen peroxide and Na₂WO₄, morpholine N-oxide (A) is generated, which is converted into cycloadducts (5-7) as a result of the process of 1,3-dipolar cycloaddition. The structure of the compounds was established by the methods of IR, ¹H, ¹³C NMR, mass-spectrometry, and the composition by elemental analysis.

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(project no 4.9288.2017BCH)
SYNTHESIS AND SOLID STATE FLUORESCENCE OF PYRROLE-2-CARBOXAMIDE BF$_2$-COMPLEXES

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We have synthesized a number of new dyes - BF$_2$-complexes of pyrrole-2-carboxamides (1), exhibiting fluorescent properties both in solution and in the solid phase. Synthesis of 1 (with a total yield up to 87.5%) was carried out according to the following scheme:

Scheme 1. Route to BF$_2$-complexes of pyrrole-2-carboxamide

Synthesized dyes exhibit solid-state fluorescence in a wide blue-violet region of the spectrum (with an absorption maximum in the region of 370–404 nm) with a quantum yield up to 40% (Figure 1). The magnitude of the Stokes shift is 38–80 nm.

It should be emphasized that the development of stable blue-light emitting organic diodes is still an urgent task, attracting considerable attention of researchers in this field.

Figure 1. Solid-state fluorescence parameters of synthesized complexes.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-01042).
NOVEL ANTIPROLIFERATIVE Pt(IV) COMPLEXES WITH LONIDAMINE AND BEXAROTENE LIGANDS

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Today clinically approved Pt(II) anticancer complexes, cisplatin, carboplatin and oxaliplatin, are used in about 50% of all chemotherapeutic regimens. However, they have a lack of selectivity and a number of severe side effects. For the last two decades, octahedral Pt(IV) complexes became an important platform for the development of new anticancer agents due to their kinetic inertness, low general toxicity and a possibility for oral administration.

Combinations of two drugs in one molecule are a widely used approach in modern drug discovery. We introduced lonidamine, a specific inhibitor of aerobic glycolysis in cancer cells, and bexarotene, a selective agonist of retinoid X receptors, as an axial ligand in Pt(IV) complexes [1].

New complexes were characterized by NMR, ESI-MS and elemental analysis. Antiproliferative activity of the complexes was investigated using SW480, A549, MCF7, MCF7D and HaCat cell lines by means of standard MTT colourimetric assay. Investigation of the mechanism of action and results of in vitro and in vivo studies will be presented.

![Figure 1. New Pt(IV) complexes with lonidamine and bexarotene ligands.](image)

References:

Acknowledgements. This work was supported by the RSF (project № 19-13-00084).
EFFECT OF PH ON RADICAL REACTIONS OF TRYPTOPHAN AND LYSOZYME PHOTOSENSITIZED BY KYNURENIC ACID

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Human eye lens contains low-molecular mass compounds, kynurenine (KN) and its derivatives, which absorb in UV-A region (315-400 nm) and protect eye tissues from harmful Sun irradiation. KNs are effective molecular UV filters but products of their thermal degradation could act as effective photosensitizers able to generate reactive triplet states under UV-A light. Reactions of these triplets with aromatic amino acid residues (mainly tryptophan, Trp, and tyrosine) yield free radicals within the eye lens, which subsequent reactions could inevitably change the eye lens proteins. As a result lens proteins accumulate various modifications during an individual lifetime that predisposes the eye lens tissue to the development of cataract, which molecular mechanisms are still weakly studied.

Oxidative stress is the necessary condition for the cataract onset. Though the origin of oxidative stress formation in a healthy lens is unclear, it could be followed by acidosis, a shift of cell pH to lower values. In this work we studied the influence of pH on the photoinduced radical reactions between Trp-derivatives and kynurenic acid (KNA), one of the most effective photosensitizer of the human eye lens.

Time-resolved optical experiments have shown that pKa value for KNA radical (KNA•) is 5.5 and for Trp radicals (Trp•) lies in the range of 4-5 depending on a substituent in amino acid backbone. Aqueous solutions of KNA and various Trp derivatives were UV-A photolyzed at three pHs, corresponding to three different pairs of protonated/neutral radicals of KNA and Trp. HPLC-MS analysis of photolysed samples have shown a decrease of decomposition yield of both reagents at pH<pKa (Trp•) without qualitative changes in the composition of formed products. This indicates an acceleration of the back electron transfer rate between KNA• and Trp• without the Trp• protonation that was confirmed by time-resolved experiments.

Experiments with model protein lysozyme have shown that protein environment could significantly redirect the radical reactions even without protonation of Trp• within protein structure. We found that Trp• in lysozyme has pKa of 3.1 and the change of pH from 7 to 5 has no effect on the lysozyme degradation, but largely increases its oxygenation and lowers the formation of covalent cross-links. To clarify pH-influence of the eye lens proteins additional experiments have to be done.

This work was financially supported by Russian Science Foundation (project 18-73-10014).
The following example describes a rare case of the diastereospecific [4 + 2] cycloaddition of maleic anhydride to 1-(vinylhetaryl)tetrahydroisoquinoline 2 [1-3].

1,2,3,4-Tetrahydroisoquinolines 2 were obtained from amides 1 by the Bischler-Napiralski reaction, followed by reduction of the C=N bond. The interaction of compounds 2 with maleic anhydride proceeds through the stage of nitrogen atom acylation and the subsequent intramolecular Diels-Alder reaction, which allows to obtain polycycles 3 or 4 as individual diastereomers in one step. Moreover, at temperatures below zero degrees, it is possible to isolate the “non-aromatic” adducts 3. At high temperatures, the adducts 3 undergo prototropic tautomerism, turning into compounds 4 with an aromatic furan (thiophene) cycle. The reaction of transformation 2 to 4 can be carried out without isolation of intermediate product 3.
Reference


*This work was supported by the Russian Foundation for Basic Research, grants № 17-53-45016 and 16-03-00125.*
Homogeneous gold catalysis provides wide opportunities for heterocycles synthesis from simple organic “building” blocks. In particular, multicomponent reactions of gold-activated acetylenes, pyridine N-oxides and nitriles lead to formation of 1,3-oxazole scaffolds with different functional moieties (Figure 1). [1-2].

Figure 1. Gold-catalyzed multicomponent reactions leading to different 1,3-oxazoles scaffolds.

At this work we investigate reactivity patterns of ynamides (acetylenes with amide, sulfonamide or carbamate moiety) in gold-catalyzed multicomponent reaction with pyridine N-oxides and cyanamides to achieve 2,4-bisamino-1,3-oxazoles scaffold.

Figure 2. Gold-catalyzed multicomponent reactions leading to 2,4-bisamino-1,3-oxazoles scaffold.

References

This work was supported by Russian Foundation for Basic Research (project No 18_33_00277).
Aza-Michael reaction is one of the most widely used in modern green organic synthesis of bioactive compounds. As a rule, it proceeds under mild conditions and does not require the use of toxic solvents and organometallic catalysts. Despite aza-Michael addition has already been studied rather thoroughly, there are some unsolved items. In particular, regioselectivity of the nucleophilic addition to alkenes bearing two vicinal electron-withdrawing moieties is still a challenge task for chemists.

In our work the reactions of primary and secondary amines (benzylamine and morpholine) with acrylic esters bearing acetyl-, cyano-, or trifluoromethyl groups were studied. The influence of the introduction of bulky groups (methyl or phenyl) is also discussed.

To explain the observed ratios of regioisomers, we applied a modified model, which had been originally proposed by Mayr at al. in [1]. We have found that the model is in good agreement with the results obtained.

Figure 1. General scheme of the reaction

References

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SYNTHESIS OF URACILS WITH PHENYL CARBAMATE FRAGMENT

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The interaction of 5-acetyl-4-hydroxy-2H-1,3-thiazin-2,6(3H)-dione (1) [1] with cyclohexyl- and benzyl-N-(4-aminophenyl)carbamates (2,3) when boiling in ethanol in the presence of a catalytic amount of glacial acetic acid the corresponding cyclohexyl (benzyl) N-(4-{[(E)-1-(4-hydroxy-2,6-dioxo-3,6-dihydro-2H-1,3-thiazin-5-yl) ethylidene]amino}phenyl)carbamates (4,5) were prepared. Boiling the obtained Schiff bases (4,5) in DMF for two hours is accompanied by release of COS and the formation of cyclohexyl (benzyl) N-(4-[6-methyl-2,4-dioxo-3,4-dihydro-1(2H)-pyrimidinyl]phenyl)carbamates (6,7) (Figure 1).

Figure 1. Synthesis of uracils with phenylcarbamate fragment.

Structure of the compounds (4-7) was confirmed by $^1$H, $^{13}$C NNR spectroscopy.

References

Acknowledgements. The work was financially supported by the Ministry of Education and Science of the Russian Federation (project no. 4.9288.2017BCH).
4 section

COMPUTER MODELING AND CHEMINFORMATICS
EXTENDED INTERACTIVE GREENE’S REACTIVITY CHARTS

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Multi-stage organic synthesis very often leads to using protective groups for selective blockade of undesirable interactions with certain functional groups. Chemists usually obtain information on the reactivity of protective groups either on the basis of their own experience or on the basis of such literary sources as "Greene's Protective Groups in Organic Synthesis" [1]. Unfortunately, in the latter case, it is not clear how the authors assessed the reactivity of the protective groups in one-step and selective reactions with molecules containing several protective groups. In addition, it is not indicated what exactly the number of reactions was the basis for the conclusion about the degree of reactivity of a particular protective group.

The use of chemoinformatics methods allowed us to overcome these shortcomings [2] and create spreadsheets, equivalent to tables from Greene's book [1]. As a source of data, we used the dataset of one-step catalytic hydrogenation reactions, which was extracted from Reaxys database [3]. Retrieving information about the reactivity of the protective groups included the following steps. The protective group and its class were determined (namely, the protective group leaves or remains) by using the Condensed Graph of Reaction (CGR) approach [4] and the substructural search. Reaction conditions were pre-standardized using a synonyms dictionary that includes “raw” and “standard” compound names.

Moreover, we expanded our equivalent of Greene’s Reactivity Charts by adding some interesting, frequently occurring combinations of conditions, for example, Pd with amines. The results of this system are presented in the form of a web interface containing a list of accessible protected groups for catalytic hydrogenation reactions and an interactive table including the reactivity estimates of the protective groups (corresponding to those presented in Green).

This system is fully automatic, in addition, it allows us to look in Reaxys, on the basis of what kind of reactions was made predictions about the reactivity of protective groups.

References

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MODELING THE BASIS OF HOMODESMIC REACTIONS OF CHEMICAL COMPOUNDS

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Thermodynamic calculations are a common and important element of many chemical studies. They underlie the development of highly efficient technologies for the industrial synthesis of compounds. Thus, it becomes necessary to accumulate reliable information about the thermodynamic properties of individual substances [1]. Experimental data on thermodynamic properties are available for a limited number of compounds, and therefore the development and improvement of methods for calculating thermodynamic quantities is an important and urgent task. The development of computer technology and the development of new quantum-chemical methods allows one to carry out theoretical calculations of the thermodynamic properties of chemical compounds with an accuracy comparable to experimental errors.

The principle of maximum similarity, implemented in the form of the concept of isodesmicity, was proposed as early as the 70s of the last century. This approach proved to be very fruitful for analyzing the relationship between the structure of organic compounds and their energy content, but the accuracy of thermochemical calculations was limited to a low level of development of computational quantum chemistry. It was quickly found out that the quality of calculations can be improved by adding to the set of balances of the isodesmic reaction with the requirement of group balance. This approach was called homodemic [2-3]. Any chemical compound can be represented as a molecular graph. The vertices of the graph are the atoms that make up the molecule, the edges are the bonds between the atoms. The experience of using the homodemic method has shown a high reliability of the theoretical prediction of the enthalpies of formation of various compounds.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-07-00584 A).
MOLECULAR DYNAMICS SIMULATIONS OF GAS PERMEABILITY IN THERMOPLASTIC R-BAPB POLYIMIDE

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Gas separation is among the key processes in chemical and petrochemical industry. During recent years polymer gas separation membranes have emerged as a promising class of materials in various applications including air enrichment with oxygen, extraction of such valuable resources as helium and hydrogen and reduction of carbon dioxide emissions into the atmosphere. Along with improving transport properties of the existing polymers, another important problem is developing new polymers with high selective properties. Aromatic polyimides (PI) are widely used to create such polymeric gas separation membranes due to their unique physico-chemical properties. Various methods are actively used to access this issue. Recent years have seen active development of computer simulations methods employing fully-atomistic models to evaluate transport properties of various polymers. In the present work, molecular dynamics simulations are for the first time used to determine transport properties of promising crystallizable thermoplastic R-BAPB PI synthesized from 1,3-bis(3', 4'-dicarboxyphenoxy) benzene (dianhydride R) and 4,4'-bis-(4 "-aminophenoxy) diphenyl) (diamine BAPB) in the Institute of Macromolecular Compounds. For this purpose diffusion coefficients and solubilities of various gases including helium (He), oxygen (O₂), nitrogen (N₂) and methane (CH₄) were determined. It was found that R-BAPB PI has a high selectivity with respect to He/CH₄, which makes it a promising candidate to be used for the separation of helium from natural gas. The results of computer simulations are in good agreement with the recently obtained experimental data, which provide a strong basis for further investigations of transport properties of nanocomposites based on R-BAPB PI by means of molecular dynamics simulations.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (RFBR), (grant No. 18-29-17040). The simulations have been performed using the computational resources of the Institute of Macromolecular Compounds of the Russian Academy of Sciences, Lomonosov-2 supercomputer at Moscow State University, Joint Supercomputer Center of the Russian Academy of Sciences and resources of the federal collective usage center “Complex for Simulation and Data Processing for Mega-science Facilities” at NRC “Kurchatov Institute” (http://ckp.nrcki.ru/).
Studying of the confined water/hydrocarbon mixtures is important for understanding and improving of the ways of oil recovery. The extraction of hydrocarbons from narrow pores is an essential problem for oil production industry. Methods of computer modeling allow one to describe different interactions between water solution and adsorbed hydrocarbon nearly solid surface of the different nature and define proper conditions for oil recovery. In this work computer simulation is used to study the mobility of decane and water in amorphous silica and graphite slit pores. Different systems were investigated at pore width $H = 6$ nm in a range of decane concentration from 0 to 100 vol.%. Furthermore, we investigated an efficiency of addition of different surfactants (Span 80 and AOTNa) on the diffusion coefficients of decane and water in a different range of concentrations in pores.

Figure 1. Water/decane mixture in graphite pore at 30 vol.% decane.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-03-01238 A).
Ultracold molecules have, in recent times, become a highly useful tool in many fields of experimental physics, such as fundamental physics, metrology, ultracold chemistry, and experimental modelling of quantum computers. However, in order to employ ultracold molecules, one must first create them. This typically requires comprehensive and exact foreknowledge of rovibronic levels, the calculation of which requires highly accurate potential energy curves (PECs) and coupling matrix elements between the states involved.

In this work, the spin orbit coupled D1Π-d3Π complex of LiRb is studied. Using high level ab initio data of the PECs and spin-orbit couplings (SOCs), the available experimental terms [1-2] assigned to the D1Π and d3Π states are described through a nonadiabatic perturbation treatment to within experimental accuracy (0.01 cm⁻¹).

Figure 1. The a) PECs, b) SOCs, and c) term energies for the D1Π- d3Π complex of LiRb, as well as d) the error in describing the experimental terms.

References

Acknowledgements. The study was funded by RFBR according to the research project N18-33-00753.
EFFECT OF BRANCHING OF SIDE GROUPS ON SELF-ASSEMBLY OF OLIGO(PHENYLENE-THIOPHENE)S ON GRAPHENE

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Nowadays, conjugated compounds are of considerable interest for application in a field of organic electronics. Rigid and planar oligo(phenylene-thiophene)s are excellent candidates for the design of electronic devices with relatively high conductivity values. However, one of the priority tasks in the field still remains the increase in efficiency of the devices by precise control over morphology in organic layers. This is usually a complicated task due to the fact that even a small change in chemical structure of either the backbone or the side groups of the molecules significantly affects the conductivity values. Thus, present study aims at investigating the effect of branching of side groups on self-organization of oligo(phenylene-thiophene)s on monolayer graphene via the molecular dynamics simulations. The results obtained demonstrate that highly ordered molecular aggregates are observed only for unbranched alkoxy side chains, while branching, on the contrary, hinders the ordering.

Figure 1. Typical top views of the monolayers of oligo(phenylene-thiophene)s on graphene: a) the formation of molecular aggregates in the systems with alkoxy side groups; b) disordered structure of the systems with ethyl-hexyl side groups.

Acknowledgements. The simulations were performed using the computational resources of the Institute of Macromolecular Compounds of Russian Academy of Sciences and the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University. This study was supported by the Russian Foundation for Basic Research (project No 18-29-19123).
Reverse micelles are called associates of non-polar organic solvents in which hydrophilic groups form a core, in which, as a rule, is water, a hydrophobic outer shell. Micelles have the ability to solubilize (that is, include in their composition) molecules and even ultrafine particles of surface-inactive substances. Surfactants are essential to the phenomenon of life.

In this work, we investigated the systems using the molecular dynamics method of the structure of the surfactant AOT and the location of organic substances (benzene and pyridine oxy derivatives) in reverse micelles in the dean – water system of ionic surfactants AOT. To achieve the goal, the tasks were set: to establish the dependence of the position of the molecule in the reverse micelle.

Figure 1. Organic molecules.

Figure 2. Reverse micelle AOT.
DFT CALCULATIONS OF NAPHTHOQUINONE FLUOROSULFATE DERIVATIVES WITH POTENTIAL CYTOTOXIC ACTIVITY

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Naphthoquinone derivatives, including plant-derived naphthoquinones, exhibit a variety of pharmacological properties, including antimicrobial, antiviral, anti-inflammatory, and antitumor effects [1]. Electronic properties associated with the ability to accept electrons, such as energy of the lowest unoccupied molecular orbital (E_{LUMO}), vertical electron affinity (VEA), and general chemical reactivity (ω), are the most important characteristics related to cytotoxic activity of the naphthoquinone derivatives studied here. These properties are important in accordance with the general concept of donor-acceptor and nucleophile-electrophile interactions with target molecules, which are to a great extent defined by the energies of frontier molecular orbitals [2]. Hydroxyl derivatives of naphthoquinones can be converted into fluorosulfates by using the SuFEx reaction, which was successfully applied in the synthesis of small molecules, protein labeling, polymer synthesis, and surface derivatization [3]. Such derivatives potentially have greater potential to accept electrons, which is why they may have higher cytotoxic activity. Thus, the aim of this research was to investigate electronic properties of naphthoquinone fluorosulfate derivatives by the DFT method.

We performed a DFT study for a group of naphthoquinone derivatives to identify characteristics of their electronic structure related to cytotoxicity. Geometry optimizations were performed with BP86 functional, triple-zeta basis set def2-TZVPP, and D3BJ dispersion correction. This level of theory provides high-quality results for geometries of organic molecules [4]. Subsequent single-point calculations were then performed for each compound with ωB97X-D3 functional and the largest Pople basis set 6-311++G(3df,3pd) in order to obtain improved results for orbital energies [5].
In comparison with naphthoquinone hydroxyl derivatives, the fluorosulfates possessed higher chemical reactivity and lower LUMO energy. For example, plumbagin (1), a natural compound that has anticancer activity [6], has higher LUMO energy than its fluorosulfate derivative 2 (-1.719 eV and -1.812 eV, respectively), lower chemical reactivity (3.27 eV and 4.31 eV, respectively) and lower VEA (33.99 kcal/mol and 47.214 kcal/mol, respectively). We also observed such a tendency for other naphthoquinone fluorosulfate derivatives, e.g. 3 and 4. The results suggest that these derivatives can be used for future investigation as biologically active compounds. Synthetic routes for introducing fluorosulfate groups into the naphthoquinone scaffold are exemplified below.

![Synthesis of fluorosulfates](image)

**Figure. General method for the synthesis of fluorosulfates**

References


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Recently, more attention has been focused to use the molten salts for the interests of developing safe and efficient power engineering, and for nuclear technologies as well as. Herewith, data about the stability of compounds and phase boundaries are first priority in the problems related to materials science. Therefore, the thermodynamic data and state diagrams of salt systems are important in electrochemistry, metallurgy, energetics, nuclear engineering, etc.

Simulations of phase equilibria in molten salts are carried out by means of thermodynamic modeling, ab initio and molecular dynamic methods. The difficulty of statistical-thermodynamic calculations is the absence of exact solutions for realistic models of the interactions (e.g., with polarizabilities); therefore, in the framework of the statistical theory, this problem for molten salts has not been considered so far. In report, simulation results for fusion characteristics and thermodynamic properties of rubidium halides by means of variational thermodynamic perturbation theory will be given. Within this approach, the free energy for a molten phase has form

\[
F_{\text{liq}} \leq F_{\text{chs}} + 2\pi \rho \sum_{i,j} x_i x_j \int_{0}^{\infty} \phi_{ij}^{\text{pol}}(R) \cdot g_{ij}^{\text{chs}}(R) \cdot R^2 dR.
\]

Here \( F_{\text{chs}} \) is the free energy for the reference system of charged hard spheres within mean spherical approximation, \( g_{ij}^{\text{chs}}(R) \) is the radial distribution function of the reference system, \( \phi_{ij}^{\text{pol}}(R) \) is the additive to the pair potential. The free energy for an ionic crystal can be written as sum of the potential energy in Born-Mayer formula and vibrational contribution in Debye’s model:

\[
F_{\text{sol}} = \frac{N A z_i z_j e^2}{R_0} \cdot \left( 1 - \frac{\rho_e}{R_0} \right) + N k_B T \cdot \left[ 3 \ln \left( 1 - e^{-\frac{\theta_d}{T}} \right) + \frac{9}{8} \cdot \frac{\theta_d}{T} - \frac{\theta_d}{T} \right].
\]

Then the position of phase equilibria can be found using the rule of equality of the chemical potentials for each phase at the equilibrium point.
Transition metal complexes with redox non-innocent ligands are among the most interesting objects of the modern coordination chemistry. The most popular redox non-innocent ligands are the dioxolene type ligands derived from o-quinones (Q), which can be in the dianionic catecholate (Cat), o-semiquinone (SQ) or neutral (Q) forms. Recently, two manganese complexes with dioxolene ligands, Mn(3,6-DBCat-pipe)(3,6-DBSQ-pipe)$_2$ (1) and (4-NIT-Py)$_2$Mn(3,6-DBCat-pipe)$_2$ (2), were synthesized and characterized using X-ray diffraction, EPR and magnetic susceptibility measurements [1]. The authors proposed the localized oxidation state for 1 – Mn$^{IV}$(Cat)(DBSQ-pipe)$_2$ – and the presence of valence tautometric equilibrium for 2. This work presents the *ab initio* multi-configurational study of the electronic structures and properties of both complexes and the analysis of their valence states.

References

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Investigation of the ordering of heterocyclic polymers on the graphene is a promising research area to develop heat-resistant substrates with controlled mechanical properties for different industrial applications. The orientation of polymer chains on the graphene plane could lead to different mechanical properties in various directions upon applying mechanical field. However, it remains unclear how the heterocyclic polymer chains are ordered on the graphene plane with respect to the symmetry axes at different temperatures and how this orientation might influence on the mechanical properties of polymer nanocomposites. In the present study, all-atom molecular dynamics (MD) simulations have been carried out to preliminary investigate the thermal, dynamic and structural properties of oligomers of crystallizable polyimide (PI) BPDA-P3 ordered by the graphene surface. The chemical structure of BPDA-P3 repeating unit consists of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and diamine 1,4-bis[4-(4-aminophenoxy)phenoxy]benzene (P3). BPDA-P3 oligomers with polymerization degree $N_p=1$ or 2 have been simulated in wide range of temperatures from 300 to 600 K. It was found that with increase of BPDA-P3 chain length, the value of glass transition temperature ($T_g$) also increases, that might be due to high mobility of oligoimides with $N_p=1$ near the graphene surface than mobility of oligoimides with $N_p=2$. The formation of oligoimide regions with a preferable orientation relative to the graphene symmetry axes was observed close to the graphene surface at the temperature higher and below $T_g$.

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The adequate account of solvation effects is crucial in the calculation of the thermodynamic states of chemical substances in solution. This is particularly important if one considers a complex homogeneous catalytic process under non-standard conditions. Such systems are quite common in hydrogenation reactions catalyzed with transition metal complexes, where parallel processes and side reactions are ubiquitous. We present here the computational research of the thermodynamic parameters of competitive reaction pathways in the homogeneous hydrogenation of carbon dioxide [1-4].

This reaction takes place in a non-aqueous solution at high hydrogen pressures. To model such reactions adequately, the accurate calculation of the free energies of the substances in solution is necessary. The energies of the intermediates and transition states are highly non-standard in this case. We thus evaluated the available quantum chemical methods for solvation modeling to find the most effective method on the chosen model example. This in turn led to new insights into the mechanism and kinetics of the catalytic homogeneous CO$_2$ hydrogenation. Moreover, the performed computational modeling allowed us to rationalize the optimal operating conditions for the catalytic process.

We performed DFT calculations at the RI-TPSS-D3/def2-TZVP level of theory to model the molecules in the gas phase and used COSMO-RS to account for the solvation effects. The dependences of the free energy of the reactions were calculated under varied temperature, pressure, and reaction components concentrations.

References:
The key challenge in the computer planning of chemical synthesis is generation of new compounds from the set of available molecules. As part of this work, we have developed an algorithm that generates new chemical structures from a given molecules, using transformation rules extracted from database of chemical reactions. This approach has one major advantage: information about mechanism of the transformation is saved.

List of possible reactants was extracted from databases of commercially available chemical building blocks, which were stored in reactant database based on our in-house Python-based CGR-DB cartridge. Chemical structures were indexed based on functional groups present in them. Transformation rules were classified into one-, two- and multi-component based on number of molecules required to perform reaction transformation. Based on extracted transformation rules, functional groups that are subjected to transformations were identified.

At the stage of generation of products, system identifies functional groups present in the initial molecule, and extracts from database only those transformation rules that can be applied to a given molecule. If selected transformation rule requires two or more reactants, the second reactant is also selected based on the list of functional groups. The groups absent in starting molecule but required for transformation rule is identified and corresponding molecules are extracted from the database. Having all required molecules reaction product is generated based on the transformation rule. In such a way, algorithm does not try to do unnecessary transformations with unsuitable molecules and it quickly generates new compounds and reactions.

Possibility to generate the whole reaction was also implemented. Algorithm was tested, speed and quality tests were performed.

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The systematic study of the consistency of available experimental thermochemical data for the set of structurally close molecules allows to analyze the accuracy of measured values and predict the properties of unexplored compounds. The standard approach of calculating of the gas-phase enthalpy of formation uses the atomization reactions and requires exceptionally high levels of theory, that is widely available only for small organic compounds. Isodesmic reactions scheme as a concept of balanced reactions (isogyric, isodesmic, homodesmotic) results to better error cancellations and thermochemical predictions of chemical accuracy (<4 kJ/mol) when composite ab initio methods are used. A large number of calculations for different CHON organic compounds by Gaussian-4 method applied isodesmic reactions shows clear advantage in accuracy of theoretical values.

For consistent treatment of data of the group of compounds from one class the high-accurate data on enthalpies of formation of simplest reference species are needed. However, even for the smallest organic CHON compounds (for example methylamine and nitromethane) results of measurement are not always known or there are significant disagreements in published results. So careful prior analysis is required for these molecules.

This limitation can be avoided by considering of thermochemical network of reactions where the known experimental data is optimized in conjunction with data for other structurally close molecules. The simultaneous least-squares solution of a network of isodesmic reactions connecting enthalpies of formation of studied compounds provides the set of self-consistent data. The accuracy of these calculations was shown to be comparable to the accuracy of the experimental data and higher-level calculations.

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Despite the success of Ru-based polyhydride catalysts [1], their replacing by less expensive and less toxic Fe-based analogues can open new ways in applications where these parameters are particularly important [2]. Accordingly, we studied the reactivity of the tetrahydrides for common structural motifs of Fe and Ru precursors (Figure 1) [3] in hydricity and acidity terms, which can be predicted experimentally as well as by computationally [4]. We estimated them as Gibbs free energy of hydrogen species shuttling from metal complex to solvent molecule at D3-TPSS/ma-def2-SVP//ma-def2-TZVP level of theory in conjunction with COSMO-RS corrections for accurate accounting of the solvation effects. Moreover, observed classical and non-classical binding H$_2$ modes [5] studied by QTAIM analysis.

References
Nowadays, chemoinformatics have high variety of solutions for molecular characteristics modeling. The opposite situation is for prediction of reaction characteristics that tend to stay challenging. Such characteristics as reaction rate and equilibrium constants are crucial for calculation of reaction yield, conversion, time etc. Taking into account rising interest to reactions and lack of straightforward modeling schemes for them it was decided to develop workflow for automatic reaction preprocessing and modeling. The designed workflow includes several stages: (i) Condensed Graph of Reaction (CGR) based data curation and analysis, (ii) modeling and validation, (iii) model applicability domain outline.

The first stage are the vital, so it was resulted into standalone CGR based data cleaning procedure. It includes chemical structure standardization, atom-to-atom mapping check, reaction condition verification (based on expert rules, e.g. temperature should be lower than the boiling point and higher than the melting point of solvent, etc.), duplicates filtering with following rate constant or equilibria constant verification. Additional Matched Molecular Pairs approach was proposed for reactions to assess substituent effect on reaction rate. It was shown that this approach can be used to identify reactions that were wrongly attributed to unimolecular substitution mechanism. Different types of fragment descriptor were used in the modeling of the reactivity parameters: Marked Atoms-based, CGR-based and mixture-based descriptors. The models predicting reaction rate of bimolecular substitution (S_N2), elimination (E2), cycloaddition as well as tautomeric equilibrium constants were built and validated. The pitfalls in model validation and applicability domain application will be discussed.

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Chemical and phase equilibrium data for reactive systems are of obvious interest to those who are engaged in designing processes involving reactive mixtures, such as processes combining product synthesis and isolation. One of the most important examples of combined processes in chemical engineering is reactive distillation. However development of new effective methods of organization of reactive distillation process requires the development of an experimental database. Presently, the most studied are chemical and phase equilibrium in systems with the reaction esterification carboxylic acids alcohols. This is due to the practical significance of the production of products this reaction - esters. Nevertheless, some experimental data on combined processes are lacking even for the above systems: the available database should be also augmented for advancing the fundamental theory of complex equilibria [1].

This report presents data on the chemical equilibrium in the systems with the ethyl acetate [2] and ethyl propionate [3] synthesis reaction. Present model calculation of the equilibrium between chemically equilibrium solutions and their vapor at different temperatures for these systems (Fig.1).

![Figure 1. Isotherm–isobar lines on the chemical - equilibrium surface.](image)

References

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ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF
NITROXIDE RADICALS, DIRADICALS AND THEIR COMPLEXES
WITH 3d-METALS: AB INITIO AND DFT STUDY

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One of the most effective approaches to the design and synthesis of
molecule-based magnetic materials is the metal-radical (diradical or
dyrad) approach.[1] Thus there is a growing interest in the diradicals
and their complexes with transition metals.[2]

This report will present and discuss our recent results on the
computational study of the magnetic properties of the nitronyl-nitroxide
(NN) and iminonitroxide (IN) radicals, diradicals and their mono- and
dinuclear complexes with transition metals (Cu(II), Ni(II), Mn(II)). These
paramagnetic molecules and their complexes have been recently
synthesized and characterized using XRD analysis, EPR spectroscopy and
magnetic susceptibility measurements in a wide temperature range.[2-4]
To understand these properties on a molecular level we performed a large
series of calculations using both the DFT and high-level CASSCF/NEVPT2
calculations.

Diradicals under study belong to the non-Kekule structures with both
the disjoint or non-disjoint SOMOs. The DFT calculations predict well
parameters of the EPR spectra (ZFS and HFC constants) of these diradicals,
however, fail to predict singlet-triplet energy splitting for diradicals with
disjoint SOMOs. Thus, high-level calculations (e.g. CASSCF/NEVPT2) are
required in this case. Report will present analysis of a large series of
calculations for diradicals, their transition metal complexes and clusters.

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RFBR (project 18-33-00143).

References
Methane is one of the widely used fuels, thus searching for the new sources of natural gas is an important task. It was shown that significant amount of methane can be obtained from its hydrates. A promising way of methane extraction from hydrates is the replacement of CH$_4$ by other gases, such as N$_2$ and CO$_2$.

In this work Grand Canonical Monte Carlo simulation was used to study the occupancy of SI and SII hydrate frameworks by ternary CH$_4$/CO$_2$/N$_2$ (1:1:1) gas mixture (Fig. 1). Simulation was carried out at 270 K and in the pressure range from 1 to 70 atm.

Figure 1. Snapshots of SI (left) and SII (right) mixed hydrates at 70 atm. 
Hydrate framework – cyan, CO$_2$ – orange and red, N$_2$ – blue.

Total and partial occupancies of hydrate frameworks by gases were obtained. Occupancies of various types of hydrate cavities (large and small) were also calculated. For SI structure the composition of gas in completely filled hydrate is approximately 2:7:1 (CH$_4$/CO$_2$/N$_2$), and for SII structure this ratio is ca. 1:7:1. It was shown that CO$_2$ completely displaces CH$_4$ in large cavities, and N$_2$ competes with CH$_4$ for the small cavities.

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ARE WE OPENING THE DOOR TO A NEW ERA OF MEDICINAL CHEMISTRY OR BEING COLLAPSED TO A CHEMICAL SINGULARITY?

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The paradigm of “drug likeness” dramatically influenced medicinal chemistry community for a long time[1]. In recent years, scientists have empirically found a significant increase in key properties of drugs that have moved structures beyond the rule-of-five[2]. Herein, we show that for the past decade, the number of molecules claimed in patents by Big Pharma companies has dramatically decreased, which may lead to a “chemical singularity”. New compounds with increased 3D complexity are generally larger, slightly more lipophilic and polar. A core difference between this study and recently published papers is that we consider the nature and quality of sp\(^3\)-rich frameworks rather than sp\(^3\) count[3]. We introduce the original descriptor MCE-18, which stands for Medicinal Chemistry Evolution, 2018, and this measure can effectively score molecules by novelty in terms of their cumulative sp\(^3\) complexity[4].

Figure 1. Medicinal Chemistry Evolution described with MCE-18 Score.

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References
Molybdenum disulfide, MoS$_2$, is one of the most intensively investigated sources of inorganic nanotubes. The properties found make MoS$_2$ nanotubes very useful in catalysis, tribology, hydrogen storage, and in electronics for the fabrication of field-effect transistors [1].

*Ab initio* quantum-chemical modelling of structural, phonon, and thermodynamic properties of MoS$_2$ multi-walled nanotubes of real size are practically impossible even using powerful computers. However, such simulation can be performed using the classical force field approach. Several versions of potential fields for MoS$_2$ systems have been proposed before. Further study of these potentials has shown that some of them do not well reproduce such substantial quantities as the unit cell parameters of two most stable bulk crystalline phases $2H$-MoS$_2$ and $3R$-MoS$_2$, and the formation energy of a monolayer from a bulk crystal.

In this work we present a new force field (SWMB-C) fitted to measured and calculated properties of $2H$-MoS$_2$ and $3R$-MoS$_2$ bulk phases, $2H$-MoS$_2$ monolayer, and some single-wall nanotubes. Preliminary calculations show that the proposed field successfully reproduces structural and vibrational properties of single- and double-walled nanotubes obtained by DFT quantum-chemical simulations using CRYSTAL 17 [2] code and hybrid exchange-correlation functional HSE06. The optimization of the geometry of triple-wall nanotubes has also shown that the use of the proposed potential gave physically reliable results. In all considered cases the nanotube binding energy (difference between multi-wall tube and single-wall tubes) estimated by proposed force field agrees well with the quantum-chemical result.

References

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Computer drug design can be divided into two approaches. The first approach is based on the structure of the target protein. But it is not always possible to determine the structure of the protein. The second method is screening for ligand structure – pharmacophore modeling.

Development of an approach to search for an active pharmacophore molecule based on the use of 3D pharmacophore signatures An approach has been proposed to identify active pharmacophore based on a set of active and inactive molecules. The approach is based on the use of the pharmacophore signature algorithm proposed by us, a unique identifier that takes into account the distances between pharmacophore centers and their spatial location. The use of the signature made it possible to calculate the occurrence of pharmacophores in a set of molecules. The active pharmacophore was considered to be one that was found in highly active molecules and was not found in the set of inactive molecules.

The approach was validated on three different datasets: AChE, CYP450 3A4, A2a. Performance of the developed 3D pharmacophore models was comparable to or higher than the performance of a 2D pharmacophore similarity search. The developed 3D ligand-based pharmacophores were able to match important ligand-protein contacts of known ligands in their observed poses taken from PDB protein-ligand complexes.

The developed tool is open-source software, whereas the available free tool for ligand-based.

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A superhalogen $\text{F}@\text{C}_{20}(\text{CN})_{20}$, named $\text{X}$, was designed on DFT and DLPNO-CCSD(T) levels of theory. Some of its derivatives were considered: fluorine superhalogenide $\text{FX}$, superhalogen dimer $\text{X}_2$, hyperhalogen $\text{BX}_4$ and superacid $\text{HX}$. The latter is expected to be much stronger acid than fluorocarbon superacid $\text{H}[\text{CHB}_{11}\text{F}_{11}]$. Antimony pentafluoride was suggested as a possible solvent for $\text{HX}$ to attest its strength. Both $\text{HX}$ acid and $\text{X}^-$ anion were predicted to be thermodynamically stable, while neutral $\text{X}$ radical is expected to have only kinetic stability at low temperatures. Various ways of possible improvements to superhalogenic structures were investigated. The instability of some earlier-claimed superacids of record strength was established. [1]

![Figure 1. A fluorine atom is encapsulated into a dodecahedrane cage decorated with twenty cyano groups. The resulting superhalogen has outstanding calculated electron affinity of 10.8 eV, forming a very non-nucleophilic anion of $I_h$ symmetry with calculated gas-phase basicity of just 208 kcal/mol.](image)

References

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Nowadays chemists all around the globe try to solve actual environmental problems. Particularly, there are issues of reducing emissions of different volatile compounds, improving the technology of production energy from renewable sources and water purification. Deep eutectic solvents (DESs) are able to be the new generation of “green solvents”, due to its biocompatibility, biodegradability and sustainability. DES is a eutectic mixture composed of two (or three) high-melting point pure components at given stoichiometry and having a much lower melting point in comparison with parent compounds. These solvents are characterized by pronounced hydrogen bond interactions. According to recent researches [1], DESs can replace commonly used organic solvents as extractants for separation of azeotropic mixtures formed by alcohol and ester in esterification reaction, which has a broad application in chemistry. In this contribution we continue the investigation of liquid-liquid equilibrium (LLE) data in DESs choline chloride – dibasic carboxylic acids in alcohol-ester systems [2,3]. Herein we consider the ability to separate mixtures of alcohols with its propanoate esters (ethyl propanoate, n-propyl propanoate, n-butyl propanoate) using choline chloride – urea and choline chloride — glycerol deep eutectic solvents. Tie-lines were obtained at temperatures 293.15 K and 313.15 K and atmospheric pressure. The compositions of coexisting organic and DES phases are determined by \(^1\)H NMR-spectroscopy. The extraction performance was characterized with distribution coefficients and values of selectivity for used alcohols. NRTL equation was used for LLE data correlation.

References

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PARAMETRIZATION OF PHOSPHINE LIGANDS TO REVEAL AN EXPLANATION OF SELECTIVITY IN HYDROSILYLATION REACTION OF PLATINUM COMPLEXES

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A series of platinum(0) dialkylbiarylphosphine complexes with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) were synthesized with 72-96% yield and structurally characterized using NMR, IR and XRD. Prepared complexes found to be efficient catalysts in hydrosilylation reaction between phenylacetylene and diphenylsilane in mild conditions and in cross-linking process of PDMS. The ligand set was based on commercially available XPhos, JohnPhos and SPhos and their tailored derivatives and in total contained 7 ligands. These catalysts sufficiently increased the selectivity of β-(E) isomer formation up to 98% with increasing of total yield up to 95%. The structural parameters were extracted from both XRD structures and optimized phosphine oxide derived template structures. Parameters were set as percent buried volume, sterimol values, and percent buried volume values of phosphines in 4 quadrants. Constructed library of complexes allow to include other types of ligands with the same structural scaffold for further optimization of hydrosilylation processes and study QSPR for selectivity and activity of homogeneous catalysts in Si-H activation processes.

For complex 1a platinum(0)-ortho carbon atom from aryl group distance averages 3.204 Å platinum(0)-ipso carbon distance was 3.293 Å, these values are less than the sum of platinum and carbon Van der Waals radii (3.57 Å) [1]. The same effect, when d(metal-Cortho) is quite shorter than d(metal-Cipso) observed in palladium (0) diphosphine complexes [18], in contrast to gold(I) complexes of JohnPhos [2] which prefers interactions with ipso atom rather than ortho, preferred ipso-coordination also occurs in allylpalladium complexes of dialkylbiarylphosphines with formation of strong Pd-Cipso bond, as it seems from bond length varying from 2.3 to 2.5 Å which refers to monohapto coordination of palladium to benzene ring [3]. Estimation of hapticity for Pt-arene interaction in 1a using Kochi and co-workers proposed equation [4] equation gave hapticity value of x=1.68, this is comparable with gold(I) complexes with x in range 1.55-1.95.


Figure 1. (i) Chemical structure of part of the crystallographically determined complex 1, used in the calculation of buried volume, 34.9% $V_{\text{bur}}$. (ii) Chemical structure of the crystallographically determined complex 2, 45.0% $V_{\text{bur}}$. 
Enhancement of discovery speed in synthetic chemistry has led recently to accumulation of big amount of data. It opened the door for applications of big data analytics and data mining technologies (including artificial intelligence approaches) in synthetic chemistry [1]. We will review four applications: synthesis design, selectivity prediction, reaction kinetics and condition prediction. Condensed Graph of Reaction [2] is a cornerstone of the developed methodologies.

Two main approaches to synthesis design will be considered: older, based on manual rule coding, and newer, based on machine learning application. Machine learning classification algorithms can be applied to predict reaction selectivity, which will be shown on Markovnikov/antiMarkovnikov addition reactions. The importance of substrate structure, electrophile/nucleophile and reactions condition will be demonstrated.

Regression algorithms of machine learning can be naturally applied to predict reaction rate and equilibrium constants. It will be shown how structure of reactants and products, solvent and physical conditions can be encoded in descriptor vector used for modeling.

Assessment of optimal reaction conditions can be effectively solved using ranking algorithms, whose task is to rank applicable conditions as high as possible.

In such a way, despite synthetic chemistry introduce rather new challenges to chemoinformatics and artificial intelligence, there are quite universal approaches to address them.

References

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Formation of micelles and stability of the spatial structure of proteins, as well as a number of other phenomena in aqueous solutions are governed by the hydrophobic effect. Experimental data show that such phenomena are typical not only for water. The hydrophobic effect is a particular case of a more general phenomenon, the solvophobic effects. In the studies of solvation properties, the concept of cavity formation is often used. Unlike water, for which the thermodynamics functions of cavity formation have been extensively analyzed, there were almost no studies of the cavity formation process in other solvents exhibiting solvophobic effects. In this work, we calculated the thermodynamic functions of cavity formation in a number of models of individual solvents using molecular dynamics trajectories (NPT-ensemble). The Gibbs free energy of cavity formation $\Delta_{\text{cav}} G$ was calculated from the probability of existence of a cavity of certain radius at the random point of simulation cell. For probability calculation, 10000 configurations were chosen from 10 ns-long trajectory. For each configuration, $10^5$ random points of space were selected. The enthalpy of cavity formation $\Delta_{\text{cav}} H$ was determined from the temperature dependence of $\Delta_{\text{cav}} G$. The calculation showed that $\Delta_{\text{cav}} G$ increases in the solvent series hexane $\approx$ acetone $\approx$ benzene $\approx$ propylene glycol $\approx$ ethylene glycol $<$ formamide $<$ glycerol $<$ water $<$ hydrazine, which generally corresponds to the order of increase in the Gibbs energy of solvation of inert gases. The enthalpies and entropies of solvation processes of inert gases and cavity formation also change in the same order. The link between the solvophobic effects and thermodynamics of the process of cavity formation is clearly seen on the plots in coordinates $\Delta_{\text{cav}} G$ – $\Delta_{\text{cav}} H$. For solvents that do not exhibit solvophobic effects (hexane, benzene, acetone, THF, acetonitrile), the lines representing relationships between $\Delta_{\text{cav}} G$ and $\Delta_{\text{cav}} H$ for the cavities with different sizes lie parallel to each other at a relatively short distance. For the solvents exhibiting solvophobic effects, similar lines on the plot lie much higher, and their slope is larger. Comparison of positions of various solvents on these graphs for a cavity of the same size shows that solvophobic effects are weakening in the series water $>$ glycerol $>$ formamide $>$ ethylene glycol $>$ hydrazine $>$ propylene glycol, dimethylformamide, which qualitatively corresponds to the results of experimental studies of these effects. 

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Colchicine (Figure 1) is the main representative of the family of colchicine alkaloids, which has a unique biological property to bind to the special fragment of the tubulin macromolecule (colchicine site), preventing the formation of microtubules and, as a consequence, the mitosis of tumor cells. Because of the high nonspecific toxicity, colchicine cannot be used in the treatment of cancer. Therefore, one of the main tasks of medicinal chemistry is the search for and synthesis of molecules similar to colchicine and possessing higher antitumor activity.

To assess the biological activity of colchicine analogues, we studied the coordination ability of more than 30 [2H, 3H]oxepinoallocolchicinoids to the colchicine site of tubulin using the method of molecular docking. All calculations were performed with the Autodock 4.2 program [1] using the AutoGrid software to create a docking area and the MGLTools 1.5.6 shell for initial data preparation and visualization. Each docking run was carried out using the genetic algorithm LGA (200 conformations, 25000000 calculations per each conformation). The α- and β-subunits of the stathmin-like domain 1SA0.pdb [2] were taken as the source protein structure. The geometry of allocolchicinoid molecules was optimized using Gaussian 03 [3] by DFT at the B3LYP/6-31G(d,p) theory level. The highest binding energies were found for colchicinoids 1, 2, 3, 4 and 5 (Figure 2) and ranged from 9.42 kcal/mol (5) to 9.98 kcal/mol (1). These compounds are synthesized, their structure is confirmed by the method of 1H and 13C NMR spectroscopy. At the moment, their activity is being investigated by biological methods.

References
Quantitative structure-property relationship (QSPR) modeling mathematically connects the structure of a molecule formalized in a set of descriptors with its physicochemical properties [1]. QSPR approach was successfully employed for the prediction of metal-ligand interactions in liquid extraction processes [2] and studies of metal toxicity [3]. The response of polymeric membrane potentiometric sensors is also based on metal-ligand interactions. Therefore, the application of QSPR modeling to develop a relationship between the ligand structure and electrochemical behavior of the corresponding polymeric sensor membrane could significantly facilitate the development of sensors with desired properties and save the resources required for the electrochemical characterization of new ionophores.

In this work, the feasibility of QSPR modeling was studied in the prediction of the potentiometric Mg/Ca selectivity of Mg-selective electrodes based on the ionophore structure. The dataset was created using literature data on various lipophilic di- and triamide magnesium ionophores with selectivity constants determined by the separate solution method.

The ISIDA/QSPR program package [4] was used for modeling and prediction with multiple linear regression as a machine learning method and substructural molecular fragments descriptors as independent variables. The evaluation of the model predictive performance was performed with 20-fold external cross-validation. The coefficients of determination were 0.95 and 0.63 for calibration and test sets, respectively, showing good promise for reliable prediction of sensor properties based on the ionophore structure.

References

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Molecular logic gates (MLGs) are molecules that implement logic operations. Nowadays, they can detect ions in a living cell[1]. It is expected that in the next two decades autonomous therapeutic systems based on MLGs will come into practice[2]. Such systems should have suitable computing capabilities. However, “quantum problems” have stalled development the system[3]. Guliev was able to connect two gates using energy transfer like a signal[4]. The goal of this study is to discover suitability of electron transfer as a signal in a large logic system.

The model logic system was based on TTF moieties linked as a chain. The terminal moiety was modified to alter HOMO and LUMO energies.

It was proposed that an electron in such system moves together with a hole, as an exciton in a semiconductor. The process is ongoing while exciton recombination is forbidden - more specifically, the electron cannot transfer from an excited state to a ground state. A hypothesis is right only if a transfer rate is greater than a recombination rate. We used Marcus model to evaluate rates[5]. Parameters were calculated by MCSCF method in Gamess[6]. A basis is 6-31G(d) with SBKJC, an active space is (8,8). Radiative transition was calculated by CASSCF, 6-31G(d), (8,8).

The calculated transfer rate is $3.59 \times 10^9$ sec$^{-1}$, while the recombination rate is less than $2.45 \times 10^7$ sec$^{-1}$. The exciton transfers in several steps. In the first phase, the exciton is located on the first moiety. Then it spreads over the entire molecule. Then the exciton finally transfers to the second moiety. Exciton transfer is preferable to electron transfer because needs less energy.

References
Multicomponent mixtures and the examination of mutual solubility of their components attract steady interest of scientists nowadays, because of the fact that information about phase equilibria in such systems is demanded not only for fundamental studies but for modern industry. Moreover, predicting of liquid-liquid equilibria (LLE) in these systems is one of the main tasks of scientific basic research. That is why both the experimental obtaining of solubility data and development of different approaches to description of phase equilibria are relevant today. Experimental part of our investigation includes studying of mutual solubility in ternary mixtures acetic acid - amyl acetate - water, acetic acid - amyl alcohol - water, amyl alcohol - amyl acetate - water at 318.15K and atmospheric pressure. During the theoretical study an semiempirical equation was derived, that can describe LLE in ternary systems with one splitting subsystem based on solubility data for splitting binary subsystem. The equation was used to describe phase equilibria in systems that have already been studied at present, such as mixtures acetic acid - ester - water, acetic acid - alcohol – water [1-4]. The results, obtained by using this equation, were compared with widely used model describing LLE - UNIFAC and NRTL model for those mixtures.

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References
CALCULATION OF VAPOR PRESSURE USING EXCESS MOLAR ENTHALPY OF BINARY MIXTURES OF NON-ELECTROLYTES

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Studies of liquid vapor equilibrium is largely used for optimization of various chemical and physical processes, in particular, for extracting and separating elements of mixtures. As part of systematic studies from NRNU MEPhI's chemistry department, cluster model equation, connecting vapor pressure of a solvent and some excessive properties with liquid phase composition has been justified before [1]. This model is applicable to binary solutions of completely miscible nonelectrolytes, showing positive deviations from Raul't's law and nonideality of them is mainly from association of one of its components.

Using mixes of aliphatic alcohols with alkyl halides [2] as an example, the objective of modelling vapor pressure of a solvent above a solution with concentration dependence of molar excess enthalpy with fixed temperature. Initial data for the task is concentration dependence of molar excess enthalpy with fixed temperature. Because multitude of parameters, describing dependency of vapor pressure of a solvent above a solution, is a subset of parameters of the equation, describing molar excess enthalpy, it is possible to directly substitute solution of parameter identification task in a equation, describing vapor pressure of a solvent above a solution.

Modelling has been done via minimising of RMS error function. As a consequence of the fact that there are a lot of approximately the same local minima, the objective was completed via clusterization. Mass center of the most dense cluster was added to the equation, describing dependency of vapor pressure of a solvent above a solution. Alcohol association was assumed. For 1-bromobutane + 1-butanol, 2-methyl - 2-propanol systems, solutions were obtained, describing vapor pressure of a solvent with a relative error no more than 10%.

References


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We used an integrated approach to reveal fine changes in the surface–normal structure of DMPS monolayers at the air/lipid/water interface occurring during the monolayer compression. We performed MD simulations at several points (circles, Fig. 1) of monolayer compression, validating calculated electron density profiles to those reconstructed from X-ray reflectivity data [1]. From MD simulations, we found that the extrusion of water molecules from lipid headgroup region is responsible for Volta potential changes during monolayer transition (Fig. 1, red curve).

Figure 1. Compression diagrams of the DMPS: surface pressure (black) and Volta potential (red) are plotted against area-per-lipid. Circles marks the area-per-lipid values used in MD simulations.

References

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One of the most prospective areas of the application of reverse micelles (RMs) is biochemistry. [1] In particular, RMs are used as biological extractors and bioreactors that can solubilize proteins and enzymes into a water aggregate surrounded by an organic medium. Many researchers studied biological properties of RMs and pointed out that some physical and chemical factors like pH and ionic strength have the extensive influence on extraction processes. [2] The sodium chloride increases ionic strength inside the water pool of the RM. In this work, we used molecular dynamics simulations to find how the electrical potential and dipole moment of RMs depend on the presence of salt and its concentration.

Figure 1. The snapshot of the AOT reverse micelle in isooctane.

References
Halogen bond (XB) is one of the most abundant non-covalent interactions, which can be formed by electron donors and halogen-containing (Cl, Br, I, in some cases F and At) molecules and ions, in which halogen atom is bonded to an electron-withdrawing group. Therefore, halogen atom has an electron poor region, so-called σ-hole, due to which it acts as an electron density acceptor (i.e. halogen donor). Various molecules, ions and individual atoms (e.g. Hal, O, S, Se, N etc.) can act as electron-donating halogen bond acceptors.

Halogen bonds can be observed in solids, in solution and in gas phase. They play an important role in catalysis, drug design, crystal engineering and design of new materials with various useful properties (e.g. luminescent emitters). Halogen bonds are usually detected by their geometric (valence angles and bond lengths) or energetic characteristics. While geometric parameters can be rather straightforwardly determined for single crystals by X-Ray analysis, complexation energy is notoriously hard to determine, especially in other media (liquids and solutions, where the information on interatomic distances is absent) and especially for intramolecular halogen bonds (where the complexation energy needs an additional definition). Besides, it is desirable to design tools for prediction of the complex’s characteristics based on the electronic properties of halogen donor molecules.

In this quantum-chemical work we consider a series of more than 100 halogen bond donors (F-, Cl-, Br-, I- and At-containing) and their complexes with (CH₃)₃PO as a probe halogen bond acceptor. All calculations were performed in vacuum at the DFT level of theory using Def2-TZVPPD basis set and hybrid functional M06-2X, which is one of the most effective functionals for the study of non-covalent interactions.

Our first goal is to evaluate the possibility to use ³¹P NMR chemical shift, δ(³¹P), and P=O stretching vibrational frequency, ν(P=O), as descriptors of halogen bond energy and geometry. Our second goal is to analyze the QTAIM (Quantum Theory of Atoms In Molecules) parameters at the halogen bond critical point (3; –1) in order to construct correlations that would allow one to use topological analysis of the electron density in order to predict the energy and geometry of O···XR halogen bonds.

This work was supported by RSF grant 18-13-00050.
Figure 1. Equilibrium structure of halogen-bonded complex of trimethylphosphine oxide (CH$_3$)$_3$PO and trifluoriodomethane CF$_3$I
In this study, the molecular dynamics (MD) simulation of vitamin D receptor (VDR) was performed with the Desmond package of Schrödinger Small-Molecule Drug Discovery Suite. The structure of VDR was obtained by refining 1VD2 crystal structure, which is analogous to 1DB1 from PDB but with higher resolution and less residues missing. First, the validation procedure was done according to the protocol described in [1]. We used a VDR structure, with a peptide derived from TRAP220 coactivator complexed with calcitriol (VD₃). Validation procedure revealed the important role of histidine rotamer states. It is known that the ligand in the binding pocket of VDR should maintain at least six hydrogen bonds: HIS305 and HIS397 with 25-OH, ARG274 and SER237 with 3β-OH, TYR143 and SER278 with 1α-OH [2]. However, after the standard minimization performed by Protein Preparation Wizard (Schrödinger) both HIS305 and HIS397 were in HID conformation. This led to their constant competition for the hydrogen atom in ligand and, consequently, to the formation of extra water bridges inside the binding pocket. This obviously weakened ligand binding to the VDR, thus the solution was to manually change the HIS397 conformation to HIE rotamer with Interactive H-bond Optimizer tool (Schrödinger). After validation procedure had been finished, we ran 18 experimental simulations. For this, VDR has been set up with different motifs from two coactivator peptides (hSRC1 and hPGC1α) and with three ligands (VD₃, Gemini, TX527). The various peptides used from hSRC1 and hPGC1α contain one LXXLL-motif, which interacts with VDR. The final parameters of MD simulations were 300K at 1 bar for 10 ns using the water model TIP3P. The binding energies for all the complexes after MD simulations were calculated using MM-GBSA method. MD simulations showed stabilization of the VDR regions important for allosteric communications and interaction with coactivators such as helices H3, H4-5 and H12.

References
MODELING OF THE EFFECT OF GRAPHENE EDGES ON THE ELECTRON TRANSFER KINETICS

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Using the method of classical molecular dynamics, we have obtained the structure of the electrode/electrolyte interface for various types of surface — a single-layer graphene edge, a multilayer graphene edge, a graphene plane [1-3]. We have obtained the distributions of mass and charge densities in the near-electrode layer, the distribution of the electrostatic potential, and the orientational ordering of the solvent. Also, the kinetics of oxygen adsorption to the model surfaces and the corresponding distributions of the equilibrium concentrations were calculated. Within the framework of the density functional theory, we studied heterogeneous electron transfer from two clusters of graphene with different edge types. Using the Landau-Zener and Marcus theory, the values of electron transfer constants with spatial resolution both along the surface and varying the distance to the surface of the clusters were obtained [4, 5]. The effective electron transfer constants were calculated, taking into account the equilibrium distribution of the oxygen molecules in the near-electrode region. The edge of graphene showed a less ordered interface structure with less dense layers of electrolyte compared with the plane of graphite. As a result, the edge of both single and multilayer graphene is an effective surface for adsorption of the oxygen molecules. Also, the accelerated kinetics of the electron transport from the zigzag graphene edge was found in comparison with the graphene plane. At the same time, the armchair graphene edge does not show such electrocatalytic activity.

References

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PHASE EQUILIBRIUM IN THE QUATERNARY SYSTEM WITH THE ESTERIFICATION REACTION OF N-PROPYL PROPIONATE: EXPERIMENTAL AND SIMULATED BY NRTL MODEL DATA

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The relevance of phase equilibria studying of liquid-phase systems is associated with the extraction processes. Classic examples of extractants are the innocuous esters of carboxylic acids. The advantage of the non-toxic n-propyl propionate discussed in this study is its low cost and dissolving ability of a wide range of compounds. Thus, it can be a full-fledged replacement for deficient butyl acrylate [1]. However, data on the thermodynamic behavior of systems involving such ethers as biodegradable n-propyl propionate which are necessary for optimization the technology of synthesis of organic substances, are practically absent.

The aim of the work is a detailed experimental study of phase equilibria in a multicomponent reaction system with n-propyl propionate (fig. 1) and using the NRTL [2] model to simulate the liquid-liquid equilibria data.

![Figure 1. The surface of phase equilibrium in the system propionic acid - n-propyl alcohol - n-propyl propionate - water at 303.15 K.](image)

References

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New insights into non-classic phenomena in cross-coupling reactions are often obtained via DFT computations; understanding phenomena as formation of M(0) nanoparticles or M(II) oligomers \textit{in situ}, metal-metal cooperativity, redox processes, and processes involving radical species can direct design of new catalysts [1]. In Pd systems, dynamic interconversions of Pd nanoparticles and Pd complexes often determine the activity [2].

Figure 1. The proposed model of evolution of Pd catalytic systems in reactions that involve ArX oxidative addition. Adapted with permission from Ref. 3.

We have recently proposed a model of interconversions of Pd species in coupling reactions with ArX [3]. The model allowed to determine, which pools of species can form under reaction conditions (Figure 1). In this presentation, we will report results of our DFT modeling of mechanisms of activation and deactivation of Pd catalytic systems in couplings involving ArX.

References
Boron-dipyrromethene dyes (BODIPY) are of great interest nowadays mostly due to their valuable optical properties. Nevertheless, no systematic research of optical properties dependence on the structure of a dye has been done yet. So, at first we carried out calculations of electronic spectra of BODIPY derivatives using the available methods and proposed the best method that allows to predict experimental data with high accuracy. Next, using the suggested method, we studied the influence of the nature of the substituent and its position in BODIPY core on the optical spectra of the dye.

All the calculations have been performed with Gaussian program. Accuracy of eight different DFT functionals was analyzed. Solvation effects upon excitation were considered using SMD model in terms of Linear Response (LR) and State Specific (SS) schemes. Eleven BODIPY and aza-BODIPY derivatives with absorption and emission maxima in the range of 490 – 850 nm were considered. Comparison of linear regression coefficients showed that M062X functional is the most accurate for LR-scheme of calculation of absorption and emission spectra, while wB97XD functional is the most accurate for SS-scheme. Model structures with various donor and acceptor groups in different positions of BODIPY core were proposed to evaluate the influence of substituents on optical properties of BODIPY dyes. The calculations of their absorption and emission maxima revealed complex pattern of red- and blue-shifts (Fig.1), nature of this pattern was explained in terms of HOMO and LUMO energies.

The results of this work provide the way for efficient design of BODIPY derivatives with desired properties.

Figure 1. Influence of the substituents on absorption and emission maxima.
BENCHMARKING ANALYSIS OF APPLICABILITY DOMAIN DEFINITION: CHEMICAL REACTIONS CASE

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One of the OECD principles for model validation requires clearly defining the Applicability Domain (AD) for the QSAR/QSPR models. This is important since the models provide the reliable predictions only for those objects, that are structurally similar to the training set objects used to build the models. Currently, more and more attention is drawn to chemical reactions as objects of QSAR/QSPR modeling. When building quantitative structure-reactivity relationship (QSRR) models and their applicability domains it is necessary to take into account the structures, conditions and types of chemical reactions.

In this study AD definitions extensively used in QSAR/QSPR studies, their modifications and proposed by us for reactions were benchmarked. In the study more than 10 simple AD definitions, 24 combinations of AD and 2 types of consensus AD approaches were compared. Four criteria (coverage, ability to exclude wrong reaction types, ability to improve model performance and to detect outliers) for assessing quality of model with applicability domain were used. Four data sets of reactions were used for benchmarking study. Some applicability domain definitions requires selection of optimal hyperparameters, for doing that we developed especial procedure that includes both internal and external cross-validation of model and applicability domain.

Generally, most applicability domain definition approaches are quite good in ability to exclude wrong reaction type and to improve model’s performance. Combination AD approaches with fragment control or reaction type control led to much better model performances than single AD definition approaches. Based on ranking we selected optimal AD definition approaches suitable for reactions.

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EXTENDED ISING MODEL FOR SOLID SOLUTIONS OF LaFeO$_3$ IN LaGaO$_3$ AND LaAlO$_3$

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Perovskite-type oxides have been widely investigated for the last decades for their potential applications as advanced materials for solid oxide fuel cells, sensors, electrochemical devices, etc. The experimental studies [1] indicate the existence of Fe-clusters with the ferromagnetic exchange in LaGaO$_3$-LaFeO$_3$ solid solutions, whereas they are not observed in LaAlO$_3$-LaFeO$_3$ system. In our work, we focus on $ab$ initio modeling of the magnetic properties of these solid solutions.

Calculations were performed with CRYSTAL14 computer code [2]. The solid solutions were presented as an average over a set of configurations with distributions of different species over a given set of atomic positions. We treated all symmetry non-equivalent configurations, including not only all the possible distributions of Fe-atoms on the $p$-metal positions (Ga or Al) but also the different spin distribution of the Fe-atoms. Statistical weights and probabilities were estimated for each configuration within the canonical ensemble. Magnetic moments were calculated considering these probabilities.

We used a simple Ising model to describe the contribution of the magnetic exchange to the total configuration energy of considered structures. However, the accounting of the magnetic contribution was not sufficient to explain the differences between the two solid solutions. To account for non-magnetic contributions, a new «extended Ising model» has been proposed, using the lattice approach based on the concept of interchange energy. Two model parameters (the magnetic coupling constant and interchange energy) were fitted to the calculated energies of configurations for both LaGaO$_3$-LaFeO$_3$ and LaAlO$_3$-LaFeO$_3$ solutions.

The extended Ising model confirmed the benefit of Fe-clustering in doped lanthanum gallate against aluminate. The different sign of the estimated interchange energy enables to explain the reasons for such differences.

References

Acknowledgements. The authors are grateful to the Computer Center of St. Petersburg State University for providing the high-performance computations.
Experimental study of phase equilibrium in systems involving ethyl propionate is of enormous importance for both practical and theoretical purposes. Ethyl propionate is one of the most used in the production of esters. It is used in paint and varnish production, the perfumery and food industry and so on. Therefore, to optimize and modernize production processes, knowledge of the physicochemical properties of ethyl propionate is necessary. In addition to the experimental method of studying phase equilibrium, computational methods are also used to predict liquid-liquid equilibrium.

This work is devoted to the prediction of phase equilibrium in a liquid-phase splitting system propionic acid - ethyl alcohol - ethyl propionate - water at 20 and 30°C using the thermodynamic model NRTL. The non-random two liquid (NRTL) model is based on the concept of a local composition, namely the difference in concentrations near the molecule and in the depth of the solution. This difference is due to different energies of interactions of molecules of the same type ($U_{ii}$) and molecules of a different type ($U_{ij}$). Based on this concept, an equation was obtained that relates the activity coefficient of one component to the energy parameters of all system components (Fig. 1).

To verify that the model is suitable for predicting the phase equilibrium of this system, the calculated data were compared with the experimental ones and the error was calculated.

The data obtained in the future will be used as the basis for the development and modernization of ethyl propionate production processes.

\[
\ln y_i = \frac{\sum_{j=1}^{n} \tau_{ij} c_{ij} x_j}{\sum_{j=1}^{n} c_{ij} x_j} + \sum_{j=1}^{n} \left( \frac{\sum_{k=1}^{n} \tau_{ij} c_{ij} x_k}{\sum_{k=1}^{n} c_{ij} x_k} \right)
\]

\[
\tau_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad \tau_{ij} = \frac{\Delta g_{ij}}{RT} = \frac{g_{ij} - g_{jj}}{RT}
\]

Figure 1. NRTL equation

Acknowledgements. Maria Toikka is grateful to Russian Foundation of Basic Research for the support of this study (RFBR project 18-33-20138)
THE STRUCTURE OF GRAPHITE OXIDE AND THE ROLE OF WATER

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Graphite oxide as a promising material is studied widely in experimental field. Structure of graphite oxide remains still unknown exactly. Different methods of synthesis lead to different kinds of material specimens with different composition. A lot of models were suggested since 1959. Nowadays, Lerf-Klinowski model [1] is commonly used. It assumes the existence of hydroxyl and epoxy groups located close to each other in the inner part of carbon layers, and carboxyl and hydroxyl groups at the edges. Based on comparative analysis of theoretical and experimental IR spectra, it was suggested [2] that lactones can also be present in graphite oxide layers.

The model of graphite oxide structure can further be extended based on a more thorough analysis of theoretical IR spectra. The effect of water on IR spectra and its probable interaction with functional groups in graphite oxide layers are studied with a particular attention to the properties of graphite oxide as an individual material and a membrane, through which gases like He, H₂, or CO₂ do not penetrate in a dry state, but do in a wet state [3].

Nonempirical simulations were carried out for clusters of a general composition CₓHₙ(OH)ᵢ(OH)ₓ(COOH)ₓ(SO₃H)ₘ(NO₂)ₙ(H₂O)ₚ, and theoretical IR spectra were constructed. In calculations [4], density functional method with B3LYP hybrid exchange-correlation functional and extended Gaussian basis set was used: DFT/B3LYP/6-31G(d,p). For reliable interpretation, experimental IR spectra, X-ray diffraction patterns, and X-ray photoelectron spectra were recorded for graphite oxide specimens synthesized by Tour method (I-GO) [4].

References
Today, it is a matter of routine to simulate the Raman spectra of organic compounds by DFT calculations of a single molecule in vacuum, but this method is hardly applicable for predicting the surface enhanced Raman scattering (SERS) spectra, which usually differ sharply from the ordinary Raman profiles. To date, our research team has collected a lot of high quality vibrational data (SERS, Raman and IR spectra) for the stilbene derivatives [1]. In this work, we present the results of DFT simulations the vibrational spectra of these compounds for the molecules coordinated to the small silver clusters. In order to find the best model system we studied a dependence of simulated Raman spectrum on cluster size, solvent accounting and charge localization using a similar level of theory, which was applied in the analogous studies [2]. The obtained results show the applicability of this approach.

![Figure 1. Top to down: calculated Raman spectra of 4,4'-diaminostilbene (DAS), DAS*Ag$_6$ complex and experimental SERS spectrum of DAS.](image)

References

Acknowledgements. The Russian Science Foundation (grant № 17-73-10209) supported this work. All experimental spectra were collected in the Center for Optical and Laser Materials Research of SPbU. The DFT calculations were performed in the Computing Centre of SPbU.
The study of the liquid-liquid equilibrium (LLE) in systems containing biofuel components is of great interest in the production of alternative energy sources. However, biofuel production is inefficient because it needs an excessive amount of raw materials. Nevertheless, the organization of production can be optimized with the help of scientifically sound methods and taking into account basic thermodynamic and kinetic positions [1]. In addition, prediction of LLE in heterogeneous systems also can be useful for optimization biofuel production.

The objects of investigation were chosen ternary splitting systems including components of liquid biofuel: acetic acid – n-butanol – water, acetic acid – n-butyl acetate – water, n-butanol – n-butyl acetate – water.

The purpose of this research is prediction of LLE in above mentioned heterogeneous ternary systems by UNIFAC equation. Furthermore, comparison the LLE data modeling by UNIFAC with the experimental data of LLE obtained for the same systems by Gas chromatography method analysis. Experimental data of LLE were obtained in the work [2]. The UNIFAC method (UNIQUAC Functional-group Activity Coefficients) is one of the popular and examined models for describing the thermodynamic properties of heterogeneous systems. The modeling LLE data for ternary systems were presented in triangular phase diagrams.

Calculated LLE data have a good correlation with experimental data from work [2]. It confirms correctness the experiment in work [2] and corroborates reliability of this model.

References

Acknowledgements. Maria Toikka is grateful to Russian Foundation of Basic Research for the support of this study (RFBR project 18-33-20138).
Interest in systems consisting of molten salts is due to their broad application in various fields of industry and chemical sciences. When studying certain characteristics of such systems, it is first necessary to have reliable information about phase diagrams in order to avoid undesirable processes. Therefore, much attention is also directed to the development of theoretical approaches to describe the thermodynamic characteristics and phase equilibria in molten salts.

To carry out correct calculations of phase equilibria in salt systems, polarization interactions between ions must be taken into account. This task is successfully solved using ab initio and molecular dynamic modeling. However, within statistical theory, this problem for molten salts has not been solved so far. Within the statistical theory, task associated with polarization interactions is more conveniently to consider using the thermodynamic perturbation theory (TPT), taking into account more complex polarization interactions based on simple model of charged hard spheres (CHS) that have analytical solutions:

\[
F_{liq} \leq F_0 + \frac{1}{4\pi^2} \sum_{i,j} \sqrt{x_i x_j} \int_0^\infty \left( S_{ij}^0(k) - \delta_{ij} \right) \cdot \varphi_{ij}^1(k) \cdot k^2 \, dk + \frac{\rho}{2} \sum_{i,j} x_i x_j \varphi_{ij}^1(0)
\]

where \( S_{ij}^0(k) \) is the structural factor of the reference system, \( \varphi_{ij}^1(k) \) is the additive to the pair potential, \( F_0 \) is the free energy of the reference system of CHS, and other two terms describe the polarization additive to the free energy.

Within this variational TPT-approach, the authors carried out calculations of the polarization contribution to the energies of the molten alkali halides. On this basis, the statistical-thermodynamic model is constructed to calculate phase equilibria in salt systems. In the report, this model will be presented on the example of calculating phase equilibria and thermodynamic properties in halide systems of sodium and cesium.

Acknowledgements. The reported study was funded by RFBR according to the research project № 18-33-01234.
VALIDATION OF LIGAND DOCKING ASSAY RESULTS APPLYING ADVANCED DFT CALCULATIONS AND IMPLICIT COSMO-RS SOLVENT MODEL CORRECTION

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According to the theory of the transition state, the energy of the activation barrier can be represented as the sum of the energies of the conformational transformations of the reactant molecules and the repulsion energy between the reactant molecules. The calculation of the energy of the true transition state for large biological systems can only be done by applying extremely costly molecular dynamics modeling methods which are inapplicable for the validation of scanning docking results with a large number of ligands. From the thermodynamics point of view, the possibility of chemical reactions and the stability of conformers is described by the Gibbs free energy functions (see Fig. 1). We translated the ligand molecule into a conformational state corresponding to the docking result geometry ($\Delta E_1$), the energy difference between this state and the initial one is indirectly related to the activation barrier of the observed reaction. $\Delta E_2$ corresponds to the energy of dispersion interactions and conformational changes in the protein binding pocket and could not be accounted due to the margin of error of the employed methods. $\Delta E_3$ is the ligand binding (docking) energy. Neglecting the value of $\Delta E_2$, we concluded that the described chemical reaction could run only if $\Delta E_1 + \Delta E_3 < 0$.

Figure 1. Possible ways of protein-ligand interaction reaction

We suggested that the activity of ligand molecules may be related to their form of existence in aqueous solution, which is correlated with the significant flexibility of the studied ligand structures and the intramolecular hydrogen bonds formation possibility. The optimization of some large and flexible structures by DFT methods could be extremely computationally expensive. To narrow down the number of possible conformations, the search
for conformers based on the molecular mechanic's approach and geometry optimization based on the PM6 semi-empirical method was consistently applied. For DFT simulations, the composite RI-D3-B97-3c method [1] was used. Obtained structures were used in docking assays and DFT simulations. The energies of the most profitable ligand conformations obtained by DFT calculations were taken as reference values for the subsequent comparison with the docking energies. On the next step, ligand conformations, obtained after successful docking assays, were optimized using the DFT method. The reaction energy in the gas phase was calculated as the sum of the energies of the conformational transformation and the protein-ligand interaction. To account the influence of an aqueous solution on the ligand energy, the implicit solvent model COSMO-RS [2] was applied.

The described pipeline could be extremely useful for complex pharmacological search especially in combination with the QSAR approach. It was successfully applied in structural bioinformatics project, related to the nodulation (Nod) factors recognition mechanism by *Pisum sativum* protein heterodimer. Calculated solvation energies clearly show the large effect of water on the ligand conformational stability, which leads to a significant stabilization of the desired Nod factors in protein dimer and can serve as indirect evidence of the docking results. On the contrary, the results obtained for inappropriate Nod factors indicated a sufficient energy barrier that can impede the protein-ligand interaction.

References:
VESICLES AND STOMATOSOMES SELF-ASSEMBLED IN MIXED SURFACTANT SOLUTIONS: MOLECULAR THERMODYNAMIC MODELING

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Perforations which are known to spontaneously occur in flat bilayers, lamellae, and vesicles are important both for living matter and technology. Studying regularities of pore formation in a vesicle membrane seems to be promising as it may shed light on a mechanism of rupturing of cell membranes. Furthermore, vesicles are used in micellar catalysis and for synthesis of nanoparticles. Up to now, stable perforated lamellae as well as perforated vesicles, called stomatosomes, have been detected by SANS or cryo-TEM in a diversity of amphiphilic solutions including lipids, block-copolymers, surfactants and their mixtures [1 - 3]. A reliable theory of pore formation in self-assembling membranes is needed.

The classical molecular thermodynamic model [4, 5] is used to predict the most stable aggregate's shape and size basing on the aggregate's molecular parameters and temperature. In the present work we propose an extension to this model describing formation of stable vesicles and stomatosomes using our previous result for the mechanism of pore formation in lamellae [6]. We chose catanionic surfactant mixture C_{16}TAB (cetyltrimethylammonium bromide) - SOS (sodium octyl sulfate) in aqueous salt solution as a model system. To calculate an electrostatic term into the free energy of aggregation we derived an equation for electrostatic potential which allows inner part of the vesicle not to be electrically neutral. We obtained the equation showing that transmembrane potential depends on the geometrical parameters of the vesicle, compositions of both vesicle leaflets and the ratio of electrical permittivities in the solution and hydrocarbon membrane.

As a result, our model predicts temperature and solution salinity which stabilize vesicles or stomatosomes as well as optimal geometrical parameters and compositions of these aggregates. The obtained results are in agreement with experimental data for mixed surfactants [7].

References

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INTERACTION OF TAXIFOLIN AND P-GLYCOPROTEIN IN SILICO
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Taxifolin (TAX) exhibits pleiotropic effects including anti-oxidant activity [1]. This compound produced industrially as an active pharmaceutical ingredient, however it has a low bioavailability. Recently 191 metabolites of TAX were identified [2]. P-glycoprotein (P-gp) is multidrug transporter. The study objective is to investigate the ability of interaction TAX and its metabolites with P-gp via molecular docking. The structure of P-gp (6C0V) was used as a biotarget [3]. MarvinSketch 19.8 (ChemAxon, Hungary), AutoDock Tools 1.5.6 (TSRI, USA), AutoDock Vina 1.1.2 (TSRI, USA) [4] were used. The results were validated by redocking of the native ATP. Figure 1 demonstrates the docking TAX in ATPase site. Figure 2 shows a positive correlation between the molecular weight of ligands and this affinity energy. TAX and ATP bound with P-gp via the same amino acids residues, also they have a similar binding energy (9,8 kcal/mol and 9,9 kcal/mol respectively). TAX demonstrated good affinity energy, so the design of new TAX forms with higher bioavailability may be useful for new complex cancer therapy development.

Figure 1. The types of interactions between TAX and P-gp.

Figure 2. Comparable analysis of docking results.

References

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The discovery of the argonium ArH\(^+\) compound in the spectrum of the Crab nebula [1], and the recent detection of the molecular cation HeH\(^+\) [2], stimulated the investigations for other compounds of noble gases, which supposedly may exist in the interstellar medium (ISM). The purpose of the study of this work were complexes of the general formula Rg\(_2\)H\(^+\) (Rg = He, Ne, Ar), since it is known that complexes of this type have bright vibrational modes corresponding to the displacement of the proton between the atoms of the noble gases, which somewhat simplifies the task of detecting these molecular cations in ISM.

This work is dedicated to a quantum-chemical study of the mentioned molecular cations, including, preliminary geometry optimization, calculation frequencies of complexes. Further steps were aimed at obtaining the potential energy surface (PES) of the presented triatomic molecules. Using the resulted PES, also were calculated energy levels and rovibrational spectra. The calculations presented in the work were carried out using the method of coupled clusters of the CCSD(T) level. As previously assumed, the investigated complexes are stable and have a linear structure, corresponding to the available literary data [3].

It is expected that the results obtained in this work, in particular, the calculated frequencies of vibrational-rotational transitions, will be of use to eliminate the existing shortage of experimental information about the spectra of cations, and may also contribute to their identification in the ISM.

References
Metformin (N,N-dimethylbiguanide, BG) is an antidiabetic drug. The structure and energy (in Hartree units) of possible tautomeric forms of the N,N-dimethylbiguanide (BG) molecule are calculated using the Jaguar program using the DFT/B3LYP-D3/6-31G**++ method. Tautomeric forms were obtained using the Epik program. Typically, the structure of the BG molecule is depicted as Cis 1 or Cis 2. The calculations have shown that the Tauto 1 form, which is in equilibrium with the Trans form, has the minimum energy. The calculations explain the existence of BG in the form of monohydrochloride (protonation of the form of Tauto 1), and not of dihydrochloride (protonation of the form of Cis 1 or Cis 2) and the possibility of the formation of stable BG complex with metal cations (Trans form). The formation of complexes is accompanied in this case by the closure of the chelate cycle.

\[
\begin{align*}
\text{Cis 1} & \quad -432.84958924092 \\
\text{Tauto 1} & \quad -432.86728774376 \\
\text{Trans} & \quad -432.85635091027 \\
\text{Cis 2} & \quad -432.85009933538 \\
\text{Tauto 2} & \quad -432.85772848497 \\
\text{Antitrans} & \quad -432.85094510760
\end{align*}
\]
Presently, a lot of effort is required for associated petroleum gas (APG) utilization [1]. Large volumes of gas are flared due to high dew point temperature which leads to inexpediency of gas transportation to gas processing plants. Using of gas as a fuel to generate electricity comes across certain difficulties as well because of unstable gas composition, detonation risks and coke formation. Thus, a method of gas treatment which would allow obtaining normalized gas mixtures is necessary. Low-temperature steam conversion of light hydrocarbons (LTSC) represents a perspective method of APG treatment. The process occurs at 250-320 °C over Ni-based catalysts and results in increasing methane content. The brutto-reaction is as follows:

$$4C_nH_{2n+2} + 2(n-1)H_2O \rightarrow (3n+1)CH_4 + (n-1)CO_2 \ (n > 1).$$

Process conditions depend on initial gas composition, catalyst activity and gas requirements to be satisfied.

This work represents the results on mathematical simulation of the LTSC process. An array of experimental data on the reaction kinetics was obtained which included effective reactions orders and activation energies. The LTSC of realistic APG over an industrial Ni-based catalyst was simulated using a two-step macrokinetic model suggested. The areas of reaction conditions (GHSV and temperature) which would allow one to obtain normalized gas were determined. The calculations took into account such parameters of the produced gas as dew point temperature, methane number, net calorific value and Wobbe index. The macrokinetic model proposed can be used to predict optimal reaction conditions of the LTSC process for various applications thus being of much importance in terms of actual gas processing.

References

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HYDROGEN BOND AND PROTON TRANSFER IN COMPLEXES OF HOMOCONJUGATED ANIONS OF PHOSPHOROUS-CONTAINING ACIDS

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Carboxylic [1] and phosphoric acids can form different anionic complexes with strong hydrogen bonds. In this work the complexes of homoconjugated anions for phosphinic and phosphoric acids with different substitutes have studied by quantum chemical calculations (DFT method). In complexes with more than one hydrogen bonds there is a cooperativity between these bonds. Thus in complex 1:2 length of hydrogen bonds decrease on 0.07 Å and energy increase on 3.52 kcal/mol per bond than hydrogen bond in complex 1:1 (see Fig.1). As a result $^1$H of bridged protons and $^{31}$P NMR chemical shifts have changed on ~3 ppm and 2 ppm, respectively. In figure 1 in blue, orange and black colors $^1$H and $^{31}$P NMR chemical shifts (ppm) and lengths (Å) of hydrogen bridges are presented, respectively.

Figure 1. Calculated structures of monomers (a), complexes 1:1 (b) and 1:2 (c) of homoconjugate anions of hypophosphorous acid in vacuum.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-13-00050).
Cyclic oligosiloxanes have attracted a great experimental and theoretical interests due to their wide practical usage. Siloxanes are used in various areas of medical, catalytic and synthetic chemistry. Siloxane monomers usually exist as viscous colorless liquids. Thermodynamic properties are important in computational chemistry and high-quantity physical and chemical calculations. Therefore, the joint usage of quantum chemical and X-ray diffraction studies would help to discover interesting dependences.

One of the most commonly used siloxane monomers is octamethylcyclotetrasiloxane (D4) [1]. At the same time, its physical and chemical properties are still poorly understood. To establish the relation between physical properties and crystal structure the series of X-ray experiments at various temperatures were carried out (Figure 1). As a result, the structures of high- and low-temperature phases were established (Figure 2). We performed several MD calculations for the unit cells of D4 at various temperatures to found transition state.

It was found that the phase transition is related to the change of molecular conformation. The driving force of the conformational changes is inharmonic low-frequency vibration of siloxane ring.

References
THEORETICAL ANALYSIS OF BINDING INTERACTION BETWEEN SHORT PEPTIDES AND SOMATOSTATIN RECEPTOR TYPE 2

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Neuroendocrine tumors are characterized by high expression of somatostatin receptors on their surface. For the treatment of such diseases, peptide analogues of the somatostatin hormone are widely used. The lack of peptide hormones is their rapid hydrolysis under the action of protein kinases, therefore the development of shorter somatostatin analogues seems to be an actual task.

In this work we study two short tetra- (P1) and pentapeptide (P2) as potential biological vectors for radiopharmaceuticals (Fig.1), therefore the binding interaction between shorter peptides and somatostatin receptors needs to be shown.

The affinity of the studied peptides to somatostatin receptor type 2 was evaluated using computational methods: homology modeling [1], molecular dynamics simulation [2] and molecular docking [3]. The peptide-receptor binding energies were obtained, and receptor’s amino acids that are responsible for binding were also identified.

Figure 1. Structure of studied tetra- (P1) and pentapeptide (P2).

References

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MULTI-INSTANCE LEARNING FOR PREDICTING PROPERTIES OF MOLECULES

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The development of new drugs, chemicals and materials with desired properties is one of the key tasks of chemistry. Computational chemistry has developed many methods for predicting the properties of compounds. In drug design, the most popular methods for prediction of compound properties are docking, pharmacophore search, similarity search, and QSAR modeling. One of the key limitations of conventional structure-property modeling is the requirement that each molecule has to be represented by a single instance with fixed conformation, protonation state, tautomeric form, etc. However, a molecule is a dynamic object and simultaneously exists in many forms/instances (conformers, protonated states, tautomers, mixtures of stereoisomers, etc) in equilibrium.

To overcome these limitations we propose the methodology based on multi-instance learning (MIL) method. The main idea of the approach is that an object (molecule) can be represented as a set of instances which may simultaneously exist, in our case, different molecular forms, which are encoded by their own vectors of descriptors. The property of the object is associated with one or more instances from the entire set, but it is not known which one. Thus, each object is characterized by a set of instances represented by vectors of descriptors and a single property value. The task is to build a model that finds the correlation between the set of vectors corresponding to the object instances and the property value.

We have developed and implemented the new algorithm for multi-instance learning based on special neural networks that will enable to train regression and classification models on large The MIL approach was compared with classical QSAR techniques based on application of features of 2D molecular descriptors and features of lowest energy 3D structure. We use proposed approach to model the biological activity of chemical compounds. Molecules were represented by several conformations (instances). The model, built on several instances (conformations) within convolutional MIL architecture shows better results than models based on one instance (conformation). The study shows that MIL approach, based on neural networks are very promising for modeling chemical object properties.

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5 section

COST-EFFECTIVE
ANALYTICAL METHODS
Energy Dispersive X-ray Fluorescence (EDXRF) is a nondestructive analytical method which is very important for the determination of elements in a large variety of matrices. The advantages of EDX are simple sample preparation, non-destructivity, multielemental capabilities and short analysis time. Because of that the method has found broad application in material and environmental science, biology, chemistry, industrial process monitoring, etc. Nevertheless, most of the serial production EDX spectrometers cannot provide quantification of the elements with atomic numbers below 11 (sodium). This makes EDX hardly applicable for analysis of organic materials. The EDX spectrum contains not only the fluorescence lines of the elements composing the sample, but also the signal from reflected X-ray tube radiation which consists of deceleration radiation and elastic/inelastic scattering of cathode radiation. The intensity of scattered radiation is influenced by average mass absorption coefficient of the sample, which in turn depends on elemental composition. In this way, scattered radiation can be employed as a source of information on integral properties of the samples as determined by its “average” molecular mass. A general feasibility of studying various light elements through the analysis of scattered radiation was explored in the previous studies but the lack of selectivity was the reason for significant imprecision. In this study 46 samples of various plastics were measured with EDXRF. The resulting spectra were processed with principal component analysis (PCA) in order to explore the clustering of the samples. Moreover, using partial least square (PLS) it was possible to construct predictive models relating EDX signals with the content of organic elements C% and H% and integral physical properties (density, mass per atom and others). The derived performance metrics of the models have shown the general applicability of the approach. The use of redundant chemical information hidden in the scattering spectra can be done through chemometric modeling and can provide for novel interesting opportunities in EDX application.
The development of fast and simple methods for determining thyroxine concentrations is of great interest. Being the main thyroid form of thyroid hormones thyroxine plays an important role in the body. The content of this compound depends on the rate of metabolism, the supply of body tissues with oxygen, the work of the heart. Therefore, it is necessary to control the content of this compound to identify pathology and conduct drug therapy. Voltammetry with chemically modified electrodes (CME) is a promising method of analysis, because it is characterized by high sensitivity and selectivity in the determination of organic compounds.

In the present study the catalytic activity of gold nanoparticles immobilized on the surface of a carbon paste electrode (Au-CPE), bare and modified by single-walled carbon nanotubes (SWCNT) during electrooxidation of thyroxine was studied.

A small signal of thyroxine oxidation is observed on the bare CPE in an alkaline medium. It was found that immobilized gold nanoparticles show catalytic activity during the thyroxine oxidation, which is exhibited in an increase in the oxidation current of the modifier in the presence of the substrate and a decrease in the oxidation potential of the substrate in comparison with the unmodified electrode. The using of the CPE modified by gold nanoparticles immobilized on carbon nanotubes leads to a significant increase of the oxidation signal of thyroxine. It is established that functionalized SWCNT exhibit greater catalytic activity than unfunctionalized SWCNT. Oxidation of thyroxine on the Au-SWCNT-CPE occurs at the potential E 0.65V.

The method of voltammetric determination of thyroxine on Au-SWCNT-CPE is proposed. Calibration graph is linear in the concentration range from 1×10^{-9} to 1×10^{-3} M. The developed method was used to determine thyroxine in drugs.

Acknowledgements. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.
MAGNETIC NANOPARTICLES BASED ON Fe$_3$O$_4$ AS A SORBENT FOR GAS ADSORPTION MICROEXTRACTION: HPLC-UV DETERMINATION OF VOLATILE PHENOLS IN MEAT

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A smoking technology is widely used for the production and preservation of meat products. It assumes the penetration of smoking substances into the smoked meat products during the thermal destruction of wood [1-2]. As a desired consequence of smoking, phenolic substances are generated. Though phenol and phenolic substances are of considerable importance to the organoleptic properties of smoked meat products, they cause potential toxic and carcinogenic effects on humans [3]. According to this fact, there is a need to control the quality of smoked foods to detect the excess content of phenols, which threatens the health and life of the consumer. Taking into account the complexity of sample matrices, sample preparation plays an important role during the analysis. Thus, in this research a new simple and effective scheme of phenols extraction for its following determination was developed. According to this scheme at the first step phenols generation and sorption on magnetic nanoparticles in specially developed vessel equipped with external magnetic field was performed. At the second step, the phenols were eluted from the magnetic nanoparticles, and finally, the analytes were determined by HPLC-UV. The magnetic nanoparticles based on Fe$_3$O$_4$ were used as a sorbent for phenols gas sorption for the first time. Large adsorbing surface, high magnetic properties and stability to oxidizing can explain the choice of magnetic nanoparticles in this research.

References
Nowadays, the quantitative determination of glutathione is of great interest. Silver based electrochemical sensors can be used for determination of glutathione. We present the template electrochemical synthesis of an array of micron silver particles on a solid substrate developed by our scientific group, based on the application of a template obtained by the sol-gel method using a structure-forming polymer dopant [1]. The final material is a polished titanium coated with an array of silver microparticles separated by a dielectric xerogel of titanium oxide. The resulting material was used as an analytical electrode: a method was developed for determining glutathione in aqueous solutions in the range from $10^{-9}$ to $5 \times 10^{-7}$ M, based on the removing of cyclic voltammograms.

![Figure 1. Electron micrograph of the sample made in pulse mode.](image)

![Figure 2. Dependence of the difference between the maximum current densities in the background electrolyte and with glutathione additives.](image)

References

The team of authors thanks the Science Park of St. Petersburg State University for their invaluable research assistance.
Greenhouse hydroponic experiments were carried out to examine the impacts of citric acid on Zn uptake and phytoextraction potentials of sorghum (*sorghum bicolor* L.M). Two-week-old seedlings transplanted in hydroponic solutions were treated with different doses of Zn in the concentration range of 5, 25, 50, 100 and 200 mg/L alone or in combination with 10 mM citric acid. After 21 day of culture, the plants were harvested, separated into roots and shoots and then dried. Fresh and dry weights, Zn uptake, translocation factor (TF), bioconcentration factor (BCF), proline, ascorbate and pigment contents were determined. The results indicate that Zn uptake, fresh and dry weights, TF, BCF, proline and ascorbate contents were concentration dependent with more significant increase (P < 0.05) after application of citric acid. Pigments and protein contents were however, severely decreased with increasing Zn concentrations and appreciated gradually with the addition of citric acid. Thus, citric acid efficiently increased phytoextractability of Zn and *Sorghum bicolor LM* was non-hyperaccumulator of Zn; but may be used for phytoremediation of Zn contaminated environments with assistance of citric acid.

References
An important condition for the effective development of agriculture is the justified and controlled use of drugs in veterinary medicine. To control the quality of the products obtained, simple, fast, efficient and environmentally friendly methods of chemical analysis are needed.

To solve this problem, within the framework of this study, a simple and effective method was proposed for isolating drugs of the sulfonamide group from chicken meat samples using a new type of effective extractants - deep eutectic solvents (DES) [1]. This type of extractants is a mixture of hydrogen bond donor and acceptor, the formation of which leads to a lower melting point of the system.

The developed method includes the extraction of analytes into DES synthesized from natural substances, such as choline chloride, glycerin, ethylene glycol, acetic and formic acids. The sample preparation procedure is a liquid extraction of analytes into the DES phase with their subsequent HPLC-UV detection. The developed method allows to determine analytes at the level of mg / kg and could be used to control the quality of meat products. The developed approach made it possible to eliminate the use of toxic organic solvents at the sample preparation stage without losing the efficiency of analyte extraction.

References

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IN-SOURCE DERIVATIZATION: AN EXPRESS METHOD FOR ALCOHOLS DETECTION BY DART MASS SPECTROMETRY

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Fast growing popularity of ambient ionization mass spectrometry methods is caused by the ability of these techniques to provide express qualitative and, sometimes, quantitative analysis without or with minimal sample preparation. At the same time, all of these approaches inherited mainly such ‘soft’ ionization processes as protonation, cationization and deprotonation. Thus, analytes, which are not capable of these processes, have high detection limits or cannot be analyzed by such methods at all. Furthermore, some compounds readily eliminate leaving groups after ionization. Some of these problems can be overcome by using the chemical modification approaches providing the permanent charge derivatization or yielding the readily ionizable derivatives. The main requirement for probable derivatization methods involved in analysis by ambient ionization mass spectrometry is the application of extremely simple and fast reaction procedures. Herein, we describe the first example of such approach for analysis alcohols by ‘direct analysis in real time’ (DART) mass spectrometry. The proposed method is based on reaction of alcohols with pyridine directly in DART sample gap yielding fixed-charge derivatives.

Figure 1. Gas-phanse reaction of alcohols with pyridine in DART ionization gap.

This approach has been tested on linear and branched fatty alcohols, cyclic alcohols and sterols. It was shown that the process proceeds only at rather high helium flow temperatures and is suitable only for relatively high-boiling alcohols. The registered DART mass spectra contain only the peaks of the cationic part of the derivatives. The resulting salts have a high ionization efficiency, and the detection limits of the corresponding compounds are reduced by two orders of magnitude.

The proposed method was applied for profiling of sterols in complex food matrices. It was shown that the obtained results are identical to gas chromatography / mass spectrometry data. At the same time, the latter approach requires much longer sample preparation and analysis times.

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Fe₃O₄ NANOPARTICLES MODIFIED BY SURFACTANTS AS NOVEL SORBENTS FOR MAGNETIC DISPERSIVE MICRO-SOLID PHASE EXTRACTION OF TETRACYCLINES FROM BIOLOGICAL FLUIDS

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A novel magnetic Fe₃O₄ nanoparticles coated by surfactants were investigated for a magnetic dispersive micro-solid phase extraction of tetracyclines (tetracycline, oxytetracycline and doxycycline) from biological fluids for the first time. It was established that Fe₃O₄ nanoparticles coating with cetyltrimethylammonium bromide allowed to improve tetracyclines extraction efficiency and nanoparticles stability without deterioration of their magnetic behavior. Moreover, Fe₃O₄ nanoparticles coating with surfactants is fast and simple. A magnetic dispersive micro-solid phase extraction procedure based on novel nanoparticles was developed for the HPLC-UV determination of tetracyclines in biological fluids. The developed procedure involved the floating of the nanoparticles in a liquid sample phase for extraction of the analytes followed by their elution and determination. The procedure was applied for the determination of tetracyclines in human plasma and serum samples. The reported procedure proves to be fast, simple, and inexpensive.

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In recent years, methods for early lung cancer diagnosis, based on the measurement of the volatile organic compounds (VOCs) profile in exhaled air are rapidly developing. The advantages of this approach are the simplicity and non-invasiveness of sampling, relatively small matrix effects, the possibility of online analysis [1]. In this work, a new version of VOCs chemical ionization in glow discharge was developed.

The Lumas-30 time-of-flight mass spectrometer with pulsed ionization source and copper hollow cathode was used. All measurements were carried out using air or a mixture of VOC with air. The several compounds, which belong to different classes of VOCs, such as acetonitrile, benzene, toluene, o-xylene, p-xylene, m-xylene, heptane were analysed. Ionization processes in glow discharge were studied. The VOCs ionization mechanism of efficient VOCs association reaction with metal ions (from auxiliary cathode material) was discovered. Also, efficiency of electron ionization mechanism [2] was shown for determination of VOCs. Additional mechanisms such as Penning ionization, a proton transfer reaction were also used to increase the reliability of VOC identification and increase the informative value of the analysis. The optimal parameters of discharge (pulse duration, repelling pulse delay time, pressure and voltage) were determined for each mechanism. It has to be noted, that in this case it is possible to implement all mechanisms, as well as each of them separately by optimizing the operating parameters. The detection limits of the compounds studied were determined; the values were about ppm level. Moreover, the mixtures containing two organic compounds were analyzed. The mutual influence of the compounds and the ability to control this effect are shown.

References

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VOLTAMMETRIC DETERMINATION OF NOREPINEPHRINE ON ELECTRODES MODIFIED BY BIMETALLIC SYSTEMS OF GOLD


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Norepinephrine (NE) is an important catecholamine neurotransmitter in the mammalian central nervous system. It mediates increase in heart rate, blood pressure, pupil dilation, and dilation of the airways, and the constriction of blood vessels. NE is critical for attention and focus, learning, memory, and the sleep-wake cycle. Alteration in its level is related to many diseases and other complications in body functions.

For measuring NE use HPLC, gas chromatography, spectrophotometry, fluorometry, chemiluminescence. Most such methods are complicated, requiring derivatization and suffering from low sensitivity and high cost. These drawbacks have been overcome through the use of electrochemical methods with various modified electrodes, simplifying the fabrication with the desired composition, in turn improving their sensitivity. But NE on the indicator electrodes oxidizes with high overvoltage. However, the effects of overvoltage can be reduced by using of modifiers. Thus voltammetric methods of analysis based on the use of chemically modified electrodes (CME) with electrocatalytic properties are of interest.

In this work, the catalytic activity of gold, cobalt, palladium, copper and bimetallic systems of gold (Au-Co, Au-Pd and Au-Cu), electrodeposited on carbon screen-printed electrodes (SPE) at the electrochemical oxidation of NE is established. Catalytic properties are appeared in a multiple increasing of peak current compared with the oxidation modifiers current and in decreasing the overvoltages of the oxidation of the NE compared with unmodified electrode.

The linear dependence of the analytical signal on the concentration of NE is observed in the ranges from $5 \times 10^{-7}$ to $5 \times 10^{-3}$ M on the SPE modified by bimetallic systems of gold particles. CME with electrodeposition bimetallic system Au-Co, distinguished by the best analytical and operational characteristics in the oxidation of norepinephrine, were used in the analysis of drugs.

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Polyphenols antioxidants activity plays an important role in the prevention of chronic diseases such as cardiovascular and neurodegenerative disorders, cancer, type 2 diabetes, and osteoporosis. One of the main sources of polyphenol antioxidants are tea and coffee. Main tea polyphenols are catechins and in coffee are hydroxycinnamic acids. So, the content of polyphenols in tea and coffee is one of the criteria for analytical quality control of these beverages. Along with target analysis, a promising approach is to obtain characteristic profiles of sample components with subsequent chemometric processing to determine the suitable identification criteria and the quality of the analyzed samples. These tasks are set and solved in this work.

Polyphenol antioxidants (catechins, gallic acid, chlorogenic, caffeic, ferulic acids, etc.) were selectively separated by reverse phase (RP) HPLC with photodiode array in various samples of tea and coffee. Caffeoyl-, feruloyl- and dicaffeoylquinic acids (chlorogenic acids) in infusions from roasted coffee beans were identified by RP HPLC with MS detection in negative ionization mode. Chromatographic profiles of polyphenol antioxidant in tea and coffee were obtained. Their chemometric processing was carried out using multivariate classification techniques including principal component analysis (PCA). It allowed identification of a variety of marker compounds responsible for differences among green teas and coffee of different origin and processing methods. Gallocatechine, gallocatechine gallate, epigallocatechine gallate and epicatechine gallate were contributing to most variances in tea samples.

The special task of the research was the investigation of polyphenol composition in varieties of tea obtained from the Institute of Floriculture and Subtropical Crops of the Russian Academy of Sciences (Sochi). The chemometric processing of its characteristic profiles will provide an independent classification criterion for new varieties of tea.

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One of the fundamental problems of modern analytical chemistry is a non-invasive diagnostics of pathologies in the human body. The assessment of the condition of the oral cavity of electronic cigarettes smokers is one of the illustrations of medical diagnostic tasks. The lack of sufficient information about the effects of smoking electronic cigarettes leads to various pathologies (diseases). The markers of the state of the oral cavity can be the content of anions of mineral acids in the oral fluid (OF), such as chloride, sulfate, fluoride, nitrite, and nitrate ions. The most appropriate method for their determination is capillary electrophoresis.

Experimental instruments: ‘Kapel-104-T’ capillary electrophoresis system (Lumex).

A technique of sample preparation of OF and optimal capillary electrophoresis conditions for determination anions in OF have been developed. Overall, there are observed underestimated values of the content of anions in the electronic cigarettes smokers with nicotine OF compared with the OF of smokers of electronic cigarettes without nicotine.

The maximum values of the linear correlation coefficients (values are in brackets) between the content of anions and cations in the case of smokers of electronic cigarettes without nicotine show a linear relationship between the contents of: chloride ions and cations potassium (0,85), magnesium (0,95), manganese (0,73), sodium (0,93); phosphate ions and magnesium (0,87).

In smokers’ of electronic cigarettes with nicotine OF, there is a linear correlation between the contents of: strontium and chloride ions (0,89); potassium and sulfate ions (0,83); fluoride anions and cations of calcium (0,96), potassium (0,94); phosphate anions and cations of calcium (0,81), potassium (0,77).

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The creation of national standards for the quality of medicines based on objective methods is a guarantee of the effectiveness and safety of drugs. Determining the quality of drugs to regulated standards involves the use of various analytical methods. At the same time, the final conclusion about the quality of drugs largely depends on the quality of the method itself, which must meet certain requirements. Generally accepted worldwide recommendations for the production of medicines in the form of GMP rules — good manufacturing practices — contain test method requirements that are used to assess the compliance of pharmaceutical products with established specifications for accuracy and reliability.

The purpose of this work is to select the optimal conditions for determining the content of framycetin sulphate in the preparation of eye and ear drops “Framidex” using HPLC.

Studies were performed using an “LC-20 Prominence” chromatograph with a spectrophotometric detector (manufactured by Shimadzu Corporation, Japan). As a mobile phase used three-component mixtures: acetonitrile for HPLC : 1 N sulphuric acid solution: tris (hydroxymethyl) aminomethane buffer solution. Considered the effect of the amount of the organic modifier, and the eluent supply mode on the retention time and separation of framycetin sulphate from other components of the investigational medicinal product, such as gramicidin and dexamethasone.

The developed method for the quantitative determination of framycetin sulphate, validated as required by EP (European Pharmacopoeia) and BP (British Pharmacopoeia). According to the results of the laboratory experiment, it was found that the metrological characteristics of such validation parameters of the methodology, such as convergence, linearity and internal laboratory precision, do not exceed the validation criteria. The stability of the technique can be reproduced in the laboratory, the deviation of a single value is 100.2% with a confidence level of 95%.

Thus, in the chemical laboratory of the quality control department of “ASEPTICA” LLC (Republic of Uzbekistan), methods were carried out to develop and improve for determination of framycetin sulphate in the eye drops and ear drops “Framidex” using the HPLC method.
Deep eutectic solvents (DES) are a mixture of two or more components capable of self-association, most often through the formation of a hydrogen bond, with the formation of a eutectic mixture, the melting point of which is significantly less than the melting point of the individual components [1]. In analytical chemistry, DES have proven to be effective extractants, with the stage of preliminary synthesis of DES.

In this study, we demonstrated a new approach for the extraction of nonsteroidal anti-inflammatory drugs (NSAIDs), based on the in situ formation of DES. The procedure includes two stages. First: extraction of the analyte from the sample into the acetate buffer solution. Second: extraction of the analyte into the pre-melted menthol to form DES in-situ. The resulting DES is easily separated from the matrix and used for HPLC-UV detection of analytes.

This technique was used for determination of diclofenac and ketoprofen in beef liver samples. The detection limit was 0.7 mg / kg for ketoprofen and 1 mg / kg for diclofenac. At the same time, this approach completely eliminated the need to use organic solvents during the sample preparation procedure and allowed the use of natural menthol as an extractant.

References
Hydrophilic anions both organic and inorganic are of a wide interest for analytical chemists since they are abundant species in industry and environment. Although a lot of methods for sensing of hydrophilic anions have been proposed over decades including chromatography and various optical methods [1], potentiometry might have the biggest advantages, such as low cost, suitability for field-based experiments, and miniaturization. Potentiometric membrane sensors have attracted a lot of attention as simple and effective tools for anion quantification.

Developing sensitive and selective potentiometric sensors for such ions as carbonate, phosphate and sulfate may be a hard nut to crack. The reasons for this are low charge-to-radius ratio, variability in geometry, dependence of anion form on pH of a solution, as well as low permeability of target analyte into the sensing membrane matrix. These challenges lead to development of new anion carriers [2] later used as ionophores in electrochemical sensors.

In this study a set of perfluorinated diketones with various chemical structures was used as ionophores to prepare membranes for potentiometric sensors. Substances which bear fluorine atoms or CF₃ substituents are considered to be the most highly effective anion carriers [3]. They provide effective complexation of hydrophilic anions via hydrogen bonding. The prepared PVC-plasticized sensor membranes were studied for selectivity and sensitivity towards variety of anions. It was found that sensitivity patterns of these new sensors deviate from Hofmeister series. This shows a good promise for development of a new class of anion-selective ionophores with high potential in selective quantification of hydrophilic anions.

References

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The biological coenzyme NADH plays very important role as an electron carrier in oxidize-reduced reactions in cells [1]. As known, total fluorescence intensity in NADH can be presented as a sum of three exponents with lifetimes $\tau_1$ and $\tau_2$, and rotational diffusion time $\tau_{rot}$ [2]. However, the nature of the multiexponential decay as well as the correlation of decay parameters on NADH microenvironment are so far not known enough. In the present work, the effect of solvent viscosity and polarity on the decay parameters of polarized fluorescence of NADH have been studied. Two-photon excited fluorescence decay in NADH has been determined and analyzed in water-methanol solutions.

Based on the polarized fluorescence signals obtained, we determined decay times $\tau_1$ and $\tau_2$, rotation diffusion time $\tau_{rot}$, a fluorescence anisotropy $r_0$, and the ratio of pre-exponential factors $a_1/a_2$. It was found, that rotational diffusion time $\tau_{rot}$, the absorption anisotropy $r_0$, and the values of and $a_1/a_2$ depended nonlinearily on the methanol concentration. The decay time $\tau_2$ increased with increasing methanol concentration. A theoretical model has developed showing that the fluorescence parameters are influenced by both the solution viscosity and energy exchange between two NADH chromophores, adenine and nicotinamide. As known, there are two conformers of NADH related to folded and unfolded geometrical configurations [3]. We believed that when the concentration of methanol in solution changed, relative concentrations of these conformers changed also resulting in the changes of rotational diffusion time $\tau_{rot}$, fluorescence anisotropy $r_0$, and the ratio of pre-exponential factors $a_1/a_2$. The data obtained suggest a new way of investigation the processes of denaturation of NADH in solutions and cells.

References
DETERMINATION OF MUSCLE STRESS MARKER 3-METHYL-L-HISTIDINE IN BIOLOGICAL FLUIDS USING DNA APTAMERS

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Determination of the 3-methyl-L-histidine content in human body fluids (urine and blood) has an important diagnostic value in the clinic and sport medicine since this compound serves as a biochemical marker for the degradation of myofibrillar proteins. Thus, it can be utilized for example to monitor the Duchenne disease or muscle stress during intensive trainings. Existing methods for 3-methylhistidine determination have a number of disadvantages: low expressiveness, high cost of analysis, high interferences caused by the presence of other compounds in the analyzed sample.

A new approach based on the use of aptamers - short-chain DNA molecules (sequences up to 80 nucleotides) which have high affinity for the target compound was applied. A key advantage of using aptamers to develop express test systems is the high sensitivity of detection in the presence of other compounds. Currently, there is no information on the use of aptamers for express detection of 3-methyl-L-histidine in available literature.

SELEX (Systematic Evolution of Ligands by Exponential Enrichment) procedure was used for the selection of aptamers specific to 3-methyl-L-histidine from the DNA-aptamer library. Seven rounds including two counter rounds were carried out. Selected aptamers were amplified by PCR procedure after each round. The enriched pool of aptamers after the seventh round of selection has been cloned into cells of the E. coli strain and identified after sequencing. The physico-chemical parameters of the aptamer-target binding were measured. Dissociation constants of aptamer-target complex were in low μM level, which is sufficient to effectively apply these aptamers as specific binding agents in biosensor systems for determination of 3-methyl-L-histidine in biological fluids. The test system developed using oligonucleotide aptamers to 3-methyl-L-histidine can be the basis for new generation methods in clinical and laboratory diagnostics for medicine and sports.

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TiO$_2$ catalysts for the purification of sulfur-containing gases are used in gas and oil treatment processes, chemical industry and metallurgy enterprises. At the same time TiO$_2$ and impregnated sorbents were employed to remove hazardous ions and applied in analytical chemistry.

The goal of this work was to obtain highly efficient and inexpensive inorganic solid-phase sorbents from spent catalyst (TiO$_2$) manufactured by the Shurtan Gas Chemical Complex (Uzbekistan). The catalyst TiO$_2$ matrix was thermal treated (500°C) and impregnated by different organic ligands like 2-amino-1-methylbenzimidazole (MAB), benzo hydroxamic acid (BGK), 5-sulphosalicylic acid (SAL), dithizone (DTZ).

The metal complex formation with the surface of the impregnated matrix increases the sorption capacity (mmol L$^{-1}$) of prepared impregnated sorbents.

Figure 1. Effect of impregnation on sorption

References
Ion-selective sensors are widely used in routine analysis. Their response mechanism is based on equality of the electrochemical potentials of all the species in the sensor and sample phases. Therefore, the boundary potential at the sensor/sample interface plays a crucial role in the signal formation both for potentiometric sensors (ion-selective electrodes, ISEs) and for optical chemical sensors (optodes). The possibility of controlling the electrical boundary potential would open broad prospects for tuning the sensor characteristics.

Herein, we report on theoretical and experimental investigation of the mechanism of the boundary potential formation. The potential at the polymeric sensor/solution interface was simulated numerically. The effect of the lipophilic electrolyte partition [1, 2] between the two phases was quantified. Furthermore, strong influence of the co-extraction of the solution anion on the interfacial potential of the cation-selective sensors was predicted theoretically and verified experimentally.

The obtained results allowed developing and quantifying a strategy for tuning and stabilization of the boundary potential at the sensor/solution interface. The latter is strongly required for obtaining optodes that respond to individual ionic activity [1], liquid junction-free reference electrodes for all-solid-state potentiometric devices [2], color standards for digital color analysis [3], and calibration-free optode arrays [4].

References

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A CLOUD POINT MICROEXTRACTION APPROACH FOR THE SEPARATION AND PRECONCENTRATION OF PESTICIDES IN FOOD

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Pesticides are widely used during the cultivation and the post-harvest storage of crops to prevent the destruction of crops by agricultural pests, fungi and weeds [1]. However, pesticides misuse can result in unacceptable high levels of the compounds in the food products can it cause potential harm to human health [2]. Therefore, the pesticide residue monitoring in foods is an important challenge of analytical chemistry. In the current study, a novel cloud point microextraction technique for pesticides determination has been developed. The new approach assumes the addition of extraction mixture consisting from water, fatty amine and carboxylic acid to the sample followed by phase separation using salting-out reagent and centrifugation. The developed approach is rapidly, simple, high sample throughput, low cost and environmentally-friendly, which can be used for simultaneous pretreatment of a large number of samples without any specific equipment. The proposed technique was successfully applied to the GC-MS determination of pesticides in vegetables.

Figure 1. Schematic representation of the developed procedure.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-33-01176_mol_a).
The problem of pollution in the Arctic has been discussed for more than a decade, and it becomes obvious that the economic activity of countries around the world leads to man-made pollution of Arctic ecosystems. The Arctic nature is extremely vulnerable to the contamination, which in the future may lead to irreversible worldwide ecological processes. This region is under an ever-increasing man-caused impact of both local industrial centers and changing transportation ways of pollutants by air masses, water flows and sedimentary material of arctic rivers. The main contaminates of the Arctic territories along with persistent organic pollutants (POPs) are heavy metals (HM) and petroleum products. Among the prevailing pollutants, a special place is occupied by heavy metals which concentrations must be controlled. Thus, the purpose of this work was to study the prevalence of xenobiotics in this region and to assess the pollution level and accumulated environmental damage.

In this work, we studied the soil, water and vegetation samples from the Arctic meteorological station located on the Yamal Peninsula. Analysis of the level of oil pollution showed the presence of strong oil pollution of the soil on the territory of the station, the depth of oil penetration reached \( \geq 20 \) cm.

Also experiments were conducted to determine the content of such xenobiotics as heavy metals and organic pollutants.

Analysis of the experimental data showed that the soils of the Arctic region were subjected to anthropogenic man-made impact. On the territory of the station there are abandoned radio-relay communication lines, a number of household buildings for their maintenance, destroyed equipment and fuel and lubricant storage sites. The likely sources of oil pollution were the storage facilities for fuel and lubricants needed for the operation of the station. A number of heavy metal accumulations were obtained. The possible sources of this pollution could be, as well as destroyed buildings, equipment, etc., and transboundary transport. The presence of higher plants intensifies the processes of biomediation, the root system contributes to the loosening of bituminized / oil-contaminated soils, and also plants are able to accumulate xenobiotics.
The search for novel antioxidant express assays as well as for polyfunctional antioxidants is still of great interest [1]. Novel ligands 1-6 and their hydrochlorides 1a-6a containing N-donor pyridine rings and 2,6-di-tert-butylphenols fragments were synthesized and the electrochemical properties of these compounds were studied by cyclic voltammetry (CV) method. The feasible schemes of redox-transformations were proposed.

Antioxidant activity of 1-6 and 1a-6a was measured using electrochemical method [2] based on the reaction with stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) rate measuring. It was shown that the redox behavior of phenols as well as antioxidant activity strongly depends on the structure of pendant in para-position and the length of hydrocarbonyl linker. The compounds 4-6 and hydrochlorides 1a-6a demonstrated high activity. The correlation of redox-properties and antioxidant properties was demonstrated. The data of electrochemical study are in accordance with the results obtained spectrophotometrically in CUPRAC test thus proving the efficiency and reliability of approach proposed.

References

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VOLTAMMETRIC DETERMINATION OF ASCORBIC AND MALIC ACIDS AT SCREEN PRINTED ELECTRODES MODIFIED BY GOLD-COBALT BINARY SYSTEM

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Determination of organic acids such as ascorbic acid (AA) and malic acid (MA) in fruit juices is an important task, because these compounds are responsible for the taste characteristics and organoleptic quality, and may also effect the stability of the product. Quantification of organic acids in juice is a way to identify the product authenticity. Thus, the development of fast, simple, and selective methods for the determination of AA and MA in juice is of great interest.

For quantitative determination of AA and MA various physical-chemical methods are used, such as titrimetry, spectrophotometry, chemiluminescence, high performance liquid chromatography (HPLC). Along with advantages, these methods have some limitations. Low sensitivity and selectivity are disadvantages of spectrophotometry and titrimetry. In conditions of HPLC one can determine several components but after preliminary preparation of samples, frequently including preliminary derivatization. Besides, these methods are complicated in conduction, time, and cost taking. Therefore voltammetric method with chemically modified electrodes (CME) that have the advantage of simplicity in experiment conduction, high analytical characteristics, and non-expensive equipment represents interest.

Gold-cobalt binary system electrodeposited on the surface of screen printed electrode exhibit catalytic activity during AA and MA electrooxidation. It is exhibited in decreasing of overvoltage of substrate oxidation and in increasing of oxidation current of modifier. The method of voltammetric simultaneously detection of organic acids at the screen printed electrode with two working electrodes modified by gold-cobalt binary system was suggested. The linear dependence of analytical signal from the analyte concentration is observed in the range from $5 \times 10^{-7}$ до $5 \times 10^{-3}$ M of AA and from $5 \times 10^{-7}$ to $5 \times 10^{-3}$ M of MA. This method was used in the analysis of fruit juices.

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INVESTIGATION OF ASSOCIATION OF TRIS-PILLAR[5]ARENE WITH PHENOTHIAZINE DERIVATIVE: COLOMETRIC RECOGNITION OF ANIONS

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Due to pillar[n]arenes capability to recognize anions through forming supramolecular complexes, creating sensors based on them is attractive concept for modern chemistry. Pillar[n]arenes are also able to form inclusion complexes and associates with aromatic compounds, which makes them suitable structure blocks for receptor systems working on the dye-displacement principle for inorganic anions and biologically relevant anion substrates, e.g., adenosine triphosphate.

We have developed a synthetic procedure to functionalize TREN with three terminal pillar[5]arene terminal fragments linked to the core by amide linkers. UV-spectrophotometry titration was used to study complexation of tris-pillar[5]arene with phenothiazine dye. The structure of the complex is discussed and supported by NMR \(^1\)H spectrometry, amide fragment of TREN participates in a hydrogen bond with imino group of phenothiazine dye resulting in significant red shift of the absorption band. Anion binding leads to dye displacement with the attendant color change from blue (complex) to pink (free phenothiazine dye). Taking into account electrochemical activity of phenothiazine and polyphenothiazine derivatives this approach might be also promising for further applications in electrochemical sensors.

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NOVEL APPROACHES TO ELECTROCHEMICAL SENSING WITH IONOPHORE-BASED MEMBRANES

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Ionophores: neutral or charged molecules capable of selective complexation with various ions and neutral species are widely used in potentiometric sensors (ion-selective electrodes, ISEs), conductometric sensors and optical sensors (optodes) [1]. These sensors are routinely applied in clinical analysis, agriculture, environmental monitoring and industry. Recently, the family of ionophore-based sensors got new members: voltammetric [2] and ampero-coulometric sensors [3, 4].

In this work, a comparative study of K⁺-selective ISEs was carried out in different measurement modes: potentiometric, voltammetric and ampero-coulometric modes. Sensor membranes were drop-cast or spin-coated on top of PEDOT-PSS layer formed on glassy carbon substrate. The sensor membranes contained polyvinylchloride (PVC) as matrix polymer, bis(2-butylpentyl)adipate (BBPA) as plasticizer, neutral ionophore valinomycin (0.02 m), potassium tetrakis(p-Cl-phenyl)borate (KClTPB, 0.01 m) as cation exchanger, and a lipophilic electrolyte tetraddodecylammonium tetrakis(p-Cl-phenyl)borate (ETH 500, 0.01 m).

The ISEs showed linear Nernstian response to K⁺ over the range from 10⁻¹ to 10⁻⁶ M with the slope of 56.8 mV/log(aK) and high selectivity over Na⁺ and other interferences. In voltammetric mode clear oxidation/reduction peaks were registered. Most interesting results have been achieved in ampero-coulometric mode. The existing response model [3] was generalized, and this allowed for a dramatic improvement of the fitting of the experimental curves to the theory. Importantly, for the first time, ISEs in coulometric mode were successfully applied for K⁺ quantification in blood serum samples.

References

Acknowledgements. The resource center “Innovation technologies of composite nanomaterials” is greatly acknowledged for spin-coating of the membranes.
VOLTAMMETRIC DETERMINATION OF CAFFEINE IN ENERGY DRINKS USING AN ELECTRODE MODIFIED BY COMPOSITE BASED ON NAFION AND BIMETALLIC SYSTEM OF BISMUTH–IRIDIUM


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Caffeine (1,3,7-trimethylxanthine) is an alkaloid from xanthine group that is widely found in plant products and beverages. The popularity of caffeine-containing products is connected with her physiological effects, such as stimulation of the central nervous system and gastric secretion. However, high amounts of caffeine can cause trembling, nausea and nervousness. For these reasons, it is very important to control the concentration of caffeine in its different sources.

In this work, we developed a method of voltammetric determination of caffeine using a glassy carbon electrode (GCE) modified by composite based on Nafion film (NF) and bimetallic system of bismuth–iridium (Bi-Ir) for analysis of energy drinks.

Bimetallic system Bi-Ir electrodeposited at the GCE show catalytic activity in the electrooxidation of caffeine. It is exhibited in decreasing of overvoltage of substrate oxidation and in increasing of oxidation current of modifier. When the NF is applied to the surface of the electrode Bi-Ir-GCE, a two-fold increase of caffeine oxidation current has been achieved compared to its oxidation on the modified electrode without the NF. It is due to the accumulation of the substratum in the polymeric matrix. The signal height is linearly related to the caffeine concentration in the solution.

The procedure was verified by the introduced-found method. The relative standard deviation $S_r$ does not exceed 5% in the whole range of concentrations studied.

Developed method was used for detection caffeine in energy drinks. The determined values of caffeine contents in energy drink samples are in good agreement with a content declared by manufacturer as well as with results obtained by HPLC as independent method.

The results obtained using both methods were statistically compared by the paired t-test. Its results indicate that there are no important differences between the obtained results at the 95% confidence level. On the basis of these results it can be stated that the proposed procedure can be applied successfully for caffeine determination in pharmaceutical formulations and beverage samples.

Acknowledgements. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.
Hydroxyapatite is the main mineral component of teeth, bones and one of the most common minerals in pathologic masses in human body. The solubility of hydroxyapatite has been the subject of extensive studies for several decades and many works devoted to this topic were published, but the reported data poorly fit together. One of the reasons for this may be the incongruent dissolution of hydroxyapatite. Difficulties of study of hydroxyapatite solubility are also caused by extremely low solubility and long duration of the setting of chemical and phase equilibria. Therefore, until now, no studies of influence of electrolyte and protein composition of body fluids on the solubility of hydroxyapatite have been carried out.

Low solubility of hydroxyapatite complicates the study of phase equilibria, because even a small sampling can shift the equilibrium in the system. In this regard, it is important to provide non-destructive analysis of the composition of a solution that is in contact with hydroxyapatite. This can be done by a direct ionometry with membrane electrode selective to calcium ions. The use of calcium ion-selective electrode (Ca-ISE) allows a continuous measuring the composition of the solution in time, directly in the cell without sampling. This method has an important additional advantage: the signal of the sensor depends on the activity rather than the concentration of calcium ions in solution.

The main goal of the present work was to get reliable data on the solubility of hydroxyapatite as a function of the solution composition. The results demonstrate that the concentration of calcium ions in solution non-monotonously changes over time: the respective curves contain a maximum.
VOLTAMPEROMETRIC DETERMINATION OF GUANINE ON ELECTRODES MODIFIED WITH COMPOSITE FILM FROM NATHION AND OSMY HEXACIANOMETALLATES

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Heterocyclic nitrogenous base - guanine is the initial structural element of deoxyribonucleic acid (DNA), the primary damage to which in the DNA molecule leads to mutations and changes in the genotype. The level of guanine concentration in DNA is considered to be an important parameter in the diagnosis of mutagenic factor and therapeutic treatment of diseases number.

In this work, the electrocatalytic activity of films based on osmium (III) hexacyano-ruthenate (HCRO) and osmium (III) osmium hexacyanocobaltate (HCCO) deposited on the surface of glass-carbon electrode (GCE) covered of nafion (NF) cation-exchange film during electrooxidation of guanine is established. The highest electrocatalytic effect is registered on the GCE with a film of osmium (III) hexacyanoruthenate. Using the composite NF-GCRO leads to registration the larger catalytic currents due to a combination of accumulation stage of protonated guanine molecules in the nafion polymer matrix and principles of electrocatalysis. The optimal conditions for obtaining the composite NF-GCRO, under which the highest catalytic effect are recorded. The mechanism is proposed and the kinetic parameters of guanine oxidation on the NF – GCRO – GCE electrode are calculated.

The method of voltamperometric determination of guanine on GCE with a composite film NF-GCRO was developed. The dependence of the catalytic current from substrates concentration is linear in a wide range. The detection limit of guanine on the NF-GCRO-GCE is 5*10⁻⁷ M. The relative standard deviation is less than 5%. The developed voltamperic method of guanine determining was tested in sample of salmon sperm DNA.
Switchable hydrophilicity solvents (SHSs) have been recently introduced into sample preparation as an alternative to toxic and environmental polluted organic solvents. The unique facilities of SHSs to switch reversibly between hydrophilic and hydrophobic forms provide formation of large surface area between the extraction solvent (SHS) and the aqueous phase resulting in rapid phase equilibrium, followed by phase separation.

In the present research, we implemented a switchable hydrophilicity solvent rotating membrane disk-based microextraction (SHS-RMDME) strategy for simple and highly-available analytes preconcentration. The SHS-RMDME procedure (Fig. 1) assumed in situ generation of microdroplets of a hydrophobic medium-chain fatty acid (extraction solvent) from homogeneous sample solution containing water-soluble medium-chain fatty acid salt by acidification. A rapid mass transfer of target analytes from aqueous sample phase to extraction solvent microdroplets followed by collecting of extract microdroplets on a rotating membrane disk was obtained. Afterward the analytes were eluted from the disk. The SHS-RMDME strategy was applied for the determination of tetracycline, oxytetracycline and chlortetracycline in urine samples by HPLC-UV.

Figure. 1. The extraction process diagram.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-01176).
INVESTIGATION OF NON-STOICHIOMETRY IN F- AND O-CONTAINING KTP SINGLE CRYSTALS USING PULSED GLOW DISCHARGE TIME-OF-FLIGHT MASS SPECTROMETRY

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The quality control of nonlinear optical materials and the correlation between crystals growth conditions (solvent composition, growth rate, dopant distribution, etc.) and their composition and optical and electrochemical properties are necessary steps in growing of high quality single crystals used in nonlinear optical instruments. However, the direct analysis of dielectric materials including light elements with high ionization energy is a difficult task.

To solve this problem, the method based on time-of-flight mass spectrometry with pulsed glow discharge has been developed [1-3]. Advantages of the method include high sensitivity and accuracy, simple sample preparation and low matrix effects. The method was used to study the stoichiometric composition of KTP single crystals both pure and doped with KF and Rb+ as well as its dependence on crystals growth conditions. The effects of growth rate, solvent composition and temperature on the distribution of the components in the crystal were also investigated. Moreover, it has been shown, that the largest concentration differences in one crystal were observed along the crystal growth axis and in different growth faces, such as (011) and (201); (201) and (100). The last effect is due to differences in the growth mechanisms of the faces [4]. The analysis of electrical conductivity along the cross section of the crystal, in different facets of growth and crystals with different concentration of doped components was provided. It was shown that the concentrations of the main and doped components and the electrical conductivity change regularly.

References

Acknowledgements. The research has been supported by a grant from the Russian Science Foundation (grant №. 17-73-20089).
In recent years, there has been an active interest in the use of ionic liquids (ILs) in methods of separation and concentration due to their unique properties. A promising direction is the application of ILs in electrokinetic chromatography methods (micellar (MEKC) and microemulsion (MEEKC) variants) as components of electrophoretic system. The variety of combinations of cations and anions in the composition of ILs provides their use both as a surfactant and as “oil” in microemulsion or as modifies of background electrolyte (BGE). It will make possible to control the separation selectivity of such hydrophobic compounds to effect on efficiency and prevent the sorption of analytes on the walls of the capillary.

In this work the possibility of using imidazolium ionic liquids (C$_{16}$MImCl, C$_{12}$MImCl, C$_{6}$MImBF$_4$, C$_{6}$MImN(SO$_2$CF$_3$) for the separation of polyphenol antioxidants and steroid hormones by MEEKC were investigated. The influence of various factors on the efficiency and selectivity of separation of analytes was determined: the concentration and the nature of ILs, the type and concentration of the “oil” and co-surfactants in the microemulsion, the nature and pH of the BGE, the component ratios in microemulsion, the various additives that may undergo some additional interactions with the analytes (cyclodextrins, organic solvents). The addition of 15 mM 2-hydroxypropyl-β-cyclodextrin (HP-β-CD) has been found to increase the separation selectivity of steroid hormone. The results are compared with the use of a traditional cationic surfactant, cetyltrimethylammonium bromide.

The use of on-line preconcentration technique (sweeping) made it possible to reduce the limits of detection of analytes upto 50 ng/ml. As a result, a rapid method for determining steroid hormones by the MEEKC method in biological fluids (urine, blood serum) is proposed.

Acknowledgements. We express our gratitude to the Resource Educational Center in the direction of chemistry of St. Petersburg State University for the equipment provided. The current study was supported by RFFI grant № 17-03-01282-a.
MERGING EFFECT OF DEEP EUTECTIC SOLVENTS AND POLYMERS FOR SIMULTANEOUS DETERMINATION OF TRACE CONCENTRATION OF OMEPRAZOLE AND LANSOPRAZOLE IN COMPLEX MATRICES

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Deep eutectic solvents as a subcategory of ionic liquids are showing great potential in many different areas of chemistry, such as separation, polymer synthesis and metal deposition [1]. Conducting polymers (CPs) have been widely applied for fabricating various electrochemical devices such as sensors, actuators or solar cells [2]. In this study simultaneous electrochemical oxidation of omeprazole and lansoprazole is investigated via a modified carbon paste electrode. The modifiers are a polymer and a deep eutectic solvent. Differential-pulse voltammetry is performed as the electrochemical method in Britton-Robinson buffer solution (0.04 M; pH 6.0) and after optimization of several factors such as pH or conditioning time, well-defined peaks are observed in a linear range of 10 to 300 nM for both drugs. In addition to buffer solution determination of both analytes were done in human serum and urine and the results were satisfactory as well quality control for pharmaceutical formulations.

Figure 1. Linear range of simultaneous determination of omeprazole (blue) and lansoprazole (red)

References
While cancer surgery is the most common method of solid tumor treatment, there is no convenient tool for accurate real-time tumor margins assessment by a surgeon [1]. Resecting a tumor, the surgeons mostly rely on their experience; a histological analysis of the excised tumor fragments is generally performed after the surgery. Thus, if the tumor was not completely removed, or, in the other words, the tissue fragment margins are positive for cancer cells, a re-excision surgery is inevitable. The lack of fast and reliable tumor margins assessment method results in extra loading on hospital resources and in higher risk of side effects associated with surgery and anesthesia. Besides, a patient’s moral state could be negatively affected; some people tend to choose radical surgery (e.g., mastectomy) as more “certain”, even if organ-conserving treatment is available as an option.

Recently, various spectroscopic methods have been extensively studied for tumor margins assessment [2]. Due to the different metabolic processes, occurred in tumor and normal cells, it is possible to distinguish them by specific spectral features (light scattering, peak intensities, etc.). In our work, a near-infrared (940-1800 nm) fiber optic probe coupled with portable spectrometer has been applied for tumor distinction in vivo and in vitro from normal and pathologically changed benign tissues (e.g., hyperplasia) on various carcinogenesis animal models (skin, brain, and breast cancer) and on tissue fragments obtained from real patients with cancer (gastric and colon cancer). In combination with several multivariate data analysis algorithms, this easy-to-use approach demonstrates promising results in tumor cells distinction.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project #18-53-53016 GFEN_a).
In recent years the development of fast, precise, accurate and sensitive methodologies in chemical analysis has become an important issue. However, despite the use of highly efficient analytical instrumentation for the end-point determination of analytes, sample pretreatment is usually necessary to eliminate the negative effect of matrix components. Homogeneous liquid-liquid microextraction is based on extraction solvent phase formation from homogeneous solution induced by altering ionic strength, pH and temperature as well as an addition of ion-pair agent. This method has been widely applied for sample preparation prior to determination of both organic and inorganic analytes. Its advantages are simplicity, versatility, rapid phase equilibrium achievement and low solvent consumption. Recently, the so-called switchable hydrophilicity solvents (SHS) have been proposed as promising extraction solvents in homogeneous liquid-phase microextraction as their miscibility with aqueous sample can be easily and reversibly changed by pH adjustment. In this report different modes of SHS-based microextraction as well as main drawbacks and benefits are discussed. Various applications to the real sample analysis are described.

Acknowledgements. Authors gratefully acknowledge the Russian Science Foundation (project no. 16-13-10117) for financial support.
THE STUDY OF LOW TEMPERATURE VAPOR-GAS STREAM
COMPOSITION USING ICP-AES AND ICP-MS TECHNIQUES

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There are many sources of atmospheric pollution both natural and anthropogenic. Gold mine tailings is the most dangerous anthropogenic one, which can produce a wide range of contaminants such as aerosol, dust and vapor containing the compounds of S, Se, As, Hg and other elements. However, low-temperature transport of volatile metal and metalloid species has not been extensively studied.

The purpose of this work was to study the chemical composition of gaseous and particulate matter in the stream emerging above the solid material taken from the sulfide tailings dump (Ursk, Kemerovo region, Russia) [1].

Atomic emission and mass spectrometry (ICP-AES, ICP-MS) and SEM EDS were applied to characterize the particles of various sizes: d>0.45μm and 0.45>d>0.2μm and the gaseous fractions as well. Metalorganic framework polymer (MOF) UiO-66 was used as gas adsorbent.

For this research, the special installation was designed (Figure 1) to collect gaseous and particulate fraction of low-temperature stream.

Figure 1. Laboratory set: 1 – water seal; 2 – membrane filter; 3 – blank sample vessel; 4 – waste material; 5 – 2-step filter (0.45 μm and 0.2 μm consistently); 6 – UiO-66 as adsorbent; 7 – laboratory pump (suction mode)

It was found that low-temperature vapor stream contains the compounds of As, Hg, Sn and Sb as adsorbed by UiO-66 at the level of 0.4 - 40 μg/g.

References
DESIGN PRINCIPLES OF MULTIANALYTE OPTICAL SENSOR ARRAYS FOR DETERMINATION OF THE IONIC ANALYTES IN AQUEOUS SAMPLES

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There is a growing demand for sensing platforms that provide simultaneous detection of various analytes in a single sample, e.g. for obtaining body electrolytes snapshot from a single drop of body fluid such as blood or sweat. Optical chemical sensors (optodes) appear to be ideal tools for developing such multianalyte sensor arrays due to their tunable dynamic range and miniature size. However, the real media impose special requirements on utilization of optical chemical sensors: the problems of the sample background color, biofouling of the sensor surface, cross-sensitivity in a complex matrix must be carefully addressed.

In this contribution, we summarize the design principles of multianalyte sensing arrays for application in real aqueous samples. Optical sensor compositions for detecting ionic analytes (K⁺, Ca²⁺, Mg²⁺, Na⁺, NH₄⁺, Cl⁻) in blood and serum, human sweat and hydroponics nutrient solutions are suggested. Furthermore, different functional designs of sensing platforms utilizing substrate and protective materials of various natures will be presented and their applicability in real samples will be demonstrated (Fig. 1).

Figure 1. Examples of optical response of optodes: (A) casted on inert substrate; (B) protected with cellulose acetate from biofouling.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-73-00109).
Over the years, the use of fluoride in toothpaste has been highly controversial. Some people argue that fluoride can cause serious health problems, while experts have found that fluoride can significantly improve dental health. In recent decades, a new field of physical and chemical research – ionometry, the main task of which is the study and development of various types of ion – selective electrodes, is rapidly developing. To create new types of such electrodes, a wide range of electrochemically active substances is used, such as liquid and solid ionites, mono- and polycrystals, synthetic membrane-active complexons and other compounds that exhibit a selective action relative to certain ions.

Fluoride-selective electrode is used for fast, simple, accurate and economical measurements of fluoride ion concentration in aqueous solutions. Ion-selective electrodes are known for the determination of fluoride ions, the membranes of which are made on the basis of fluorides of rare earth elements.

Objects of research: toothpastes of different names: Ftorodent, New Pearl and Colgate. Purpose: to determine the content of soluble fluoride ions in the toothpastes of different manufacturers. The results are presented in the table.

Table 1. The results of the values of the content of fluoride in toothpastes in %

<table>
<thead>
<tr>
<th>№</th>
<th>Toothpaste</th>
<th>Manufacturer</th>
<th>The mass of charge, g</th>
<th>Fluoride content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ftorodent «Фтородент»</td>
<td>Russia, Moscow, Savelovsky district, JSC «Cosmetic Association “Freedom”»</td>
<td>0.4090</td>
<td>1.08±0.01</td>
</tr>
<tr>
<td>2</td>
<td>New Pearl «Новый Жемчуг»</td>
<td>Russia, St. Petersburg, JSC “Neva Cosmetics”</td>
<td>0.3050</td>
<td>0.86±0.03</td>
</tr>
<tr>
<td>3</td>
<td>Colgate «Колгейт»</td>
<td>Importer: Colgate-Palmoliv, CJC, RF, 121614, Moscow, Krylatskaya St.</td>
<td>1.4740</td>
<td>0.87±0.04</td>
</tr>
</tbody>
</table>
Optodes are the sensors that change the color or luminescence intensity depending on the analyte activity in solution. These devices are miniature and easy to use. Their response is determined by the selective chemical interactions between the active components and the analyte inside the sensor phase, typically plasticized polymeric matrix. The sensing layer is usually integrated into the sensing system, which can be divided into three components: the substrate (supporting hydrophobic organic sensing layer), the sensing layer itself (providing selective binding of the analyte), and the shielding layer (protecting against possible fouling) (Fig. 1A). The reported study was aimed at optimization of the substrate material and pretreatment method, as well as of the protective material, for use in optical detectors containing hydrophobic sensors. Combinations of various materials were tested with well-known sodium-selective optodes based on Na ionophore VI and pH-indicator ETH5350.

A number of materials were tested as candidates for using as an array substrate, such as poly(propylene) and polyester films, Teflon sheets, silanized glass slides etc. They were quantitatively compared in terms of optical response amplitude and reproducibility, inertness, mechanical stability and transparency. Different methods of the substrate surface pretreatment for applying optode composition and optode geometries were evaluated in terms of piece-to-piece reproducibility (Fig. 1B). Several materials were tested as shielding layers for protection of the optode array from fouling in real samples, such as polyester hemodialysis filter and 12 kDa cellulose acetate dialysis filter. The effect of the protective film in the array response time was evaluated (Fig. 1C). The optimal
design of the functional multilayer sensing platform demonstrated high reproducibility of the results, reduced the measurement errors and was successfully verified prior and after contact with whole blood.
NEW HIGH-SENSITIVE LATERAL FLOW IMMUNOSENSORIC SYSTEMS FOR CONTROL OF PLANT PATHOGENS

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Lateral flow immunosensoric systems for control of plant pathogens have two clear fundamental advantages: selectivity provided by immune recognition, and simplicity of handling procedures. However, its place among alternate analytical approaches and perspectives of wider application are still disputable. Further use of lateral flow tests in agricultural and food safety control will depend both on the development of new assay formats that allow reaching extremely low limits of detection. This report provides a comparative assessment of the enhancing approaches that their applied in practice for the control of viral and bacterial pathogens of the potato.

We have proposed several schemes for lateral flow immunoassay enhancement. (i) Combination of magnetic nanoparticles and gold nanoparticles (GNPs) as labels. This approach was applied to the detection of potato virus X and was found to be 32 times more sensitive than the conventional immunoassay. (ii) Combination of two (specific and enhancing) GNP conjugates and alkaline phosphatase. The limit of detection was 27 times lower than that of a non-amplified immunoassay. (iii) Enlargement of the size of GNPs using catalytic reduction of metal (Ag, Au) salts. The use of the GNP enlargement method resulted up to 240-fold reduction in the detection limit of potato pathogens.

The developed high-sensitive lateral flow immunosensoric systems show significant potential for various analytical tasks due to universal and simple approaches for increased sensitivity. They are highly promising for the routine and non-laboratory assay.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-16-04108).
Hydrophilic interaction liquid chromatography (HILIC) has been actively developed in the last decade driven by the increase in the development of polar drugs within the pharmaceutical industry. The growing interest in HILIC is due to the release of special columns for the determination of polar compounds. Such stationary phase can be obtained by the dynamic modification with the hydrophilic reagents. We propose to apply the imidazolium ionic liquids (ILs) as a hydrophilic coating of C18 stationary phases for HILIC. The influence of the length of the alkyl radical (C₄, C₆, C₈, C₁₂), the nature of the counter-ion (Cl⁻, BF₄⁻) and IL concentration (1 - 60 mM), the pH of the mobile phase and the organic additive on the efficiency and selectivity of separation of polar drugs had been studied. The possibility of determining drugs (p-aminosalicylic acid and antibiotics levofloxacin, sparflaxacin) by HILIC in blood plasma was demonstrated.

In this study was supposed mode of simultaneous determination of zoledronic acid (ZA) and creatinine in biological fluids by HILIC. ZA belongs to class of bisphosphonates. These drugs have become the therapy of choice for the management of various skeletal disorders such as several types of osteoporosis, malignancy metastatic to bone. However, despite the benefits of bisphosphonates, it may cause also the disruption of the kidneys, which is controlled by the content of serum creatinine. The major factors influencing the retention of ZA in HILIC such as the type of the stationary phase (amino- and amide- phases), the percentage content of water in eluent, the concentration, pH and type of the aqueous solution of the salt were investigated. ZA as strong chelator is capable to interact with the metals of the liquid chromatographic system. This required a series of experiments with the addition of complexing agents (tartaric, citric acid and EDTA) to the mobile phase. The possibility of determining ZA and creatinine by HILIC in serum was demonstrated. The high selectivity of the separation of analytes makes it possible to use the technique for obtaining chromatographic profiles in the evaluation of drug therapy.

Acknowledgements. This work was supported by the Russian Science Foundation, project No. 19-13-00370. Results were performed at the Resource Center of Chemical Analysis and Materials, Research Park, Saint Petersburg State University.
Fluoroquinolones (FQs) are a class of antibiotics which are widely used for the prevention and treatment of various diseases in animal husbandry [1]. The excessive use of these substances can result in the presence of its residue in animal tissue, which contributes to the long-term health effects, including microbial antibiotic resistance and allergic reactions [2]. Thus, there is an important analytical task to control the residue levels of these analytes in various animal products to provide food safety and protect health of consumers.

In the current study, a novel approach for effective solid-liquid microextraction of hydrophobic analytes based on in situ formation of deep eutectic solvent (DES) was proposed for the first time. The developed microextraction procedure assumed dissolution of a hydrogen bond acceptor of DES into a solid-phase sample phase followed by heating with a hydrogen bond donor of DES. The heating the mixture promoted in situ formation of hydrophobic DES, effective analytes microextraction and final phases separation. In this procedure tetrabutylammonium bromide acted as the hydrogen bond acceptor and long-chain alcohol acted as the hydrogen bond donor promoted mass-transfer of fluoroquinolones from solid-phase sample phase to DES phase. The developed approach was coupled with high-performance liquid chromatography with fluorometric detection for the determination of ofloxacin and fleroxacin in meat samples. The limits of detection, calculated from a blank test based on 3σ, were 10 μg kg⁻¹ and 15μg kg⁻¹ for ofloxacin and fleroxacin respectively.

References
Homogeneous liquid-liquid microextraction (HLLME) is a powerful preconcentration method which assumes an extraction of target analyte from a homogeneous solution into an organic phase formed due to phase separation phenomenon. HLLME is a very simple method and requires a reagent addition to decrease a solubility of an organic solvent in aqueous phase resulting in phase separation. Polar, water-miscible organic solvents such as monohydric alcohols or acetonitrile are the most frequently used in HLLME as extractants. Nevertheless, the main drawback of methanol or acetonitrile utilization is the necessity to perform the extraction process at the ratio 1:1 (v:v) between aqueous and organic phases resulting in low enrichment factor values.

In the present research, it was found that the primary amines can also be utilized for HLLME. The homogeneous isotropic solution was observed when primary amine was mixed with an aqueous phase. Phase separation was achieved by simple addition of salting-out agent to the extraction mixture. It was investigated that tetracyclines (tetracycline, oxytetracycline, doxycycline) could be extracted into primary amines.

The parameters such as type of primary amine, the volume of extractant, the phase separation agent and its concentration were optimized. The developed procedure has been utilized for the determination of tetracyclines in biological fluids followed by HPLC-UV determination. The limit of detection, calculated from a blank test based on 3σ, was 0.17 mg L⁻¹ for tetracycline, oxytetracycline and doxycycline.
STRUCTURAL-GROUP ANALYSIS OF OIL SOURCE ROCK ORGANIC MATTER

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Fourier transform infrared spectroscopy (FTIR) has been used for many years to evaluate the mineralogy of rocks [1] and structural group analysis of organic matter (OM) in extracted bitumoids and isolated kerogen [2, 3]. However, the traditional approaches in studies of OM require long and time-consuming sample preparation (extraction of bitumoids in the Soxhlet apparatus, acid dissolution of minerals). In addition, the extraction of kerogen by dissolving mineral rock makes it difficult to completely remove pyrite and quartz.

In this paper the possibilities of IR spectroscopy for structural group analysis of OM directly in source rocks (Table 1) using the example of low-permeable carbonate sediments of the pre-Jurassic basement (Paleozoic) were shown.

It was also shown that IR spectra of kerogen, recorded in the transmission mode using KBr pellets, had more absorption bands, which characterize vibrations of aliphatic and aromatic fragments, than IR spectra obtained in the attenuated total reflectance mode.

Table 1. Parameters of structural group composition of organic matter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aromaticity$^2$, $S_{1600}$</th>
<th>Aliphatic factor$^2$, $(S_{2850}+S_{2920})/(S_{2850}+S_{2920}+S_{1600})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock</td>
<td>0.64 ± 0.04</td>
<td>0.75 ± 0.05</td>
</tr>
<tr>
<td>Rock after extraction of bitumoids</td>
<td>0.26 ± 0.02</td>
<td>0.67 ± 0.05</td>
</tr>
<tr>
<td>Kerogen</td>
<td>1.02 ± 0.23</td>
<td>0.64 ± 0.09</td>
</tr>
</tbody>
</table>

* $S$ – peak area in IR absorption spectrum

References

Acknowledgements. This work was done with the financial support of the Government of the Khanty-Mansiysk Autonomous Okrug - Ugra (order No. 1234 of August 11, 2017).
It is essential to monitor the presence and movement of impurities in various water streams used in the power generation process using nuclear power reactors. Chloride content in nuclear reactor water is the necessary parameter. Chloride has proved to destroy intensively the anticorrosive coating of constructive materials of the equipment and tubes at concentrations greater than 100 μg/L. As a result of that, these equipment components are significantly exposed to oxygen corrosion.

The existing analyzers in-situ demand a regular calibration procedure and are very expensive. We suppose that the chloride potentiometric analyzer in-situ using Hg₂Cl₂/HgS and AgCl/Ag₂S electrode pair will demonstrate stable measurements (more half-year) and will not require calibration process during exploitation.

Technological equipment corrosion products are in technological water constantly. We assume that the corrosion products can poison the electrode pair and lead analyzer failure.

In order to simulate electrode poisoning with corrosion products, we have placed them into the experimental stand which can corrode. Electrode characteristics, background solution and deposition elemental composition were determined using direct potentiometry, inductively coupled plasma optical emission spectrometry (ICP OES), and energy dispersive X-ray fluorescence spectrometry (ED XRF) and anodic stripping voltammetry, respectively during the test.

It has been found out that:

- the redox reactions involving electrode and stainless steel components do not affect electrode quality;
- iron, nickel, and zinc as stainless steel and brass corrosion products do not cause electrode pair lifetime diminishing.

Acknowledgements. ICP OES and ED XRF measurements were performed using the facilities of “Chemical Analysis and Materials Research Centre” of St. Petersburg University Research Park.
Fractal analysis is a new cost-effective analytical method. Previously we demonstrated that there is a correlation between the fractal dimension of dihydroquercetin lyophilizates and their water solubility [1]. The aim of this work was to investigate the possibility of fractal analysis using for quality assay of biotechnology-derived medicinal product, such as bifidumbacterin.

The accelerated storage for bifidumbacterin was modeled by keeping its samples at 50 °C for 5, 15, 30, 60, 120, and 240 min. The fractality of sample’s surfaces was determined by computer analysis of photomicrographs. Fig. 1 demonstrates a logarithmic dependence between the fractal dimension of samples surface and exposure time ($R^2 = 0.9599$). The pH-value of bifidumbacterin suspension is one of the quality parameters. There was a linear dependence between the pH-value and exposure time ($R^2 = 0.9751$). Apparently the fractal analysis is more sensitive for determination of improper storage than potentiometry. So the fractal analysis could be recommended for quality assay of lyophilized active pharmaceutical ingredients.

![Graph showing fractal dimension (Fd)/time and the pH-value/time relationships.](image)

Figure 1. The fractal dimension (Fd)/time and the pH-value/time relationships.

References

Acknowledgements. This work was supported by the “Russian Academic Excellence Project 5-100”.
A modern direction in analytical chemistry is the search for new, environmentally friendly solvents as analogues of widely used organic toxic substances. Such solvents can be deep eutectic solvents (DES) that have recently appeared in analytical practice. These substances are analogs of ionic liquids, obtained by mixing the donor and acceptor of hydrogen bond. Such systems have melting points substantially lower than those of the initial components. These solvents have several advantages, such as environmental safety, high dissolving ability, and compatibility with most analytical instruments. In addition, most DESs mix well with water, but they are capable of dissolving non-polar organic solvents. This property can be effectively used to use DES as an effective dispersant in dispersive microextraction, instead of widely used organic solvents.

In our study, we demonstrated the application of DES as an effective dispersant in fully automated spectrophotometric method for the determination of chromium 6 in food products and natural waters. The detection limit was 50 µg/l, the performance of the method was 4 analyses per hour.

Figure 1. Graphical Abstract.

Acknowledgements. This work was supported by the Russian Science Foundation (project № 18-73-00111)
DETERMINATION OF URANIUM IN NATURAL WATER WITH THE USE OF GLOW DISCHARGE MASS SPECTROMETRY AND OXIDIZED NANOTUBES

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Pollution of the environment with uranium dictates the need to control the concentration of this element in natural waters to the permissible limits for the stability of ecosystems and public health. Uranium enters the environment with effluents from natural sediments, with emissions from industrial enterprises and uranium enrichment plants. The presence and accumulation of uranium in the industrial effluent of these enterprises has a toxic and carcinogenic effect on living organisms. Uranium affects all human organs and tissues, causes health problems, because it is a general cellular poison. Uranium bioaccumulates and remains for many years in bones, kidneys and liver. In 2011 WHO set maximum permissible concentration of uranium in water – 0.03 ppm, due to the strong toxicity and radioactivity of uranium in water. Therefore, continuous monitoring of uranium content is an important task for the safety and health of citizens.

To determine the low uranium content in natural waters, conservation of the studied solutions is necessary. However, this method of storage and transportation is not always simple. In this paper, as a convenient method of concentrating uranium, preserving the sample and transporting it, we used the method of sorbing uranium on sorbents. Single-layer carbon nanotubes were used as sorbents. Their surface was modified using wet chemical oxidation and synthesis with Aerosil A-380 silica.

Two schemes for concentrating uranium on the surface of the sorbent are considered: individual carbon nanotubes and nanotubes modified with silica. Direct analysis was used to determine the content of uranium in the sorbent, namely, time-of-flight mass spectrometry with pulsed glow discharge (GDMS). The most effective approach to the determination of uranium in water is the sorption of uranium on a tablet consisting of oxidized nanotubes modified with silica. The limit of detection in this case was 0.2 ppb.
Due to rare earth elements (REEs) special properties, these elements have a wide range of applications. REEs are used as catalysts in petrochemical processes, as an additive to the structural materials in the space industry, in the production of semiconductors, magnets, detectors and many others [1]. The increasing consumption of these materials leads to the increased risk to the health of workers occupationally exposed to REE. The human health effect of rare earth elements is not well studied. REEs inhibit calcium metabolism enzymes, disrupt the metabolism of proteins and nucleic acids, and cause fatty degeneration of the liver [2, 3]. Therefore, it is necessary to control the content of these elements.

Determination of rare earth elements in biological media was performed for the workers of the metallurgical plant, producing chemical and rare metals products for high-tech industries. REEs concentrations were determined in whole blood using a mass spectrometer with inductively coupled plasma Agilent 7500cx. The obtained concentrations of 14 REEs were evaluated by comparison with the reference levels [4]. Exceedance of 14 rare earth element concentrations in some blood samples was found. The multiplicity of exceedance varied from 1.32 times for yttrium to 38.5 times for europium.

References
Bisphenol A (BPA) is a polyphenol compound used in the manufacturing of polycarbonates-based plastic packaging. It is known that BPA as a carcinogen can be found in food products stored in the plastic packaging. Therefore, monitoring of BPA's content in foods and drinks is an important task for analytical chemistry. Recently, deep eutectic solvents (DESs) are presently getting increased attention from researchers in analytical chemistry as high-efficiency extraction solvents. DESs are formed by mixing two or three cheap components that are capable of interacting through the formation of hydrogen bonds, to form a eutectic mixture with a melting point lower than that of each individual component. DESs are regarded as a cheap alternative to ionic liquids. DES is easy to be produced and cheaper due to lower cost of the raw materials.

In this work, deep eutectic solvents were investigated as a new kind of dispersive solvent for effective dispersive liquid–liquid microextraction (DLLME) for the first time. After optimization of extraction conditions, the proposed approach was compared with the DLMME procedure using conventional polar, water-miscible organic dispersive solvents. The obtained results shown that polar, water-miscible organic dispersive solvents increase solubility of BPA in an aqueous phase. The developed procedure was used for the determination of BPA in three beverages samples (still water, sparkling water and Orange juice). The limit of detection of proposed procedure was 0.0003 mg L⁻¹.

Acknowledgements. Authors gratefully acknowledge financial support for research from Russian Scientific Foundation (project no. 18-73-00111).
Metal-organic frameworks (MOFs) are a new promising class of materials. These materials have found several applications including storage and separation of gases, sensors, catalysis and functional materials, but in the last decade, they have also attracted interest as stationary phase in separation technologies [1]. Their key properties are high porosity, large pore volume, high surface areas, uniform structured cavities and uniform pore size, wide possibilities of direct design of polymers. Due to this properties MOFs can be regarded as promising materials for use in gas chromatography (GC), high performance liquid chromatography (HPLC), and solid phase extraction (SPE) as a stationary phase. Impressive progress has been made in research into utilizing MOF stationary phases in HPLC and SPE during recent years [2]. The utilization of functionalized MOFs as stationary phases in both HPLC and SPE will offer well opportunities for analytes in complex matrixes.

This work is aimed to investigate the possibility of using the UIO-66 family of MOFs as a stationary phase in HPLC and solid-phase extraction, particularly for element speciation.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-13-00203).
RESEARCH ON THERMODYNAMIC PROPERTIES OF COMPLEX OXIDE NdBaCo$_2$O$_6$-$\delta$

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Perovskite-like oxide NdBaCo$_2$O$_6$-$\delta$ (NBC) has a significant oxygen nonstoichiometry and quantitative determination of thermodynamic characteristics of the processes connected with change of oxygen content is very important. The aim of this work was to determine the standard enthalpies of formation of complex oxides of NdBaCo$_2$O$_6$-$\delta$ at different values of $\delta$, partial molar enthalpy of oxygen dissolution in the lattice of complex oxide and enthalpy of the process of Co$^{3+}$ disproportion. Samples of NdBaCo$_2$O$_6$-$\delta$ were synthesized using standard ceramic technology. The single-phase nature of the samples was confirmed by x-ray phase analysis. Samples with different oxygen content were obtained by quenching after holding at a given temperature and partial pressure of oxygen. The quantitative oxygen content in the samples after quenching was determined titrimetrically. Enthalpies of formation of prepared and attested NBC oxides were determined by measuring the heat of dissolution of the oxide samples in 4M hydrochloric acid with the addition of hydrazine dihydrochloride in the amount of 1 g per 200 ml of solution. The enthalpies of dissolution of Nd$_2$O$_3$, CoCl$_2$·2H$_2$O and BaCO$_3$ in a solvent of the same composition were also measured to make a thermodynamic cycle for the calculation of the enthalpy of NBC formation. On the basis of the obtained results enthalpies of formation of NBC oxides were determined. It was found that the function $\Delta H_f$(NdBaCo$_2$O$_6$-$\delta$) = $f(\delta)$ can be divided into two sections, each of which is well approximated by a straight line. The difference between the angular coefficients of these lines allowed us to determine the enthalpy of the Co$^{3+}$ disproportion process, which was 16.6 kJ/mol Co$^{3+}$. To verify the correctness of the results obtained, the enthalpy of formation of complex oxide SmBaCo$_2$O$_{5.56}$ was similarly measured and the function of the enthalpy of formation of complex oxide of the composition LnBaCo$_2$O$_{5.56}$ on the number of lanthanide in Periodic table was made, which is well approximated by a straight line.
Precise calculations of the isotope shifts of X-ray transitions in heavy few-electron ions and in heavy neutral atoms are performed. The calculations include all contributions to the isotope shifts, namely, the contributions of the nuclear recoil effect (mass shift), the contributions of the finite nuclear size effect (field shift), and the related quantum electrodynamic (QED) corrections. The relativistic calculations of the mass and field shifts are based on the large-scale configuration-interaction Dirac-Fock-Sturm (CI-DFS) method [1]. The QED corrections to the field shift have been evaluated using approximate analytical formulas obtained in Ref. [2]. The contributions due to the nuclear polarization and nuclear deformation effects have been also estimated. The obtained theoretical results, in combination with the corresponding experimental data, can be used to determine the nuclear charge radius differences, and also for tests of QED in a new region: strong coupling regime beyond the external field approximation (i.e. beyond the Furry picture). The corresponding experiments with heavy few-electron ions are currently under preparation at GSI/FAIR facilities (Darmstadt, Germany). It is expected that with the new FAIR facilities the experimental accuracy of the isotope shift measurements will be improved by an order of magnitude, compared to the present one [3]. From the theoretical side, to meet this accuracy, one needs to evaluate all the contributions mentioned above.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No. 18-32-00275).
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Plenary Speakers
Prof. Silke H. Christiansen
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Professor Silke Christiansen is appointed full professor since 11/2013 at the Free University – Berlin, Physics department and running a research department for Nanoarchitectures for energy conversion at the Helmholtz Zentrum Berlin für Materialien und Energie, Germany. Moreover, she is running a research group in the department of Prof. G. Leuchs for Photonic Nanostructures at the Max-Planck Institute for the Science of Light in Erlangen, Germany. She received several awards including the MRS student award, a research fellowship award by the Bayerische Forschungsstiftung for a research stay at Columbia University, NY, USA and a Feodor Lynen Fellowship awarded by the Alexander von Humboldt Foundation to carry out research in silicon technology at TJ Watson Research Center of IBM, Yorktown Heights, NY, USA. Moreover, she is distinguished honorary professor at the Material Science Dept., Chungbuk University in Korea for 5 years (2014-2019). She has significant experience in the field of nano-materials for energy conversion, bio-medical sensing and opto-electronics. She advances materials based on correlated microscopies and spectroscopies for which she operates a lab@location with Carl Zeiss AG. She gained her scientific experience at various institutions in Germany and the USA, e.g. IBM’s T.J. Watson Research Center in Yorktown Heights, NY, USA, Columbia University, NY, USA, Max Planck Institute for Microstructure Physics and the Science of Light in Halle and Erlangen, Leibnitz Institute for Photonic Technology in Jena and the Friedrich-Alexander University Erlangen-Nürnberg. She has more than 350 peer-reviewed publications, more than 10 patents/- applications, more than 9900 citations and an h-index of 52.
THREE-DIMENSIONAL NANO-ARCHITECTURES IN ENERGY, BIO-MEDICAL, ELECTRONIC AND SENSING APPLICATIONS – OPTIMIZATION BASED ON CORRELATIVE MICROSCOPY AND SPECTROSCOPY AND MACHINE LEARNING

S.H. Christiansen

Complex nano-architectures of various material combinations (e.g. Si-nanostructures such as wires (NW) and cones (NC), GaN nanostructures, transparent conductive oxides e.g. Al doped ZnO, coinage metal nanoparticles e.g. wires, spheres, graphene and other 2D materials) integrated on Si wafer platforms will be presented for light absorption, light emission and sensing applications.

In this context we will show nano-material choices e.g. for surface enhanced Raman spectroscopy (SERS) and chemically functionalized SiNWs, SiNCs, GaN NWs with distinct resonances for optical sensing or distinct electrical performance in e.g. electronic nose devices based on resistors or field-effect transistors.

Materials and device optimization will rely on advanced correlated electron microscopy and spectroscopy (CORRMIC).

We will show how we utilize X-ray, electron- and ion microscopies and their analytics to acquire huge amounts of heterogeneous data with statistical significance to exploit deep learning strategies to further advance materials and device performance.
Prof. Sergei S. Sheiko
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Professor Sergei Sheiko aims at the design of novel polymeric materials with unique properties for biomedical implants, soft robotics, and enhanced oil recovery. He is currently focused on time-programmable materials with architecturally encoded physical properties. Sergei is a George A. Bush, Jr. Distinguished Professor of Chemistry and Fellow of the American Physical Society.

Before joining the Chemistry Department at the University of North Carolina in 2001, Sergei has been working on his Habilitation in Polymer Chemistry at the University of Ulm in Germany and as Postdoctoral Fellow at the University of Twente in The Netherlands. He received a PhD degree in Polymer Physics from the Russian Academy of Sciences in 1991 and BS in Molecular and Chemical Physics from the Moscow Institute of Physics and Technology in 1986.
ENCODING TISSUE MECHANICS IN SILICONE

S.S. Sheiko

Machines of the Future will synergize biomimetic mechanics with artificial intelligence. An ideal actuator should mimic muscle by being passively elastic while also efficiently converting potential energy into mechanical strokes. An ideal body material should mimic skin by being simultaneously compliant and strong to accommodate actuator motion. One drawback of biological tissues, however, is that their softness requires water, which is an unreliable engineering material. To overcome this challenge, we have developed a materials design platform that predicts mechanical properties of elastomers by engineering brush-like polymer networks. Adaptable to any chemistry, the platform harnesses architectural parameters to encode tissue-mimetic softness, firmness, and extensibility within single-chemical-component systems. Applying this platform to archetypal poly(dimethylsiloxane) (PDMS), aka silicone, we have designed simultaneously supersoft and extremely strain-stiffening materials without using solvent as a material “softener”.
Dr. Konstantin Yu Amsharov studied chemistry at Saint Petersburg State University. In 2002 he received his Ph.D from the Institute of Macromolecular Compounds, Russian Academy of Science. From 2002 to 2004 he was a postdoctoral fellow in the group of Prof. Shamanin (Institute of Macromolecular Compounds, Russian Academy of Science). In 2005, he moved to Max-Planck Institute for Solid State Research, Stuttgart where he worked with Prof. Martin Jansen on several projects in the area of fullerene chemistry and synthesis of higher and non-IPR fullerenes. From 2009 to 2012 he received his habilitation in Organic chemistry in the subject “Direct synthesis of carbon based nanostructures: buckybowls, higher fullerenes and nanotubes” at the Institute of Organic Chemistry, University of Stuttgart, Germany. From 2005 to 2013 he was a Group Leader of the “Fullerene group” in the department of Prof. Martin Jansen (Max-Planck Institute for Solid State Research, Stuttgart). Since 2014 he is leading a junior research group (Heisenberg program) at FAU Erlangen-Nürnberg. His current research focuses on developing alternative synthetic approaches suitable for preparative production of various carbon allotrope in isomerically pure form based on using of organic substrates - polycyclic aromatic hydrocarbons. The characteristic feature of the approach is a zipper mechanism of cyclization (regiospecific condensation via Ar-Ar coupling in a domino fashion) by which the regiospecificity of each condensation step is unambiguously predefined by the specially “designed” precursor structure, which allows rational synthesis of sp2-carbon based nanostructures.
Carbon based nanostructures such as fullerenes, nanographenes, nanoribbons and nanotubes display outstanding electronic properties and are currently considered as leading materials for future electronics. Despite great success in the total synthesis of complex organic molecules, the rational synthesis of large carbon-based nanostructures still remains challenging. Our methodology is based on the synthesis of polycyclic aromatic hydrocarbons which are “programed” for the fabrication of desired nanostructures via domino-like intramolecular condensation (nano-zipping). Following this strategy various carbon-based nanostructures can be synthesized very effectively by regioselective “rolling-up” of the precursor molecules either by cyclodehydrogenation or by the tandem cyclodehydrofluorination. We have found that the C-F bond “activation” can be used for effective intramolecular cyclization. The process discovered is characterized by unprecedentedly high chemoselectivity and regiospecificity. This strategy opens the possibility for the facile synthesis of extended polycyclic aromatic hydrocarbons in macroscopic amounts with exceptionally high efficiency, including nanographenes, fullerences, buckybowls, isomer-pure nanotubes, Zig-zag nanographenes, and allows the fabrication of carbon-based nanostructures directly on insulating metal oxide surfaces.

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Alexander Novikov was born and raised in Moscow, Russia. He graduated from Moscow State Pedagogical University, Moscow, Russia, in 2010 (summa cum laude) and obtain his Ph.D. (summa cum laude) at the Saint Petersburg State University, Saint Petersburg, Russia, in 2013. He has held several Researcher, Postdoc, and Invited Lecturer positions in Russia, Portugal, Finland, Sweden, and Germany. He currently is a Senior Researcher at the Institute of Chemistry, Saint Petersburg State University, Saint Petersburg, Russia. He is an Expert of the Russian Science Foundation in fields of Quantum Chemistry, Computer Modeling, and Supramolecular Chemistry and co-author of more than 100 articles in reputable international scientific journals (Scopus ID: 50262902200). His research interests include theoretical studies in the following topics: cycloaddition and nucleophilic addition reactions, their mechanisms, driving forces, kinetics and thermodynamics; consideration of the catalysis of hydrocarbons oxidation processes and their conversion to alcohols, ethers, aldehydes, ketones and carboxylic acids; investigations of various unusual types of non-covalent interactions in organic, organometallic and coordination compounds.
THEORETICAL STUDIES IN ORGANOMETALLIC AND COORDINATION CHEMISTRY: REACTIVITY, CATALYSIS, AND NON-COVALENT INTERACTIONS

Novikov A.S.¹

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My presentation will address some issues about application of advanced quantum chemical methods (ab initio and DFT) as well as some special techniques (e.g., QTAIM, NBO, CDA, BSSE-correction, isodesmic reactions, HSAB principle theoretical model, Hirshfeld surface analysis) in studies of catalytic reactions and organic transformations assisted by metal complexes, e.g. oxidation of hydrocarbons, nucleophilic addition and cycloaddition processes (mechanisms, driving forces, kinetics and thermodynamics), as well as properties of coordination and organometallic compounds (e.g. conformational isomerism and rotational barriers, properties of chemical bonds, orbital and charge factors). Also we will discuss results of my investigations in field of supramolecular chemistry and theoretical studies of unusual non-covalent interactions (e.g., hydrogen, halogen and chalcogen bonding, π-stacking, anagostic and metallophilic interactions).

Acknowledgements. This work was supported by the Russian Science Foundation (project No. 19-73-00001).
Roberto Paolesse graduated cum laude in Chemistry at the University of Rome “La Sapienza” on 1983. He started his academic career at the Department of Chemical Science and Technologies of the University of Rome "Tor Vergata" in 1986 as Assistant Professor. From 2001 to 2012 he has been Associated Professor and from 2012 he is Full Professor of Chemistry at the same Department. In 1992-1993 he was Visiting Scholar at the University of California, Davis, collaborating with the group of Professor Kevin Smith.

He has been responsible of several National and European research projects, and he is now coordinator of the FET-OPEN project INITIO within the Horizon2020 EU program. Roberto Paolesse authored more than 400 articles on international journals, six patents and edited two books. His papers received 10079 citations with a H-index=53 (source SCOPUS, September 2019).

His research interests range from the synthesis and reactivity of metal complexes of porphyrins and related macrocycles to their application as sensing materials for the development of porphyrin based chemical sensors. Since 1993 he has been involved in the development and application of artificial sensorial systems (E-nose and E-tongue). He has been among the founders of the Sensors Group of the University of Rome Tor Vergata (http://sensorsgroup.uniroma2.it), where he is now co-director with Professor Corrado Di Natale.
Porphyridiums and related macrocycles have been massively exploited as sensing materials in chemical sensors based on different transduction mechanisms. Practical applications are further allowed by using sensor arrays, where the cross-selectivity of sensing layers plays a key role for the analysis of complex matrices. The optimal design of sensor arrays greatly benefits from both the synthetic flexibility and molecular properties of porphyrinoids. Our group recently reported that sensors coated by corrole and porphyrin derivatives possess different sensing properties, proving to be a valuable team for gas and liquid phase sensor applications.
1 section

ADVANCED NANO CHEMISTRY AND NANOMATERIALS
SYNTHESE OF THE (HYDROXYAPATITE)GOLD NANOCOMPOSITE WITH THE TUNABLE PARTICLE SIZE

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Nanocomposites, including nanoparticles (NPs) of noble metals, are of great interest because of their tunable absorption and scattering of light in the UV and visible regions. Hydroxyapatite (HA) can be the basis for the uniform placement of metal NPs on its surface. The purpose of this study was to develop the methods of the (HA)Au nanocomposite synthesis under ultrasound conditions with the ability to adjust the size of gold NPs being synthesized. While the synthesis of (HA)Au, a 50 mM glucose or 15% glycerol, 0-1.0 mM sodium citrate, 0-0.8 mM HAuCl₄, 0.5 mg/ml HA were used. In the absence of HA, the formation of gold NPs in a solution of 15% glycerin or 50 mM glucose is not very effective. HA significantly accelerates the process of NPs synthesis.

Fig. TEM images of (HA)Au nanoparticles obtained in medium containing A — 0.3 mM HAuCl₄, 15% glycerol; B — 1 mM HAuCl₄, 15% glycerol; C — 0.3 mM HAuCl₄, 50 mM glucose.

For the synthesis of gold NPs of large diameter on the surface of HA, glycerin or glycerin together with sodium citrate are suitable reducing agents. The size and amount of gold NPs associated with HA depend on the HAuCl₄ and glycerin concentrations and the presence of sodium citrate in the synthesis medium. In general, the diameter of gold NPs associated with HA increases with increasing concentration of HAuCl₄ in the synthesis medium (Fig. A, B). The use of glucose to obtain gold NPs with a diameter greater than ~ 30 nm leads to the agglomeration of gold NPs (Fig. C). The use of glycerin or glucose as a reducing agent together with sodium citrate in the synthesis medium in vitro leads to the formation of gold NPs of smaller diameter on HA grains, than using only glycerin or glucose alone.

Thus, the obtained nanocomposites can be used in the technique of resonant light scattering, based on the effect of the migration of plasmon resonance energy.
PHYSICOCHEMICAL PROPERTIES AND BIOLOGICAL ACTIVITY OF C₆₀ FULLERENE DERIVATIVE WITH L-ARGININE

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Water-soluble fullerene derivatives including adducts with amino acids can be considered as perspective compounds due to their antioxidant, antibacterial, antimicrobial and anticancer activity [1-3]. At the same time, it is important to carry out physicochemical investigation of these derivatives and to establish interconnection between their structure and behaviour in solid state, solutions, as well as biological activity.

This research is devoted to physicochemical and biological investigation of C₆₀-Arg aqueous solutions. In the framework of our study, the measurements of density (ρ), viscosity (η), refraction index (nD), nanoparticles’ size dimensions (δᵢ), zeta potential (ζᵢ), as well as experiments on binding with human serum albumin (HSA), antioxidant activity in the reaction with DPPH were conducted. Finally, the dynamic characteristics of two C₆₀-Arg isomers (Fig. 1) in aqueous solutions with the use of molecular dynamics simulation were studied.

Figure 1. C₆₀-Arg isomers with uniform (left) and equatorial (right) distribution of L-arginine residues.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-015-00469).
SYNTHESIS AND CATALYTIC PROPERTIES OF GOLD NANOPARTICLES FORMED IN THE PRESENCE OF GUANOSINE MONOPHOSPHATE


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It has been recently shown that DNA can reduce HAuCl₄ affording particles with mean size of 2 nm [2]. Our aim was to investigate the ability of guanosine monophosphate (GmP) which is a structural unit of DNA to reduce Au(III) in the solution and to analyze catalytic properties of the formed Au NPs. The interaction of HAuCl₄ with GmP was studied at different ratios of GmP to Au in the solution. The GmP-Au complex was formed upon addition of HAuCl₄ to GmP solution. TEM analysis revealed the presence of nanoparticles only at the DNA/Au ratio below unity, after 48 hours (fig. 1). Reduction of 4-nitrophenol catalyzed by the obtained Au NPs was monitored by electronic absorption spectroscopy. No spectral changes were observed upon addition of 1000-fold excess of NaBH₄ to a solution of 4-nitrophenol and NaBH₄, evidencing that no reaction occurred in the absence of Au NPs. However, the addition of Au NPs induced rapid color change of the mixture. In summary, mixing GmP solutions with HAuCl₄ resulted in the Au-GmP complex and Au NPs formation, and the reduction of 4-nitrophenol to 4-aminophenol with sodium boron hydride was catalyzed by the Au nanoparticles obtained in the presence of GmP. The rate constant of 4-nitrophenol reduction catalyzed by Au NPs prepared in the presence of GmP 0.6s⁻¹ was an order of magnitude higher in comparison with those formed in the presence of DNA or glucose 6.54*10⁻³ s⁻¹. The difference in the catalytic properties was likely due to the difference in the particles size.

References
Acknowledgements This study was financially supported by the Russian Foundation for Basic Research (project no. 17-08-01087).
SYNTHESIS AND PHASE FORMATION OF FLUORIDES IN MOLTEN NITRATE FLUX

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Inorganic fluorides gain a lot of attention due to their optical properties. These are applied as materials for photonics. Fluoride matrixes doped with rare-earth elements have biomedical applications. Metal fluorides can be prepared using a broad variety of techniques. However, almost all of them face the problem of hydrolysis, which leads to accumulation of oxygen impurities in samples. In this work we report a molten-salt synthesis (MSS) of metal fluorides with NaNO₃ as a flux. Batsanova et al. [1] was the first who reported about preparation of metal fluorides from nitrate fluxes. The key idea of this method is to lower melt point of system by adding sodium nitrate as a flux. NaNO₃ have eutectic points with alkali-earth metal nitrates which were used as precursors. NaNO₃ acts as a medium to carry out the reaction. We have used sodium fluoride (NaF) as fluorinating agent. Typical chemical reaction can be described by following equation:

M(NO₃)₂ + 2NaF → MF₂↓ + 2NaNO₃

We have obtained individual calcium and strontium fluorides using MSS [2]. Scanning electron microscopy (SEM) images of prepared SrF₂ powder presents well-formed microcrystals with 0.8–10 μm diameter. CaF₂ microcrystals have same sizes without determined habit. Energy dispersive x-ray (EDX) analysis revealed that samples of individual metal fluorides have no major impurities and they are oxygen-free.

Up-conversion nanomaterial with fluorite matrix CaF₂:Er³⁺, Yb³⁺, Na⁺ was produced by MSS. Particles have spherical shape with 60–120 nm diameter. Sample has two emission lines in spectra 510–560 nm and 625–680 nm under 980 nm laser excitation. Obtained luminescent material does not require additional thermal treatment and have 1.2 % quantum yield.

References

Acknowledgements. Voronov V.V. Baranchikov A.E., Kuznetsov S.V., Yapryntsev A.D.
DIRECT LASER SYNTHESIS OF COPPER-SILVER MICROCOMPOSITE FOR D-glucose AND L-alanine SENSING

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Modern scientific directions in the field of biosensors involve the modification of electrodes by nanomaterials instead of the use of enzymes as sensor-active elements. This facilitates charge transfer, prevents denaturation of molecules on the electrode surface, and increases the effective surface area of an electrode [1].

There are two most used synthetic methods for preparing microcomposite electrodes: in situ laser-induced deposition technique and direct laser sintering. The first one includes continuous laser irradiation of aqueous solutions, containing metal salt as an oxidizing agent and some reducing agent. Direct laser writing is pulsed laser irradiation of the previously spin-coated mixture of metal oxide/ salt, reducing agent and some polymer (PVP, for instance) as a linking agent.

In this work, we reported in situ laser-induced synthesis of sensor-active copper-silver microcomposite. This bimetallic microelectrode exhibits highly developed surface area and good electrical conductivity, and can be successfully used for glucose and alanine sensing demonstrating decent sensitivity (31,000 μA cm⁻² mM⁻¹ for D-glucose and 11,177 μA cm⁻² mM⁻¹ for L-alanine) and low limit of detection (2.8 μM for D-glucose and 0.83 Mm for L-alanine).

Fig. 1. SEM image and EDX spectra of copper-silver microelectrode.

References

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NEODYMIUM AND CERIUM CONTAINING APATITES WITH SLOW MAGNETIC RELAXATION

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Slow magnetic relaxation is a remarkable property of so called single-ion magnets (SIM): such compounds could retain a macroscopic magnetic moment during a certain time after removing magnetic field but this is an individual property of each magnetic ion. The majority of modern SIM represents magnetic ions surrounded by a volumetric organic ligands that provides a strongly anisotropic geometry. Interestingly that such conditions could be realized inside the inorganic solid state apatite matrix. Indeed we have recently found the slow magnetic relaxation of dysprosium [1] and terbium [2] that partially replaced alkaline earth cations in hydroxyapatite. Moreover the most impressive dysprosium containing sample is characterized by very high remagnetization energy barrier up to 1043 cm⁻¹. In this work we expand our research and have synthesized and studied calcium hydroxyapatites containing neodymium and cerium.

Nearly monophasic compound with nominal composition Ca₄.₇₅Nd₀.₂₅(PO₄)₃O₀.₇₅(OH)₀.₇₅ was synthesized by solid state synthesis. Structure refinement by the Rietveld method shows that neodymium is surrounded by 7 oxygens (6 from phosphates and one that is oxygen anion) but with one much shorter distance to the last one. Thereby neodymium forms “NdO⁺” cation with highly anisotropic geometry. This sample demonstrates the slow magnetic relaxation with narrow distribution of relaxation times and high compared with other Nd-based SIM remagnetization barrier of 93 cm⁻¹.

The synthesis of analogical cerium containing compound is less successful: the product is polyphasic but the main phase is characterized by apatite structure and contains cerium cations that partially substitute calcium. This phase also demonstrates slow magnetic relaxation with high remagnetization energy barrier of 163 cm⁻¹.

References

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SYNTHESIS AND PROPERTIES OF N-METHYL-1-[4-CYTIZINOPHENYL]FULLERENE-C\textsubscript{60}[1,9C]PIRROLIDINE


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The presence of C\textsubscript{60} and lipophilic properties membranotropic important for developing drugs against the pathogen of various infectious diseases [1]. However, at the present time is not yet established common biological effects and possible toxicity when used on live sites. In asking these questions is an interesting study of the fullerene derivative known in medicine drug. In line with this trend we conduct a study of synthesis and properties of the fullerene derivative – N-methyl-1-[4-cytizinophenyl]fullerene-C\textsubscript{60}[1,9]pirrolidine (1). Reacting C\textsubscript{60} with N-methylglycine (sarcosine) and 4-cytizinilbenzaldehyde (Prato reaction [2]) in refluxing toluene under argon for 20 hours resulted in the formation of N-methyl-1-[4-cytizinophenyl]fullereneC\textsubscript{60}[1,9]pirrolidine (1). Unreacted starting materials and product (1) after the reaction were separated by column chromotatography on SiO\textsubscript{2}, eluting with hexane and then with hexane-toluene (1:1) (yield 38%).

![Chemical structure of C\textsubscript{60} and starting materials](image)

The structure of the synthesized compound (1) is proved by IR, \textsuperscript{1}H- and \textsuperscript{13}C-NMR spectroscopy.

References
α-Amino acids are among the most important biologically active substances, which in living organisms are the structural elements of proteins and endogenous compounds. Amino acids and their mixtures are widely used as additives in food production, active components of pharmaceutical preparations for parenteral and sports nutrition, treatment and prevention of diseases. The content of amino acids in foods and medicines is strictly regulated, since the therapeutic effect is achieved at a certain concentration of the biologically active substance. Arginine (Arg) is a semi-essential amino acid, an important part of the diet of animals and humans, and plays a significant role in the urea cycle and energy metabolism. Arginine promotes wound healing and stimulates the release of various hormones and enzymes. Therefore, the development of a sensitive method for quantifying Arg in biological fluids has a profound effect on the diagnosis of diseases.

A promising approach for the determination of arginine is spectrophotometric registration of the change in the color of silver nanoparticles (NPs) as a result of their aggregation in the presence of arginine. The purpose of this work was to assess the possibility of using silver nanoparticles for the spectrophotometric determination of arginine.

Silver nanoparticles were synthesized by borohydride and citrate methods and their size and optical properties were investigated. Spectrophotometric determination of arginine by its own absorption in the visible region is impossible. However, silver NPs can act as a spectrophotometric reagent for the determination of arginine in connection with their possible aggregation and the associated displacement of the surface plasmon resonance band (SPR). It was shown that in the case of silver nanoparticles synthesized by the citrate method, no changes were observed in the absorption spectra of NPs in the presence of arginine, which is probably due to the too large size of silver NPs. In the case of silver NPs synthesized by the borohydride method, a shoulder in the region of 500 nm is formed on the absorption spectra in the presence of arginine. In this case, there is a linear dependence of the optical density at $\lambda = 500$ nm versus arginine concentration in the range of $5 \cdot 10^{-4}$ - $8 \cdot 10^{-3}$ M, the square of the approximation coefficient was 0.98.
Dissolution and Dilution Enthalpies of the Ternary System MgCl₂-CsCl-H₂O at 298,15 K

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Multicomponent water-salt systems are ubiquitous in nature, and also are extremely useful for industrial applications, so their study is of particular scientific interest. Water-based systems are environmentally beneficial alternative to many of the currently available technologies. There is no problem of utilization for such systems, since their components are part of natural soils, also multicomponent water-based electrolyte solutions are refrigeration agents and exhibit properties similar to inorganic non-toxic ionic liquids [1]. The thermodynamic description of water-salt mixtures containing ions of alkali and alkaline-earth metals contributes to their spread use [2]. In this study, a multicomponent water-salt system including magnesium and cesium chlorides MgCl₂-CsCl-H₂O was studied at a molar ratio of Cs/Mg=1/1.63. The dissolution enthalpy of double magnesium-cesium chloride MgCl₂∙CsCl∙6H₂O was determined by the calorimetry method. The thermal effects of dilution were determined by the method of differential dilution calorimetry. Based on the experimental results obtained and the water activities [3], activity coefficients and chemical potentials of water were calculated. Relative partial molal enthalpies of dilution and entropy were also calculated. These dependencies were presented in the form of composition-property diagrams and analyzed for the coincidence of inflection points with the position of the eutectic region for these systems.

References:

Acknowledgements: Scientific measurements were performed in the Research Park of the Saint Petersburg State University “Thermogravimetric and Calorimetric Research Centre”
PHOTOSENSITIZERS BASED ON CYCLOMETALATED COMPLEXES OF D6-METALS FOR DYE-SENSITIZED SOLAR CELLS


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The most important component in Grätzel solar cells (DSSC) is the sensitizing dye responsible for absorbing light and participating in the charge separation process. The improvement of the photosensitizer is based on knowing how specifically the variation of ligands or metal affects the target optical and electrochemical characteristics of the complex, as well as its stability. Herein, we present the results of our study aimed at creation of a model of the dye, which establishes the main factors affecting the properties of the photosensitizer and their (factors) connection with the structure and electronic properties of ligands and metal.

\[ \text{antenna ligand} \]

M = Ir, Rh

\[ \text{anchoring ligand (X = N, O)} \]

2, 2'-bipyridines, dipyrrines, aromatic 1, 3-diketones, dipyridophenazines

Figure 1. Complexes in this study.

More than 40 new coordination compounds of iridium (III) and rhodium (III) were synthesized and comprehensively studied. The influence of both types of ligands (antenna and anchoring) on stability, as well as optical and electrochemical properties of the complexes, have been established, which made it possible to significantly improve the very primitive dye model that was previously available. Based on this model, an integrated approach has been developed, consisting in the rational selection of metal and ligands, and aimed at obtaining stable and effective photosensitizers for solar cells. The use of this strategy allowed us to synthesize a number of dyes, which demonstrated good stability and efficiency when performing in DSSC.

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INFLUENCE OF MORPHOLOGY ON THE CAPACITANCE PROPERTIES OF CeO₂ NANOPARTICLES

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CeO₂ nanostructures of different morphology were synthesized under hydrothermal conditions. The structure, elemental composition, shape and size of the obtained nanoobjects were analyzed using the X-ray diffraction, energy-dispersive X-ray spectroscopy and transmission electron microscopy. It was shown that hydrothermal treatment of cerium nitrate at 180°C, 15 MPa in strongly alkaline solutions for 24 hour leads to the formation of cubic CeO₂ nanoparticles with a wide size distribution. In case of carrying out the synthesis at lower temperatures and simultaneously increasing the alkali content in the composition of the hydrothermal medium, CeO₂ crystallizes in the form of rods with a diameter of 10 nm and a length of 200 nm.

Electrochemical properties of prepared oxides were tested in standard 3-electrode cell. The working electrodes were prepared by dispersing of oxide in the DMF solution containing carbon black, PVDF. The glass carbon electrode with working area 1.3 cm² was covered with 0.3 ml of prepared dispersion and dried at 60 °C. Cyclic voltammetry and galvanostatic charge discharge experiments were performed with the CeO₂ with different morphology in the potential range -0.2V – +0.5V vs Ag/AgCl reference electrode. The results demonstrate that CeO₂ in the form of cubes has significantly higher specific capacitance in comparison with CeO₂ rods. This can be attributed to the difference in the specific surface area of these oxides.

Acknowledgements. The reported study was funded by RFBR according to the research project № 18-03-01167 A.
A NEW WATER-SOLUBLE FULLERENE DERIVATIVES WITH FOLIC ACID

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It is known that the number of expression or activity of folate receptors on most tumor cells is significantly higher than the corresponding values for normal cells [1]. In this regard, derivatives of fullerenes and endohedral metallofullerenes with folic acid can be promising agents for targeted cancer therapy using photodynamic therapy, chemotherapy, radiofrequency thermal therapy, radiotherapy [2, 3]. In this work, new water-soluble fullerene derivatives with folic acid have been obtained. The structure of the obtained derivatives was investigated by using UV-VIS, FT-IR and elemental analysis. The aggregation properties of the derivatives were characterized by DLS.

Figure 1. UV-VIS spectra of folic acid (1) and fullerene derivatives with folic acid (2): a — in NaOH 0.1M, b — in water

References
NOVEL HYBRID CARBON FLAKES – OPTICAL INVESTIGATION USING MICROSCOPIC MÜLLER MATRIX MEASUREMENTS

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We present a microscopic Müller matrix technique [1,2] to optically characterize Danilova e a unique carbon-metal hybrid material fabricated by laser induced deposition [3]. These carbon flakes exhibit an orthorhombic carbon matrix intercalated with bi-metal nanoparticles. Due to the small lateral dimensions of the flakes (microns), standard optical measurement techniques cannot be applied. We use a custom-made system to perform a detailed polarization analysis of individual carbon flakes using two liquid crystals variable retarders [4]. The experimentally measured Müller matrix reveals the optical properties of the material such as attenuation and birefringence [5]. The investigated structure shows wavelength-dependent attenuation and strong optical birefringence on the order of 0.1, which is constant across the visible spectral range [2].

References
HALOGEN BONDING OF BROMOFLUOROBENZENES WITH BROMIDE DIMETHYLICYANAMIDE PLATINUM (II) COMPLEX

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Halogen bonding (XB) is widely applied in different areas such as supramolecular chemistry, crystal engineering, catalysis, etc. Although the vast majority of XB research does not include organometallic compounds, the application of these substances as XB participants is very useful for the design of new materials.

Iodoperfluorobenzenes are XB classic donors for both organics and metal complexes. Meanwhile their bromo-analogs were poorly investigated in cocrystallization with metal complexes.

In this work, we studied the cocrystallization of 1,2-bromotetrafluorobenzene, 1,4-dibromotetrafluorobenzene, and bromopentafluorobenzene with trans-\([\text{PtBr}_2(\text{NCNMe})_2]\), since this complex was investigated by us as an interesting XB acceptor [1]. In all structures of the adducts of the complex with bromoperfluorobenzenes, the C–Br⋯Br–Pt XB were detected by single-crystal XRD experiments. In the cases of dibromotetrafluorobenzenes, this halogen bonds provide the construction of infinite supramolecular chains.

![Figure 1. Objects of research.](image)

References
SYNTHESIS, CHARACTERIZATION AND FUNCTIONAL PROPERTIES OF COMPOSITE NANOPARTICLES BASED ON Fe3O4 AND ACYCLIC DIAMINOCARBENE COMPLEXES OF Pt(II) AND Ir(III)

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Organo-inorganic hybrid nanoparticles (NPs) are complex systems consisting of an oxide core, a NP, a spacer, and a metal complex. As the core of the NPs can act as iron oxide NPs that can exhibit magnetic properties; in the role of a spacer, various organic substances are used that contain functional groups, namely, polymers and biologically active compounds and organic complexes of transition metals with ligands of various nature act as a metal complex. The constituent components of hybrid particles are able to exhibit different physicochemical properties, but at the moment there are no studies of the mutual influence of the parts of the system on each other.

The aim of our work is to develop and optimize the approach to the synthesis of hybrid organic-inorganic NPs of a given functionality due to the combination of the nature of the core, the spacer and the metal complex. NPs of iron oxide, polyethylene glycol of various molecular weights and isoanide iridium complexes were chosen as objects of study.

The first step includes the preparation of magnetite NPs by a typical co-precipitation procedure. In the next step, the magnetite surface was coated a SnO2 layer with a thickness of 2 nm using SnCl4 and NH4OH. Then, polyethylene glycol (PEG-300 and 3000) was grafted to as-prepared NPs by activating the surface OH- group using chloride ions. The terminal PEG hydroxyl groups were modified by APTES. This allowed us to introduce amino group for the subsequent addition of the metal complex. All stages of the synthesis were characterized by a complex of physicochemical methods such as FTIR spectroscopy, elemental analysis, TGA-DSC. Magnetic and optical properties of as-prepared samples with complex structure are also under discussion.

Acknowledgements. This work is financially supported by RFBR grant 18-03-01066.
Scientific research was performed at the Research Park of St. Petersburg State University Educational Resource Center of Chemistry: Centre for X-ray Diffraction Studies, Center for Optical and Laser Materials Research, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.
NEW CHROMOPHORES CONTAINING 2,5-DI(THIOPHEN-2-YL) 1H-PYRROL-1-YL FRAGMENT: SYNTHESIS AND INVESTIGATION OF OPTICAL AND ELECTROCHEMICAL PROPERTIES

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The synthesis and investigation of a new set of N-substituted 2,5-di(thiophen-2-yl)-9H-pyrroles are presented. Spectral and electrochemical characteristics as well as the frontier orbital energies and HOMO/LUMO gaps of the compounds synthesized have been evaluated and described [1-2].

References

The work was supported by the Russian Foundation for Basic Research (project No 19-43-590014).
PEROVSKITES AS NEW CATALYSTS AND ANTIBACTERIAL MATERIALS

Chislova I.V. 1, Yafarova L.V. 1, Sokolova E.S. 1, Chislov M.V. 1, Khabibulina V.R. 1, Zvereva I.A. 1, Borodina E.M. 2, Sheshko T.F. 2

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Complex oxides with perovskite structure have long been in the focus of researchers' attention and have already found their application in the chemical, electronic industry, energy, catalysis and other fields. Despite of the extensive study of perovskites in many areas of science, the study of their antibacterial activity has only begun to develop. At present, due to the reduction of oil resources and the increase in their cost, interest in alternative sources of light hydrocarbons is increasing. Fischer-Tropsch synthesis is the most promising way to obtain them, as it allows from the simplest substances, carbon monoxide and hydrogen, to obtain the most valuable organic compounds, among which the target or most valuable components are light olefins.

In this paper, we evaluated the catalytic and antibacterial activities of complex oxides with the perovskite structure GdCo$_{1-x}$Fe$_x$O$_3$, GdMn$_{1-x}$Fe$_x$O$_3$ and GdCo$_{1-x}$Mn$_x$O$_3$ ($x=0; 0.2, 0.5, 0.8; 1$).

Studies on the catalytic activity in the Fischer-Tropsch process were carried out in a flow-through catalytic unit at different component ratios (CO:H$_2$) at atmospheric pressure in the temperature range of 523-708 K. It was found that perovskites exhibit resistance to carburization in the Fischer – Tropsch process, and stability after high-temperature processes.

Antibacterial activity was investigated using gram-negative bacteria - Escherichia coli by two methods diffusion method for agar and Shake-Flask method. MBC were determined.

As a result, it was shown that complex oxides GdCoO$_3$, GdFeO$_3$ and GdMnO$_3$ exhibit better antibacterial activity when replacing part of the transition metal atoms on other transition metal atoms.

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IMPACT OF THE ACTIVATING ABILITY OF NANOSTRUCTURED CARBON ON THE WORK OF THE NEGATIVE ELECTRODE OF A NEW-GENERATION SEALED LEAD-ACID BATTERY

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Lead-acid batteries are the most demanded ones in the world market, covering various areas of technology such as nuclear and thermal energy, military equipment and many others. One of the main problems of lead-acid batteries is the process of sulfation of the negative active plate under conditions of high-speed partial charge, which limits the battery life. The solution of this problem is the addition of carbon components to the negative active mass of the plates.

The purpose of this work was the structural and electrochemical properties studying of the negative electrode with various carbon additives for the SKA.

Carbon technical extended Art Nano GT (TU VU 691460594.004-2017)(Perspective Research and Technology, Minsk), Art Nano GT (treated with ozone), Art-nano GT (processed by DMF), (LLC Advanced Research and Technology, Minsk), carbon nanostructured technical activated Art Nano, brand NSU S (TU BU 690654933.001.-2011), Art Nano NSU “C” (ozone treatment), “Art-nano” of the NSU “S” brand (DMF treatment) (Promising Research IAOD and technology, Minsk) were used as a carbon additives in the negative mass of the lead electrode. The content of the carbon additives was 0.5, 1 and 1.5 wt.%

It was found that with the addition of carbon components, the discharge capacity and the utilization rate increase compared with electrodes without carbon additives, regardless of the concentration of carbon. And the addition of such components make pores increasing in with a radius of less than 0.1 μm, regardless of the amount of introduced carbon.

The morphology of the surface of negative electrodes with carbon additives with 1 wt.% concentration at the 6th charged cycle was investigated. It showed that samples with carbon additives have rounded crystals with smaller sizes, the structure is more branched, which is related with the addition of carbon particles into the volume of the active mass. Carbon particles are electrically conductive, and the electrochemical reaction of lead ion reduction can occur on their surface. The newly formed lead surrounds carbon grains and includes in the volume of the negative active mass.

The addition of carbon particles in the amount of 1 wt.% showed the best electrochemical properties.
Cationic metal-organic frameworks are of distinct interest due to abilities for incorporation of anions for catalytic, photochemical, selective sorption and separation applications. Using neutral ligands is the method to synthesize cationic MOFs specifically. For example, di-N oxide bridges are promising building blocks due to unusual topologies of coordination networks forming, as well as easy coordination to the wide range of oxophilic metal centers. [1] Coordination polymers based on N-oxides are quite rare. In particular, just a few examples of 1,4-diazabicyclo[2.2.2]octane di-N-oxide (odabco) - based MOFs are reported in the literature. But, odabco containing coordination polymers and organic adducts were shown to have ferroelectricity and thermally induced phase transitions [2-3] (e.g. breathing) which are related to the axial rotation of odabco bridge fragments. So, we purposed to investigate odabco as a ligand in a wide range of solvothermal systems (different solvents, temperatures, transition metal salts, reagent ratios etc.) and obtained a series of M$^{2+}$ and M$^{3+}$- based compounds. The impact of different synthetic conditions on the forming structures is discussed in detail.

References

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Currently, the use of semiconductor films as multisensory systems for analytical chemistry is being actively studied [1]. One of the main problems is obtaining reproducible, selective and highly sensitive detectors. This is impossible without a basic research of the relationship between the chemical composition of films, their morphology and functional properties. This report presents the results of the study of nanoscale films of different composition based on tin dioxide used as a detector for capillary gas chromatography. The studies were carried out using scanning electron microscopy, X-ray fluorescence and gas chromatography-mass spectrometry [2]. The effectiveness of the films is illustrated by the examples of the analysis of test systems (fig. 1). An algorithm for calculating the identification features of various classes of organic compounds is also proposed.

Figure 1. Left - scanning electron microscopy image of sensor surface. Right - The response of the sensor unit to different mixtures.

References
PHASE TRANSITIONS AND ELECTRICAL PROPERTIES OF Ag₂Se THIN FILMS FORMED BY LASER ABLATION

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Silver selenide in alpha modification has a wide range of interesting properties, first of all, high ionic conductivity. The alpha modification of Ag₂Se, stabilized at room temperature, is a perspective material for the creation of electronic elements, such as batteries and chemical current sources. The electrical properties, phase transitions, and crystallization features of thin silver selenide films obtained by laser ablation were studied. In a multilayer sample consisting of alternating layers of Ag₂Se and oxide glass silver selenide in alpha modification was detected at room temperature.

This work was supported by the Russian Foundation for Basic Research (project No 17-03-00121) All studies were carried out in the Researchpark of St. Petersburg State University.
TRANSMITTING METAL-OXIDE INTERACTION BY SOLITARY CHEMICAL WAVES: H2 OXIDATION ON ZrO2 SUPPORTED RHODIUM

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Catalytic hydrogen oxidation has been studied since the times of Faraday (1834) [1]. The increasing experimental and theoretical efforts in recent years, caused by the growing importance of hydrogen based energy generation in fuel cells, have resolved the intermediate reaction steps and shed light on the accompanying spatiotemporal effects from the nm- to the µm-scale [2]. Nevertheless, the formation of water by oxidation of hydrogen on noble and other transition metals remains a complex reaction with many interesting and unexplored features. For example, the interaction of catalytically active metal nanoparticles with the supporting oxide surfaces is still a research challenge. Particularly, the exact role of metal-support boundary effects, caused by the active sites along the metal-oxide interface, is not entirely clear. Recently, a long-range effect of metal-oxide boundaries in CO oxidation on oxide supported Pd was detected

Here we demonstrate a similar effect in a Rh/ZrO2 model system on the reactivity of Rh in H2 oxidation. The atomically narrow (<1 nm) interface between a Rh particle and ZrO2 causes a remarkable shift in the kinetic behavior of the entire µm-sized particle, i.e. affecting metal sites thousands of nanometers away from the interface. The effect was directly observed by photoemission electron microscopy (PEEM) using the kinetics by imaging approach [4], which allows the evaluation of reaction kinetics for individual supported particles within the resolution limit of PEEM. The observed effect is attributed to the critical role of the perimeter sites for the initiation of activation and deactivation fronts (chemical waves) during H2 oxidation, which transmit the metal-oxide interface effect over the entire Rh particle.

References

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SYNTHESIS AND AGGREGATION PROPERTIES OF MONOSUBSTITUTED PILLAR[5]ARENES CONTAINING \(N\)-ALKYLAMIDE AND \(N\)-(AMINOALKYL)AMIDE FRAGMENTS

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In recent decades, the attention of researchers is attracted to supramolecular polymers, due to their interesting chemical properties. Architectural and dynamic parameters which determine polymer properties, such as degree of polymerization and molecular weight, are a function of the strength of the noncovalent interaction, which can reversibly be adjusted. A unique macrocyclic platform for the synthesis of supramolecular polymers is pillar[n]arenes discovered in 2008. The introduction of various substituents into the structure of pillararenes allows the creation of new macrocyclic receptors with unique properties. The synthesis of pillar[5]arenes containing primary and secondary amino groups is a complex problem, solution of which leads to new compounds with practically useful properties. The functionalization of pillar[5]arene platform by the amide fragments, which can form hydrogen bonds, results in pre-organization of the macrocycle structure and provides coordination centers as a control element for self-organization. In the course of the study, we synthesized monosubstituted pillar[5]arenes containing \(N\)-alkylamide and \(N\)-(aminoalkyl)amide fragments [1]. The structure of the obtained macrocycles was confirmed by a complex of physical methods of NMR \(^1\)H, \(^{13}\)C and IR spectroscopy.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No. 18-33-00276 mol_a).
Layered double hydroxides (LDH) are compounds consisting of brucite-like layers, in which part of divalent cations are isomorphically substituted by trivalent ones. Arising positive charge is compensated by anions, which are located in interlayer space. LDHs can be represented by the following formula:

\[
[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-x/n}\cdot yH_2O]^{x-},
\]

where M(II) and M(III) are divalent and trivalent cations respectively, and An is n-valent anion. Incorporation of rare earth elements may allow to obtain materials possessing specific optical, electronic and magnetic properties [1, 2]. Co/Al-Ce layered double hydroxide was synthesized by coprecipitation method followed by hydrothermal treatment. The technique and synthesis conditions were chosen based on our previous work [3], in which nickel-aluminum-cerium LDH was successfully synthesized. Sample was prepared with an atomic ratio M(II)/M(III) = 3 and Ce³⁺/(Al³⁺ + Ce³⁺) = 0,05. The obtained compound was explored by powder X-ray diffraction, energy-dispersive X-ray spectroscopy, transmission electron microscopy, thermogravimetric analysis and differential scanning calorimetry.

Analysis results show that the synthesized material is layered double hydroxide with rather high crystallinity and it doesn’t contain any phase impurities. EDX indicates the presence of cerium, so we can admit an incorporation of rare earth element into the layered structure. Crystal lattice parameters were calculated using PDXL program: \(a = 3.01\ \text{Å},\ \ c = 22.811\ \text{Å}\).

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project № 18-43-310011 p_a). The work was carried out using the scientific equipment of joint research center “Technologies and Materials” of NRU “BelSU”.
MoS2 is one of the most studied transition metal dichalcogenides, and is considered to be a promising in electrocatalysis, photocatalysis, as a cathode material, and in other areas. Modifying MoS2 by doping we can produce materials with the necessary electronic properties. Solid solutions based on MoS2 doped with non-isovalent metal atoms (electron-rich Re and electron-deficient Nb compared to Mo) and chalcogen atoms are investigated within this work using X-ray photoelectron (XPS) and X-ray emission spectroscopy (XES).

X-ray photoelectron spectra and X-ray emission spectra of the core and valence levels of compounds with composition Mo1-xMxS2 (M=Re, Nb, x = 0.05, 0.1, 0.15), MoS2-xQx, (Q=Se, Te, x = 0.1, 0.15, 0.2, 0.25), which give information about the charge state of atoms included in the structure and their contribution to the chemical bond, were analyzed. The results of XPS Mo3d and S2p spectra analysis of Mo1-xRexS2 are consistent with hypotesis that Re atoms replace Mo atoms; in this case, electron density is delocalized from Re atoms to nearby Mo and S atoms. XPS Re4f spectra of the Mo1-xRexS2 samples show that the formation of Re dimers occur in a whole range of Re concentrations. When the Re concentration reaches 15% large island-like clusters are formed.

The change in partial Mo3d and S3p DOS after doping can be studied using Mo Lβ2.15 and S Kβ XES. Contributions to deeper energy range of Mo4d DOS upon doping with both metal and chalcogen are increase significantly. On the contrary, contributions of S3p to DOS after doping with metal atoms changes insignificantly and redistributes with the replacement of chalcogen. It is associated with an increase in the ionic radius of the dopant, because the difference of ionic radii leads to a significant distortion of the crystal lattice and therefore the electronic structure of MoS2.
EFFECT OF NANOSTRUCTURED CARBON IN THE NEGATIVE ACTIVE MASS OF A LEAD-ACID BATTERY: AN IMPEDANCE SPECTROSCOPY STUDY

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Lead-acid batteries (LAB) are the undisputed leaders in the field of automotive, stationary and traction batteries. However, when used in hybrid electric vehicle (HEV), irreversible sulfation of negative active mass (NAM) occurs in high-rate partial-state-of-charge (HRPSoC) conditions, which significantly limits the battery life. The actual direction of solving this problem is the introduction of additives of various types of carbon.

The purpose of this work was to study the structural and electrochemical properties of the negative electrode with the addition of carbon for the LAB. As carbon additives in the NAM of the lead electrode, multi-walled carbon nanotubes (“Art-nano” NSU “S” (TU BU 690654933.001-2011)) and multilayer graphene (“Art-nano GT” (TU BU 691460594.004-2017)) were used (manufactured by «Advanced Research & Technologies» LLC).

It was obtained that the introduction of carbon additives in the amount of 1 mass. % increases discharge capacity, NAM utilization ratio and number of cycles when tested under HRPSoC conditions.

The methods of impedance spectroscopy were used to study the processes occurring at the negative electrode. An equivalent electrical circuit was proposed, which included the ohmic resistance of the electrolyte $R_1$, the $C1-R2$ block associated with a thin tightly packed film of lead sulfate, and the parallel-connected $CPE1-R3$ block associated with the porous structure of the electrodes. The calculation of the elements of the proposed equivalent circuit showed the change in resistance values $R3$ associated with the porous structure of the electrodes. The study of the structural characteristics of the electrodes showed that in the presence of carbon additives, the formation of pores with radii of less than 0.05 microns, an increase in the total porosity and specific surface of the electrodes occurs. A mechanism is proposed for the effect of carbon additives on the process of sulfation of negative LBA electrodes.
Supercapacitors have become one of the most promising energy storage systems, since they are characterized by high power density, fast charge-discharge, and long-term cyclic stability. However, the initially low energy density is inherent in traditional supercapacitors, which limits their widespread use, prompting researchers to develop new types of supercapacitors with improved characteristics. Asymmetric supercapacitors assembled using two dissimilar electrode materials have a clear advantage due to the wider voltage window, which allows a significant increase in energy density.

The purpose of this work was to study the electrochemical properties of carbon-based electrodes based on nanostructured NSU “S” (TU BU 690654933.001.-2011) and carbon of the technical advanced “Art-nano GT” (TU VU 691460594.004-2017) (manufactured by Advanced Research and Technology LLC ) and establish the possibility of its use in an asymmetric supercapacitor in an aqueous electrolyte.

Electrochemical properties were studied by the methods of cyclic voltammetry and galvanostatic. It was found that carbon Art-nano GT is not suitable as a material for the electrodes of an asymmetric supercapacitor in an aqueous electrolyte. The electrodes prepared from this carbon grade had satisfactory mechanical properties, only after the active mass was treated with ultrasound before being applied to the tantalum substrate. The resulting electrodes had a very low specific capacitance of 2-6 F·g⁻¹.

Electrodes prepared on the basis of the carbon of the NSU "C" brand, both with and without the use of ultrasound, had satisfactory mechanical properties. The specific capacity of these electrodes was 27-57 F·g⁻¹. The resulting electrodes can be used in an asymmetric supercapacitor in an aqueous electrolyte.
We report on the novel inorganic complex $[\text{Mo}_{72}\text{Fe}_{30}\text{(NO}_2\text{)}_6\text{]}\text{(NO}_2\text{)}_x$, where $x=14\pm3$, synthesized by the exposition of giant nanocluster polyoxometalate (POM) crystals in the dry-NO$_2$ and NO stream. The vibrational spectroscopy showed the saving of Keplerate Mo$_{72}$Fe$_{30}$ structure and formation of nitrate ions: sharp intensive signal at 1385 cm$^{-1}$ and weak signal at 1287 cm$^{-1}$ in IR and Raman spectra, respectively. That coordination of NO$_2$ molecules in POM crystals occurs by the two ways – inside (in-plane, Fig.1) or above (out-of-plane) of the hexagonal POM pores as it was observed from XPS spectra. In-plane coordinated NO$_2$ molecules belong to the constitutional ligands that is opposite to out-of-plane coordinated ones, which are delocalized at 298 K. However, below 200 K, a new EPR-signal with g-factor of 4.3 appears that corresponds to localisation of all nitrate ions leading to distortion of FeO$_6$ octahedra towards the tetrahedral symmetry. Thus, in POM crystal, there are two types of NO$_3^-$ ions – constitutional strong-bonded and weak-bonded, which can be released from the crystal during the thermal destruction (above the 493 K) or the dissolution in aqueous media at neutral pH (near 7.2-7.4) and room temperature. The later is interesting for biomedical applications where such complex could play the role of NO$_x$-delivery system for in vivo production of nitrogen monoxide, which is a very important signalling molecule.

Figure 1. Model of NO$_2$ coordination in hexagonal pores of POM showing the NO$_3^-$ ion formation and octahedral-to-tetrahedral transition of FeO$_6$ polyhedra at the cryogenic temperature observed on EPR spectra. The purple and yellow colours correspond to the Mo and Fe oxygen polyhedra, respectively.
Group 13 element trihalides are strong Lewis acids which form stable donor-acceptor (DA) complexes with bifunctional N-donors. Resultant 13-15 DA complexes are adducts or group 13 metal-organic frameworks (13-MOF) of different kinds. Most of 13-MOFs described are built using poly-carboxylate linkers [1], and there are only a few examples of using N-donors. Thereby synthesis and characterization of new 13-15 complexes built up with bifunctional N-donors are important tasks.

Recently we first established crystal structures of MX$_3$ (M=Al, Ga; X=Cl, Br) complexes with 1,2-bis(4-pyridyl)ethylene (bpe). Complexes obtained exhibit a broad set of architectures: adducts, coordination polymers (CPs) (1D, 2D, mixed 1D-2D CPs), binuclear ionic complex. Due to the remarkable diversity of the possible reaction products, the target synthesis of the complex desired generally results in the hardly-splittable mixture formation irrespective of the synthetic conditions. This work, in turn, focuses on the complexes of MX$_3$ (M=Al, Ga; X=Cl, Br) with 1,2-bis(4-pyridyl)ethylene (bpa). All complexes were synthesized by direct interaction of MX$_3$ (M=Al, Ga; X=Cl, Br) with bpa without the use of organic solvents. Because of the moisture and air sensitivity of group 13 element halides and of the reaction products, all synthetic operations were carried out in whole glass apparatuses under vacuum. Either equimolar amounts of components were used or two-fold excess of one reagent was employed. Solid state structures of adducts (e.g. (MCl$_3$)$_2$·bpa) as well as coordination polymers (e.g. 2[MCl$_2$(bpa)$_2$][MCl$_4$]) were established by single crystal X-ray analysis.

References


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GREEN CHEMISTRY APPROACH TO THE SYNTHESIS OF BRIGHT BLUE EMITTING Cd-Zn-S QUANTUM DOTS

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Over the last decade, chalcogenide quantum dots (QDs) with bright and stable photoluminescence have gained much attention because of the variety applications they afford [1]. Due to the quantum size effect, it is possible to tune the band structures and thereby the optical properties of semiconductor QDs by simply controlling their sizes and shapes.

In this work, we present a study of the temperature influence on the structure, morphology, and optical properties of Cd$_{0.15}$Zn$_{0.75}$S QDs using a new sulfur source. In our recent investigations [2] we have successfully replaced harmful and expensive phosphine sulfides (such as trioctylphosphine and tributylphosphine sulfides) on eco-friendly and commercially available N,N'-disubstituted and N,N',N'-trisubstituted thioureas. All syntheses were conducted in an organic dispersion medium with a non-coordinating solvent 1-octadecene (ODE) by hot-injection and one-pot synthetic methods in the temperature range 220 – 300 °C. The structural and compositional characterization of QDs was performed by X-Ray diffraction and Energy Dispersive X-Ray Spectroscopy (EDS). It was found that nanoparticles have different particle shape with face-centered cubic structure and the average size of 3-4 nm. The crystal growth and optical features were analyzed by UV-VIS and photoluminescence (PL) spectroscopy. The obtained Cd$_{0.15}$Zn$_{0.75}$S QDs exhibit favorable narrow emission peaks and photoluminescence quantum yields (PLQY) up to 67 %.

References

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The study of the surface of α polymorph of 9,10-diphenylanthracene crystals by the THz-Raman spectroscopy method allowed us to detect zones with a modified metastable structure. Under the action of laser radiation at a wavelength of 785 nm, monotonous changes in the crystal structure in the direction of the formation of more stable α polymorphs can be observed in the detected zones. The found metastable structure of 9,10-diferinylanthracene may be associated with the appearance of surface oxygen vacancies.

Figure 1. Raman spectra of the 9,10-diphenylanthracene polymorphs.

References
ELECTROCHEMICAL PERFORMANCE OF REDUCED GRAPHITE OXIDE IN VARIOUS ELECTROLYTES

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Significant reduction of the sizes of portable devices and at the same time an increasing of clock frequency and processor power makes the development of effective energy storage devices such as supercapacitors (SC) and Li-ion batteries relevant (LIB’s). The promising materials for these applications are carbon nanomaterials, electrically conductive polymers and transition metal oxides. The selection of the most effective electrolyte is an important moment as well. In this work, the thermally treated reduced graphite oxide was synthesized as electrode materials for electrochemical devices. RGO is a graphene-like nanomaterial functionalized by oxygen-containing functional groups (OCFG). The RGO thermal treatment allows controlling the OCFG content in the material. It makes possible to control such important material characteristics as electro conductivity, wettability and specific surface area.

In this work, we synthesized a graphite oxide by modified Hummers method as a precursor for RGO synthesis. The RGO was synthesized by acid treating graphite oxide. Further, the RGO was thermally expanded at 250°C (RGOTE) and thermally annealed at 500°C (RGO-500), 600°C (RGO-600), 700°C (RGO-700). The change in OCFG content with the temperature increasing was investigated by XPS, IR and Raman spectroscopy methods. It was shown that thermal expansion allows obtain the materials with developed surface (Fig. 1). The samples specific surface areas were obtained by BET method. It was shown that the specific surface area reaches ~300 m²/g. The electrochemical performance in various electrolytes (1M H₂SO₄, 1M KOH, 1M NaCl for SC and 1M LiPF₆ in PC/EC for LIB’s) was obtained by cyclic voltammetry and charge-discharge cycling methods.

Figure 1.SEM images of: (a) RGOTE, (b) RGO-500, (c) RGO-600, (d) RGO-700.

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SYNTHESIS AND STUDY OF THE ELECTROCHEMICAL PROPERTIES OF PEDOT-BASED COMPOSITES WITH TRANSITION METAL OXIDES

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Low-cost transitional-metal oxides – tungsten trioxide (WO3) and molybdenum trioxide (MoO3) have attracted considerable interest as promising supercapacitive materials due to their non-toxicity, high electrochemical activity and environmentally friendliness. As these compounds have low conductivity, their electrochemical performance (specific capacitance and cycling stability) can be enhanced by making their composites with conducting polymers. Poly-3,4-ethylenedioxythiophene (PEDOT) is often used in supercapacitors, both as a conducting matrix and to maintain the microstructure of metal oxide deposits during charge-discharge process.

WO3 was electrochemically deposited from a metastable acidic solution of isopolytungstate on glassy carbon (GC) electrodes coated by PEDOT films [1]. The morphology of WO3 deposits was studied using SEM, TEM and EDX analysis. MoO3 was synthesized by hydrothermal method from (NH4)6Mo7O24·4H2O according to the procedure described in [2]. The PEDOT:PSS/MoO3 composite was prepared by mixing MoO3 with PEDOT:PSS aqueous dispersion and Nafion® as a binder and drop-cast onto GC electrode.

Electrochemical behavior of PEDOT/WO3 and PEDOT:PSS/MoO3 composites was investigated in 0.5M H2SO4 by cyclic voltammetry and galvanostatic charge-discharge methods. The average values of specific capacitances obtained from CV data were 67 mF/cm² (324 F/g) for PEDOT/WO3 and 93 mF/cm² for PEDOT:PSS/MoO3.

The obtained results indicate that PEDOT/WO3 and PEDOT:PSS/MoO3 composites can be promising electrode materials for supercapacitors.

References

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The VO$_2$ – TiO$_2$ system is unique in terms of the functional properties of its components. Vanadium dioxide shows a semiconductor-metal transition at approximately 68°C with a sharp change in the resistivity. Titanium dioxide is a wide-gap dielectric, a well-known photocatalyst, and is often used as transparent coatings for VO$_2$ films. Similarity of crystalline structures between TiO$_2$ and VO$_2$ allows the epitaxial growth of their layers in core-shell nanoparticles [1] and film heterostructures [2]. Such composites will provide the combination of the functional properties of vanadium and titanium dioxides and expand the area of their practical application.

The synthesis of these structures is a complicated process due to influence of many factors such as the phase composition and microstructure of the films, adhesion, and localized deformation at the film-substrate interface on materials properties. In turn, the main method of nanopowders VO$_2$ and TiO$_2$ obtaining is hydrothermal synthesis allowing change time, temperature, concentration, filling percentage of the autoclave, precursor dependence, reducing agents, with the aim to control structure, morphology and phase composition of produced particles [3]. The aim of this work is the hydrothermal synthesis of nanopowders with an interesting particles morphology and oriented films on single-crystal substrates in the TiO$_2$ – VO$_2$ system.

Hydrothermal synthesis was carried out in autoclaves with Teflon reactors with a volume of up to 60 ml at temperatures of 190 – 230°C for 1 – 24 hours using water-soluble complexes of titanium and vanadium as precursors. The powders and films on R-sapphire substrates were studied by XRD, SEM, EDX and XPS methods. To obtain crystalline coatings, the samples were annealed in a vacuum quartz-tube furnace under specific oxygen pressure. The electrical and optical (IR, THz range) properties of the materials were studied.

References

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PREPARATION AND STABILIZATION OF NANOEMULSIONS WITH LINSEED AND PUMPKIN OILS

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Recently, interest in the controlled delivery of drugs and biologically active substances has increased significantly. Targeted drug delivery has a number of significant advantages over conventional therapy, for example, they improve the pharmacokinetics with a lower content of the dosage form [1]. Nanoemulsions are promising candidates for use in targeted drug delivery. The main advantage of nanoemulsions is the ability to encapsulate hydrophobic drug compounds [2, 3], as well as the ability to protect drug compounds from destruction in the environment of the body. The purpose of this work was to obtain O/W nanoemulsions containing pumpkin or linseed oil. For the preparation of nanoemulsions, the method of temperature phase inversion was used. The concentration of the oil phase in nanoemulsions was 25 vol.%. Various mixtures of nonionic surfactants were used as nanoemulsion stabilizers. Increasing surfactant concentrations led to decreasing the sizes of oil droplets in nanoemulsions with pumpkin or linseed oil. The minimum average diameter of oil droplets was about 16 nm. Stability of nanoemulsions toward flocculation and creaming was improved by using of cross-linked acrylic polymer. The effect of the gelling agent on the stability of nanoemulsions was studied. The stability of nanoemulsions increased with increasing concentration of gelling agent. The concentration of the gelling agent of 0.2 mass.% was enough to obtain nanoemulsions stable for a long time.

References
Gold nanoparticles (AuNPs) are efficient catalysts of various reactions [1]. Since a catalyst efficiency is determined by its particles size, it is important to prepare AuNPs with tunable size and investigate their catalytic properties.

We obtained AuNPs via HAuCl\(_4\) reduction with NaBH\(_4\) in the presence of DNA, an attractive matrix to obtain stable AuNPs [2]. Catalytic activity of the AuNPs was studied using the reaction of \(p\)-nitrophenol reduction with NaBH\(_4\).

The size of the AuNPs could be tuned by changing the molar ratio between DNA and Au in the mixture (1:1, 5:1, or 20:1) and the time of NaBH\(_4\) addition (immediately after mixing DNA and HAuCl\(_4\) solutions, 2 h, or 7 days). The catalytic reaction rate constants \(k\) determined for the obtained AuNPs were systematically varied between 0.73 and 2.1 min\(^{-1}\) depending on the synthesis conditions. The lowest \(k\) value was observed for immediate reduction of the 1:1 DNA:HAuCl\(_4\) mixture (affording relatively large AuNPs, cf. Fig. 1a), while the highest \(k\) value was found for reduction of the 20:1 DNA:HAuCl\(_4\) mixture after its keeping during 7 days, which gave smaller AuNPs (Fig. 1b).

In summary, we demonstrated that ultrasmall AuNPs exhibiting high catalytic activity can be obtained in the presence of DNA matrix.

![Figure 1. TEM images and absorption spectra of AuNPs prepared under different conditions (see text for details)](image)

References

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SOLUTIONS OF BIFUNCTIONAL AMINES AND SILVER SALTS. 
FORMATION OF NANOPIRTELES

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Nowadays there are many works describes synthesis and properties of argentum nanoparticles. In many of them methods of reduction silver from solutions with polymer structures are proposed [1]. The aim of this research was to study the mechanism of the reaction and the product of oxidation.

Selected amines contains two amino groups therefore these compounds could be used as model structures in studying processes of formation argentum nanoparticles in solutions, contains polymers and silver salts.

To study formation of AgNPs through serial time intervals after mixing the solutions of amines and silver salt, absorption spectra was measured. Particle formation was observed due to an increase in the absorption intensity at the wavelength corresponding to the plasmon resonance of silver nanoparticles ($\lambda = 450$ nm, Fig. 1)

References

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An effective way of solar energy conversion is based on using a photosensitizer in solar cells (DSSC). The development of stable and efficient devices requires understanding the mechanisms of the basic processes occurring in the cell, in particular, electron transfer. Herein, we demonstrate that polyiodide chains play an important role in charge transfer in DSSC. An X-ray study of co-crystals of cationic Cyclometalated iridium(III) complexes with polyiodides gives insight into the dye-mediatior interactions and thus into the electron transfer process. Depending on the initial iodine concentration various polyiodide architectures can be obtained in the resulting co-crystals, from insular triiodides to infinite polyiodide chains. UV-light exposure leads to structural changes in co-crystals with infinite chains whereas the discrete iodides remain unchanged. We suppose that after UV-irradiation the excited dye molecules are deactivated by charge transfer to the polyiodide chains (but not to insular anions) that is accompanied with partial oxidation of the iridium ion confirmed by electron spin resonance spectroscopy.

Figure 1. Fragment of co-crystal structure containing both insular and chain polyiodides.

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NdCoO$_3$ NANOCRYSTALS FORMATION MECHANISM AND KINETICS FROM POWDERS OBTAINED IN GLYCINE-NITRATE COMBUSTION CONDITIONS

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Formation kinetics and mechanism research of perovskite-like nanocrystals is a promising direction, since it allows optimizing the conditions for obtaining crystallites with a narrow particle size distribution. This work describes the peculiarities of the phase formation processes in NdO$_{1.5}$-CoO$_x$ system from precursors obtained in conditions under glycine-nitrate combustion as well as the nucleation kinetics of NdCoO$_3$ nanocrystals at temperature treatment.

Samples corresponding to NdCoO$_3$ stoichiometry were obtained under the conditions of $G/N = 0.35; 0.55; 0.75$ ratio according to the synthesis method described in details in works$^{1,2}$. The obtained samples were annealed in air at $T = 500–800$ °C for 2-120 min. The kinetics research was performed in the annealing – quenching mode with subsequent X-ray phase analysis.

It is shown that NdCoO$_3$ nanocrystals yield with narrow particles distribution at heat treatment of X-ray amorphous precursor formed in the oxidizer conditions goes quickly enough, reaching extent of transformation equal 0.8 already in 1 h isothermal endurance at 600 °C. NdCoO$_3$ nanocrystals formation at heat treatment of the products representing crystal phases of various structure, formed in the conditions of stoichiometric glycine - nitrate ratio and excess of reducer, is complicated. It is connected with need of expenses of time for CoO oxidation ($G/N = 0.55$) and Co ($G/N = 0.75$) to Co$_3$O$_4$ at the further heat treatment, and with absence, apparently, of structural predecessors. The dependence of NdCoO$_3$ fractional conversion on time at various processing temperatures is satisfactorily described by the Avrami-Erofeev nucleation model equation. The calculated parameters of the model allow suggesting the probable mechanism of NdCoO$_3$ nanocrystals formation and estimate their apparent activation energy, the value of which is 338±32 kJ/mol.

References

Acknowledgements. This work was financially supported by the Russian Science Foundation (No. 16-13-10252). The work was facilitated by the Engineering Center equipment of the St. Petersburg State Technological Institute (Technical University).
Polyoxometalates are anionic clusters composed of early transition metals and oxygen atoms. They attract much attention in broad fields such as catalyst chemistry, magnetochemistry, photochemistry, and pharmaceutical chemistry. VO₄-based polyoxometalates construct a ring structure by corner-sharing of VO₄ tetrahedra. Tetravanadate [V₄O₁₂]⁻, which dominates in acetonitrile, is too small to capture metal cations inside the ring. However, it coordinates to various transition-metal cations. When the size of the ring is expanded to more than six VO₄ units, it can become large enough to accommodate various metal cations at the center, thus acting as a crown ether type ligand. In this presentation, we focus on the combination of rare-earth metal cations and VO₄-based polyoxovanadates. By the reaction of [Et₄N]₄[V₄O₁₂] and rare-earth metal sources in acetonitrile, three types of rare-earth metal containing polyoxovanadates was synthesized (Figure 1). The ionic radius of lanthanide is gradually decreased with increasing atomic number. The macrocyclic structures was controlled by the ionic radius of the center metal cations[1-3].

![Figure 1](image_url)

Figure 1. The molecular structures of the series of rare-earth metal containing polyoxovanadates.

References
HOW CAN WE STABILIZE AN OXIDO- OR HYDROXIDO-UNIT FROM AQUEOUS SOLUTION?

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Metal oxides have attracted much attention in various applications. To mimic the structures and the properties of metal oxides, many oxido-bridged metal complexes have been reported. In this study, we are researching intermediate oligomer species between the bulk solids and the small coordination compounds.

To stabilize such oligomer species, we are proposing protecting groups to terminate further hydrolysis. Previously, we stabilized $[\{\text{Co(tacn)\}_2\text{Mo}_3\text{O}_{12}\}]$ (1) by using an electrophilic protecting group of $\{\text{Co(tacn)}\}^{3+}$ (tacn, 1,4,7-triazacyclononane). Interestingly, cluster 1 plays an important role of a starting material leading to a key intermediate species of $\{\text{Co(tacn)\}_2\text{Mo}_3\text{O}_{13}\}$ unit for the formation of $[\{\text{Co(tacn)\}_4\text{H}_2\text{Mo}_7\text{O}_{27}\}]^{2+}$ (2) and $[\{\text{Co(tacn)\}_4\text{H}_3\text{Mo}_4\text{O}_{17}\}]^{5+}$ (3) (Figure 1) [1]. Recently, we discovered that the $\{\text{Co(tacn)\}_2\text{Mo}_3\text{O}_{13}\}$ intermediate works as a nucleophilic protecting group (i.e., ligand) to stabilize 3d-transition metal complexes. Through this study, we emphasize that the utilization of suitable electrophilic or nucleophilic protecting groups allows us to stabilize metal oxido- or hydroxido-clusters without exception on periodic table.

Figure 1. Structures of clusters 1, 2, and 3. Pink, blue, red, light blue, black, and white balls show Mo, Co, O, N, C, and H atoms.

References
This work describes the synthesis, structural and spectroscopic characterization of a new niacin hexamolybdocobaltate [C₆H₆NO₂]₂[H₂O]₂[CoMo₆(OH)₆O₁₈]•6H₂O (I), which is an efficient building block in a design of more complex supramolecular assemblies promising as catalysts or single-molecule magnets [1]. It has been prepared and studied by means of chemical analysis, single-crystal X-ray diffraction, NMR and IR spectroscopy. The crystal system is triclinic, space group P-1, unit cell parameters a=9.2303(19) Å, b=10.700(2) Å, c=10.850(2) Å, α=95.95(3)°, β=110.01(3)°, γ=105.11(3)°, v= 949.9(4) Å³ [2]. It is known the complex of nicotinic acid with dodecatungstum phosphate, in which heteropolyanions in polyhedra form cavities filled with molecules of nicotinic acid [3].

The structure of [C₆H₆NO₂]₂[H₂O]₂[CoMo₆(OH)₆O₁₈]•6H₂O includes an isolated heteropoly anion [CoMo₆(OH)₆O₁₈]⁴⁻ that can be classified as the Perloff’s-type anion, four outer-sphere cations includes two protonated molecules of nicotinic acid (C₆H₆NO₂)⁺ and two hydronium cations H₃O⁺, and six hydration water molecules.

References
AN ALIGNED OCTAHEDRAL CORE IN A NANOCAGE: SYNTHESIS AND PLASMONIC PROPERTIES

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Plasmonic metal nanostructures with complex morphologies provide an important route to tunable optical responses and local electric field enhancement at the nanoscale for a variety of applications including sensing, imaging, and catalysis. Here we report a high-concentration synthesis of gold core-cage nanoparticles with a tethered and structurally aligned octahedral core and examine their plasmonic and catalytic properties. The obtained nanostructures exhibit a double band extinction in the visible-near infrared range and a large area electric field enhancement due to the unique structural features. In addition, the obtained structures had a photoelectrochemical response useful for catalyzing the CO₂ electroreduction reaction. Our work demonstrates the next generation of complex plasmonic nanostructures attainable via bottom-up synthesis and offers a variety of potential applications ranging from sensing to catalysis.

Figure 1. Dark field TEM (a) and SEM (b) images of the structure

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CREATION OF DRUG DELIVERY SYSTEMS WITH TRIGGERED RELEASE: pH- AND ENZYME-SENSITIVE LINKERS

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Today the number of severe diseases could be effectively treated with an application of biomacromolecular drugs, as they have high specificity of action and can interact with multiple targets [1]. However, their wide application is limited by their fast rate of inactivation into the organism, as well as by their immunogenicity [2]. These problems could be mounted via the creation of special encapsulated dosage form, which allows control over biomacromolecular drug delivery and releases at the site of action. Therefore, the development of effective systems, which are capable of safely delivering a drug to the required site of action, protect the drug from degradation in the body’s environment and systemic distribution before the target cells penetrate into the intracellular space is in the list of the most important tasks for modern chemical science.

This work is devoted to obtaining and investigation of pH and enzymatically sensitive linkers to create the systems capable for inducible drug delivery based on the difference in pH and enzymatic composition of extracellular and intracellular media. Cross-linked polymer particles were chosen as such systems, in which cross-links are formed by special bifunctional molecules that are stable in the extracellular medium but degrading inside the cells, namely at acidic pH or in the presence of specific enzymes.

References

Acknowledgements. The study was supported by Mega-Grant of Russian Government "Biohybrid technologies for modern medicine" # 14.W03.31.0025.
The work is devoted to the study of the structural phase transformations of nanotubular nickel hydrosilicates Ni$_3$Si$_2$O$_5$(OH)$_4$ in air [1] and nickel-magnesium hydrosilicates of composition (Mg$_{1-x}$Ni$_x$)$_3$Si$_2$O$_5$(OH)$_4$ (x = 1 and 0.67) in reducing media in the temperature range 25 – 1000 °C. Nickel and nickel-magnesium hydrosilicates were obtained by a hydrothermal method at a temperature of 350 °C, a pressure of 20 MPa, and a 10-hour exposure to 0.1 M NaOH solution. The obtained nickel hydrosilicates were processed in air at temperatures of 400, 600 and 1000 °C. At 400 °C, the crystal structure did not change significantly, at 600 °C a nickel hydrosilicate phase transition occurred with formation of sepiolite-like Ni$_4$Si$_6$O$_{15}$(OH)$_2$. At 1000 °C, a highly crystallized phase of nickel orthosilicate Ni$_2$SiO$_4$ was formed.

Nickel-magnesium hydrosilicates were kept in a flow of argon-hydrogen mixture for 1 hour in the temperature range of 400-900 °C. Depending on the temperature, complete or partial reduction of nickel cations in the form of metal nanoparticles was observed. By using transmission electron microscopy, it was found that the size of nickel metal particles depends on the percentage of nickel in the original sample and on the temperature of the experiment. Thus, the particles formed during the reduction of hydrosilicate with a nickel content of 67% were larger, and their size distribution was wider than in the case of particles formed during the reduction of pure nickel hydrosilicate.

References

Acknowledgements. The authors are grateful to S. Bruyere, J. Ghanbaja and A. Nomine for the assistance in conducting microscopic studies and fruitful discussion.
We present a procedure to grow thin films of lead-containing materials such as lead sulfide (PbS) with ‘solution Atomic Layer Deposition’ (sALD) [1], a technique which transfers the principles of ALD from the gas-phase (gALD) to liquid processing. Pure and crystalline thin films are successfully deposited on planar and three-dimensional substrates at room temperature with a procedure that exhibits the unique ALD characteristics of self-limiting surface chemistry and linear growth. Conversion of PbS to the hybrid perovskite methylammonium iodoplumbate (methylammonium lead iodide, MAPI, CH3NH3PbI3) leads to a material which can serve as the light absorber in a photovoltaic device.

Figure 1. (a) Principle of sALD, (b) conversion of PbS to MAPI.

References

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SYNTHESIS AND PROPERTIES OF QUADRUPLE-DECKER SANDWICH COMPLEXES OF LANTHANIDES(III)

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Today phthalocyanines (Pcs) are applied in many areas, including electrochromic components in information display media and molecular magnets. Lanthanide sandwich type Pcs are among the most promising compounds in these areas.

Figure 1. Synthesis of lanthanide quadruple-deckers and NIR spectra in CCl4.

In the course of this study, a series of quadruple-decker lanthanide(III) sandwich complexes was synthesized (Fig. 1) with high yields up to 90% [1]. The compounds were characterized by a range of physicochemical methods: 1H NMR, MALDI TOF/TOF, UV-Vis-NIR, TG-MS, and electrochemistry. The UV-Vis-NIR spectra indicate that an increase in the ionic radius bathochromically shifts the main absorption bands; in the NIR region the maxima shift from 1262 to 1618 nm for Ln = Lu and Eu, respectively (Fig. 1). The completed studies allow us to offer these compounds as electrochromic components in information display media, molecular magnets, and IR labels.

References

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At the present time, the mixed (Janus) nanotubes have not yet been synthesized. Nevertheless, the rapid progress in the synthesis of nanosystems allows us to hope that such an opportunity will appear in the nearest future. Theoretical modeling of these systems will undoubtedly contribute to the achievement of this goal. To date, several computational works have been published on the study of Janus nanotubes based on MSSe (M = Mo, W). Among them, more attention was paid to the calculations of electronic structure and stability of Janus molybdenum dichalcogenide nanotubes, and relatively fewer works were devoted to similar tungsten dichalcogenide nanotubes.

In our previous work [1] we have used the hybrid density functional theory (DFT) to compare the structural and electronic properties, stability, vibrational frequencies, and thermodynamic functions of MoS$_2$ and WS$_2$-based single-wall nanotubes using for both the same calculation scheme approach implemented in the CRYSTAL17 computer code [2].

In this study we take a similar approach to obtain and compare the stability, geometry and electronic properties of MSSe (M = Mo, W) Janus nanotubes at different wall compositions, chiralities and diameters. Different types of nanotubes are considered — with S or Se atoms on the outer (inner) shell of the nanotube. It was found that nanotubes Se(out)MS(in) (M = Mo, W) with average diameter ($D_{avr}$) greater than $\approx$40 Å have the negative strain energy. Our calculations show that the band gap is direct for zigzag MS$_2$ and S(out)MSe(in) nanotubes but it becomes indirect in armchair nanotubes. For the MSe$_2$ and Se(out)MS(in) nanotubes of both chiralities, the band gap is mostly direct, except the armchair tubes with $D_{avr}$$<$18 Å and zigzag tubes with $D_{avr}$ in interval from 18 to 26 Å where it is indirect.

References

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Transformation of ligands in transition metal complexes are of paramount importance in metal complex catalysis and metal-mediated synthesis, in this report we will consider 1,3-bipolar cycle addition of acyclic nitrone p-tolC(H)=N(O)CH₃ to the nitrile ligands in complex [PtCl₂(NCC₆H₄COH)₂]. The interaction of the nitrone with the nitrile NCC₆H₄COH without the metal center is not possible even in harsh conditions (90 °C, 240 h). However coordination of nitrile to Pt(II) center leads to activation of the nitrile functionality of the interaction of the nitrone with the nitrile ligands in the complex [PtCl₂(NCC₆H₄COH)₂] via [2+3]-cycle addition becomes possible.

Scheme 1. 1,3-bipolar cycle addition acyclic the nitrone p-tolC(H)=N(O)CH₃ to nitrile ligands in the complex[PtCl₂(NCC₆H₄COH)₂]. The obtained complex was separated and characterized by ¹H and ¹³C NMR and infrared spectroscopies high resolution masses spectrometry (electrospray ionization), and also elemental analyses (C,H,N).

References

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THREE-DIMENSIONAL SCAFFOLDS BASED ON POLYMERIC MICRO- AND NANOPARTICLES FOR TISSUE ENGINEERING

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Critical-sized bone defects created due to infection, tumor resection, or traumatic fractures need external interventions in order to regenerate bone, maintain or improve its function. Although autografts are considered as the gold standard treatment [1], it remains challenging for the clinicians to select between autografts, allografts or engineered tissues [2]. This has led to the extensive research of biomaterials for tissue engineering in the last several decades [3]. Nevertheless, there is a lacks of studies, which deal with generation of scaffolds with spatiotemporal distribution of osteogenic factors and controlled micro/nanotopology. The development of such scaffolds is essential, because the combination/distribution of various materials could resemble the complexity of natural bone tissue, and allow controlled precise reconstruction of all its components.

The ideal strategy for regenerative bone therapies is to use a “smart” biomaterial scaffold that can modulate the process of healing while providing mechanical support. Particles of different nature and size, possessing various rigidity and surface area can be joined together in different combinations to tune the mechanical properties and surface topology of the pores. Moreover, the useful peculiarities of the particles are the possibilities of their surface modification and different substances entrapment into their inner volume, which allow the spatial distribution of osteogenic or angiogenic factors and their temporally controlled release.

This research is devoted to the creation of biofunctional three-dimensional matrices based on polymeric micro- and nanoparticles. The polyester, polysaccharide and gelatin-based particles were obtained. The particles were characterized using the dynamic light scattering method and their morphology was studied by transmission electron microscope. In addition, the cytotoxicity of the obtained particles as well as their printability were studied.

References

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NEW ALKOXY DERIVATIVES OF LAYERED PEROVSKITE-LIKE TITANATES HLnTiO$_4$ AND H$_2$Ln$_2$Ti$_3$O$_{10}$ (Ln = La, Nd)

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Protonated layered perovskite-like oxides are solid crystalline substances in which two-dimensional perovskite slabs alternate with interlayer spaces containing protons. Being solid acids, they are able to react with some organic compounds giving inorganic-organic hybrids, i.e. substances consisting of chemically bonded inorganic and organic parts in which the inorganic part serves as a spatial frame [1]. Their formation may occur in two ways: either as intercalation of organic bases following an acid-base mechanism, or as grafting, that is a process similar to well-known esterification in organic chemistry. The second way, as a rule, takes place in the case of reactions with alcohols and leads to covalent alkoxy hybrids. Such derivatives are of high interest as promising heterogeneous photocatalysts, materials for electronics and precursors in producing surface modified nanolayers which may become a basis for new semiconductor films and nanoparticle superlattices [2].

The present work is devoted to synthesis and investigation of covalent inorganic-organic derivatives of protonated titanates HLnTiO$_4$ and H$_2$Ln$_2$Ti$_3$O$_{10}$ (Ln = La, Nd) with saturated alcohols as organic components. Possibility of the hybrids synthesis is studied in a wide range of conditions including solvothermal and solvothermal-microwave ones. Characterization of the products is performed using modern physicochemical methods (X-ray diffraction, Raman and nuclear magnetic resonance spectroscopy, thermogravimetry, elemental C,H,N-analysis, scanning electronic microscopy) with an emphasis on hybrids structure, composition, thermal stability and morphology.

References

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THE EFFECT OF THE ACTIVE COMPONENT CONTENT ON THE CATALYTIC ACTIVITY OF NICKEL SULFIDE CATALYSTS IN DEOXYGENATION OF STEARIC ACID

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Despite the rapidly changing oil prices, interest in renewable resources persists. Triglycerides of fatty acids are one of the promising types of such feedstock. The deoxygenation of such products yield paraffins of fuel composition or higher olefins, which are important products serving as a feedstock for the preparation of detergents, synthetic oils, additives, etc. Metals such as Pd, Pt, Ni or metal sulfides, generally on supports (γ-Al₂O₃), are used as catalysts [1]. Recently, it has been shown that nickel sulfide Ni₃S₂ powder can selective catalyzed decarboxylation of fatty acid to higher olefins. These catalysts as distinct from known Ni and Ni sulfide containing ones appeared to have relatively low side activities. The aim of this work was to study the effect of the active component content in the catalyst on the catalyst efficiency in decarboxylation of stearic acid to high olefins [2].

We studied nickel sulfide catalysts supported on alumina or silica by hydrogen reduction of Ni sulfate as the precursor. The amount of loaded metal ranged from 1.5% to 9%, the reduction temperature was 400°C under a hydrogen pressure of 10 atm for 3 h. The experiments were carried out in an autoclave at a hydrogen pressure of 15 atm and a temperature of 350°C.

The results of the research showed, that in the presence of the of the alumina- and silica gel-supported catalysts, the olefin selectivity exhibits a tendency to increasing from 30 to 55% with an increase in the nickel content in the catalyst from 1.5 to 9% respectively. For the two supports the increase in the conversion is not monotonous: initially, upon switching from the 1.5%Ni catalyst to the samples containing 3-6 wt % Ni, the conversion quite rapidly increases; afterwards, the increase ceases. The catalysts were studied by TEM combined with Xray microdiffraction, the results of the analysis showed the presence Ni, NiO, NiS and Ni₃S₂ phases on catalysts. In addition to the phase composition, the particle size of the active component can be responsible for the activity of the catalysts; the average particle size for the alumina and silica gel supports, is 3.1 ± 1.0 and 5.2 ± 1.2 nm, respectively.

References
Porous glasses (PGs) (silica content >95%) - products of thorough chemical processing of two-phase alkali-borosilicate glasses of a certain composition - including nanoporous ones, and nanostructured systems prepared on their basis are modern functional materials distinguished by a very wide spectrum of possible fields of application, from highly active sorbents to matrices for producing composite quartzoid glasses. The analysis of the literature data shows that most of the research devoted to the study of the electrosurface properties of silicon oxide was carried out in 1: 1-charge electrolyte solutions. Therefore, it was of interest to study the specific features of the behavior (efficiency ratio $\alpha$, transport numbers $n_+$ and $\zeta$-potential) of micro- (MIP) and macroporous (MAP) glasses in solutions containing specifically adsorbing multivalent iron (III) and lanthanum ions in a wide range of pH values and (10$^{-1}$ – 10$^{-5}$ M) electrolyte concentrations.

When comparing the results of the study of various three-charged ions, it was shown that the low-nitratated La$^{3+}$ ion shows practically no specificity for the silica surface and is similar in behavior to the indifferent sodium ion. Whereas Fe$^{3+}$ ion exhibits distinct specificity to it. It was shown that the $\alpha$ (equal to the ratio of the specific electrical conductivities of pore and free solutions) decrease with increasing LaCl$_3$ concentration in accordance with the decrease in the contribution of ions of double electric layer (DEL) to the electrical conductivity of the pore solution. Whereas a different dependence was observed from the classical one for FeCl$_3$ solutions. It was observed that the values of $\alpha$<1, that is, the appearance of concentration regions of the equilibrium solution, in which the electrical conductivity of the pore solution becomes less than the free one. It was also found that $\zeta$-potential is negative in almost the entire LaCl$_3$ concentration range, while $\zeta$-potential becomes positive already at low FeCl$_3$ concentrations (~6.5×10$^{-4}$ M).

References

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Deflocculants in refractory concrete are defined as chemical agents who in small and miniscule amounts counteract an aggregation (floculation) of fine and ultrafine particles in high-concentrated refractory mixes [1]. The most common deflocculants in practice are PCE-based deflocculants, hydroxycarboxylic acids and sodium tripolyphosphate (STPP). Behavior and efficacy of a particular deflocculating agent depend on composition and properties of refractory mix such as pH, binder type and content of aggregates and matrix. Often in cement-free compositions based on colloidal silica widely used commercial deflocculants are rendered ineffective and decrease the stability of colloidal binder. From this perspective it’s important to look for new dispersing and plasticizing agents that could show stable behavior irrespective of composition refractory concrete based on colloidal binder.

This work was study the deflocculation properties of different agent on refractory compositions consist of matrix components (corundum filler <0.063 mm, reactive alumina, silica fume) and aggregates (mullite or corundum 0-3 mm). The binder was a commercially available NH\textsuperscript{4+} stabilized colloidal SiO\textsubscript{2} which was introduced in mixture in non-diluted or diluted with water form. A plasticizing effect was observed when introduced as few as wt. 0.005 % of pyrocatechol and its impact on flowability was proportional to amount of pyrocatechol in the mix. Meanwhile plasticizing ability of citric acid, STPP or PCE vary influenced by changes in concentration of colloidal SiO\textsubscript{2}. Matrix of all the samples in a dried state and after heat treating at 1400 °C was studied by means of XRD and SEM. The resulting matrix after sintering comprised of mullite and corundum and looked the same for all samples. All SiO\textsubscript{2} from colloidal binder and microsilica fully reacted into mullite.

References
INFLUENCE STRUCTURE OF CARBON NANOTUBES ON THEIR ELECTROCHEMICAL PROPERTIES

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Carbon nanotubes (CNT) have unique properties, such as large specific surface, high electrical conductivity, chemical stability and etc. These properties give advantage of CNTs for application them as electrode materials for supercapacitors, lithium-ion batteries, solar cells. Therefore, the structure of CNTs determines the parameters and characteristics of materials made on their basis.

The main methods of CNT production are catalytic chemical vapor deposition (CCVD) synthesis. The parameters of synthesis of CNTs, such as flow gases, ratio gases, time of synthesis, temperature and etc., are optimized for obtain of CNTs with desired properties [1].

In the research, we use of supported polyoxomolybdate cluster Mo₁₂O₂₈(μ₂-OH)₁₂{Co(H₂O)₃}₄ as a catalysts precursor for the CCVD synthesis of CNTs. The advantages of these catalysts are that there have molecular clusters structure for the formation of discrete catalyst particles with a controlled size [2]. The alloy nanoparticles mixed with MgO substrate, which has a highly developed specific surface. The oxide magnesium MgO substrate was eliminated from the product using diluted HCl treatment.

In the present work was studied influence of temperature profile of CCVD process, catalyst composition and flow rates of CH₄/H₂ on structure and properties of CNT. The obtained were tested as electrode materials for a supercapacitor performance. The deformation leads to significant changes in electrical conductivity: with an increasing deformation of CNT, its conductivity decreases.

References

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SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION METHOD FOR THE DEPOSITION OF NICKEL FERROCYANIDES, AS A NEW METHOD OF CONTROLLED SELF-ASSEMBLY OF CATHODIC MATERIALS

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Transition metal ferrocyanides are promising cathode materials for magnesium-ion aqueous batteries. Firstly, properties of the cathode material based on these compounds can be set by changing the composition, morphology and size of particles [1]. Secondly, by their nature, transition metal ferrocyanides are similar to zeolites and they can intercalate cations of alkali and alkaline-earth elements in an aqueous solution without destroying the crystal structure [2, 3].

The successive ionic layer adsorption and reaction method allows obtaining thin films of transition metal ferrocyanides possessing meso- and macropores. The presence of mesopores can favourably affect the diffusion of magnesium ions in an aqueous solution, which will ensure good cyclability of the cathode material.

In the present work nickel ferrocyanide films were obtained, containing and not containing potassium ions, on a conductive substrate of tin oxide doped with fluorine (FTO). The obtained nickel ferrocyanide films were studied by XRD, SEM, EDX, ATR-FTIR, XPS methods. The presence of mesopores in films was confirmed by the method of small-angle X-ray scattering (SAXS). Electrochemical studies in solutions of potassium chloride and magnesium chloride made it possible to establish the mechanism of magnesium ion intercalation and to reveal the negative effect of potassium ions on the process of intercalation of multiply charged ions.

References

Acknowledgements. The studies were conducted using the equipment and resource centers Science Park Saint Petersburg State University RC Geomodel, RC Innovative Technologies of Composite Nanomaterials, RC X-ray Diffraction Studies.
Acetone and methyl ethyl ketone (MEK) have the greatest practical importance among ketones. Acetone is produced through a large-tonnage cumene process. The imbalance of the phenol and acetone market creates conditions for the overproduction of the latter. Development of the technology for producing MEK from acetone would allow the excess of acetone to be removed from the market and make MEK more accessible.

The first studies of the gas-phase condensation of acetone with methanol to MEK were carried out at the turn of the 1960s-1970s. The Cu/TiO₂ system was used as a catalyst [1]. But the study has not received further development due to low activity and rapid deactivation of the catalyst. In recent years, more active and selective catalysts based on SiO₂ and Al₂O₃ have been discovered [2, 3]. However, Cu/SiO₂ catalysts have low stability. Cu/Al₂O₃ catalysts are stable but have a low selectivity of the methanol conversion to MEK, which is caused by the side reaction of dimethyl ether formation due to the acidity of Al₂O₃. The goal of our work is to develop a catalyst based on Al₂O₃, which has a low acidity due to its modification with Mg. It can be expected that a decrease in acidity will lead to an increase in the selectivity of methanol conversion to MEK.

The Cu/Mg-Al₂O₃ system was chosen as the object of research. The effect of magnesium modification of the support on the catalyst performance was investigated. The properties of the Cu/Mg-Al₂O₃ catalyst are compared with the known catalysts based on SiO₂ and Al₂O₃. It is shown that the modification of alumina with magnesium allows preparing a more active and selective catalyst.

References

Acknowledgements. The work was performed within the state task of the Institute of Catalysis SB RAS (project AAAA-A17-117041710083-5).
Layered perovskite-like oxides are complex oxides that consist of alternating perovskite blocks and blocks of different structure. Layered perovskites containing alkali metal cations in the interlayer space have been widely studied as ionic conductors, ferroelectric materials and photocatalysts. Layered oxides represent a unique class of photocatalysts, which have the ability to intercalate substrate molecules into the interlayer space, to exchange cations for different structural units. These properties already allowed creating highly efficient photocatalytic systems (e.g. for hydrogen production, organics decomposition) and open wide possibilities in the future [1]. The present research considers photocatalytic activity of the triple-layered perovskite-like titanate K$_2$Nd$_2$Ti$_3$O$_{10}$, its protonated (H$_2$Nd$_2$Ti$_3$O$_{10}$) and butylamine intercalated form (H$_2$Nd$_2$Ti$_3$O$_{10}$·nBuNH$_2$) in the reaction of hydrogen production from aqueous methanol, ethanol or butanol solutions. Effects of alcohol concentration, catalyst amount and platinum loading on the photocatalytic efficiency were investigated. The butylamine-intercalated titanate modified with platinum showed the highest quantum efficiency which was determined by ferrioxalate actinometry.

Fig. 1. Efficiency of H$_2$ evolution form alcohol solutions under UV-light

References

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ENCODED LUMINESCENT NANOCRYSTALS
FOR LASER BEAM MARKING

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Counterfeit products or reusing of decommissioned equipment carry a safety hazard. The search for the marking methods leads the scientists and engineers to the field of nanotechnology, which found a useful application in almost every technological and industrial area. Detection of the nanoobjects is only possible with the identification of their properties, which makes it possible to hide the mark inserted in the object from the eyes. Luminescence is one of the most promising properties because it has a high detection sensitivity, moreover the dependence of the luminescence properties on the structural and concentration parameters allows the creation of a unique spectral code.

Our group has developed a spectral coding system that allows creating unique fluorescent nanomarkers based on metal oxides doped with rare-earth ions. These objects are well suited for solving the problem of marking of metal products with severe operating conditions. The work is devoted to the study of the process of introducing particles into the metal surface and luminescent properties analysis of the implanted nanoparticles before and after the interaction with the laser radiation under the condition of their contact with metal alloy surface.

Metal oxides are the most promising compounds for solution of the problem. Their chemical inertness and the stability of the physical and chemical properties over a wide temperature range are the major parameters for the successful implantation of the luminescent nanoparticles in the surface layer of metal products. The implantation of the particles into the surface layer was performed with the powerful laser irradiation. The laser illumination of the metals leads to local heating followed by melting and, partially, evaporation of the surface. After the laser treatment a well-defined mark can be observed in the area of the laser spot. Translation of the laser beam on the sample surface can be used to create a visible image or a symbol. Nanoparticles can be implanted in the melting area under certain conditions. In such a way the laser-induced incorporation of luminescent nanoparticles into the metal surface allows both visible marking of the object and simultaneous spectral coding.
IMPACT OF VO$_2$ NANOPARTICLES MORPHOLOGY ON ITS ELECTROCHEMICAL BEHAVIOR

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VO$_2$ (B), layered metastable phase of VO$_2$ has demonstrated promising properties as cathode material for Li-ion batteries. Great number of publications is devoted to investigation of such battery properties but there is a lack of information on impact of VO$_2$ morphology on electrochemical behavior. In our work, using hydrothermal synthesis, we obtained VO$_2$ nanoparticles from V$_2$O$_5$ and H$_2$C$_2$O$_4$. Stoichiometric ratio of the initial reagents was determined spectrophotometrically (1:4).

The temperature regime of the synthesis was selected to obtain pure VO$_2$ (B), conforming to our previous research. To change the morphology of nanoparticles we used capping agents: etidronic (ETDR), salicylic (SAL), succinic acids (SUC), 1,10-phenanthroline (PHEN) and pyrocatechin violet (PYR). UV-Vis spectra proved that capping agents did not form complexes with VO$_{2^+}$.

Obtained nanoparticles were characterized with XRD, SEM, FTIR and Raman spectroscopy. Also zeta potential of the samples was measured. According to XRD results, all specimens represented VO$_2$ (B). However, Raman spectra showed that samples without capping agents and with phenanthroline had an impurity of VO$_2$ (A). SEM images demonstrated that all of the samples represent spherical nanoparticles consisting of different structural components.

For the specimens with the highest surface area and lowest zeta potential charge-discharge curves were investigated. The obtained data demonstrated that VO$_2$@ETDR sample possessed the highest capacity 206 mAh/g and its stability remained unchangeable after 50 cycles. To investigate the occurring processes during the charge and discharge the cyclic voltammetry was used. The samples with any capping agent and VO$_2$@ETDR showed two anodic and two cathodic peaks, apparently, related to insertion/deinsertion of Li ions into the volume and the surface of the materials.

Acknowledgements. Data was given by Centre for Optical and Laser Materials Research, Research Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Geomodel and Centre for Innovative Technologies of Composite Nanomaterials of Saint Petersburg State University.
SYNTHESIS AND LUMINESCENCE PROPERTIES OF YVO$_4$ NANOCRYSTALLINE POWDERS DOPED WITH A GROUP OF RARE EARTH IONS


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This work is devoted to the synthesis and study of the nanocrystalline particles containing the rare earth ions. Metal oxides are the most promising compounds for rare earth doping due to their chemical inertness and the stability of the physical and chemical properties over a wide temperature range. These facts allow us to use of the such materials for medical purposes (due to their biocompatibility), in the field of machine building and instrument making (thermal stability and hardness), etc. The luminescence properties of the rare earth ions can be controlled by changing the crystalline lattice, synthesis conditions, the type of the ions, and their concentration. Each rare earth ion, inserted into a specific matrix, demonstrates a set of luminescence bands with appropriate spectral positions and relative intensities. A material doped with group of rare earth ions is a unique system. The research of this system is of particular interest because of fundamental purposes and wide range of possible applications. For the synthesis of nanocrystalline particles was used the modified Pechini method. In this method the amorphous powder is prepared by the standard Pechini method and then calcined in the molten salt at high temperature. This method results in the formation of the uniformly doped weakly agglomerated oxide particles with well-organized crystalline structure. The structure ensures the high luminescence yield, while the small size of the particles affords to prepare stable colloid solutions and suspensions. The unique electron configuration of the rare earth ions, the luminescence bands position slightly depends on the particles size and the environment. The luminescence spectrum demonstrates the possibility of simultaneous excitation of the rare earth ion group by pumping through a host. In the measured spectrum, one can distinguish emission lines originated from each introduced ion (for example, for Nd$^{3+}$ - 1065 nm, for Er$^{3+}$ - 554 nm, and for Tm$^{3+}$ - 476 nm). The luminescence properties of YVO$_4$ nanocrystalline powders doped with different types and concentrations of the rare earth ions (Nd, Tm, Er) were studied. The results of the phase composition (XRD), crystal unit cell parameters, morphology (SEM) and particle size distribution were also obtained (DLS).
CRYSTAL SOLVATES AS PRECURSORS FOR SYNTHESIS OF INORGANIC MATERIALS


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At present, crystal solvates of inorganic salts with various organic solvents attract the attention of researchers due to their catalytic activity [1], the possibility of their use for the synthesis of perovskite-like structures [2], etc. However, the processes leading to the formation of solvates of a certain composition and structure are little studied. One of the most common methods for the synthesis of these compounds is their salting out of binary solutions with an indifferent solvent (acetone, ethyl alcohol, diethyl ether). This method allows to obtain only monoligand complexes. At the same time, the use of mixed ligand solvates as precursors may allow for a more subtle variation in the direction of synthesis and to obtain higher yields in the reactions.

In this work, we consider the ternary systems containing copper (II) chloride and bromide and a binary organic solvent by analogy with previously studied systems. Crystal solvates in these systems are presented in equilibrium with saturated solution and formed spontaneously. Their composition and structure directly depend on the properties of the solution. It was found that solvates containing more donor solvent molecules have a large crystallization region on the solubility isotherm in the ternary system. The evolution of the composition and structure of the equilibrium crystal solvates in the ternary system is also shown, depending on the composition of the mixed solvent. The reasons for the formation of solvates of a certain structure are analyzed from the point of view of the Lewis theory and the HSAB-theory.

References

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Owing to synergistic combination of hybrid organic-inorganic nature and chemically active porous structure, metal-organic frameworks emerged as a new class of functional materials - *soft porous crystals*. The current trend in chemical industry is utilizing such crystals as hosting flexible elements for diverse applications as gas and energy storage, filtration, catalysis and sensing. From the physical point of view, metal-organic frameworks are considered as molecular crystals with hierarchical structure providing the structure-related physical properties crucial for the future of energy transfer, data processing and storage, high-energy physics, and light manipulation [1].

I will represent the metal-organic frameworks as a new family of functional materials in modern physics: from porous metals and superconductors, topological insulators, classical and quantum memory elements, to optical superstructures, materials for particle physics and even molecular scale mechanical metamaterials. Based on complementary properties as crystallinity, softness, organic-inorganic nature and complex hierarchy I will describe how such artificial materials extend their impact on applied physics and become the mainstream in material science.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No. 18-32-20089 mol_a_ved).
Hybrid organic-inorganic compounds based on layered perovskite-like oxides is a new promising class of materials which properties could be tailored by targeted modification of both organic and inorganic parts. Preparation of such materials is recently focused on a stepwise approaches including subsequent hydrothermal and microwave-assisted hydrothermal intercalation and grafting reactions that lead to the formation of bulk hybrid compounds followed by their exfoliation into 2D organically modified nanosheets. [1] Such hybrid compounds and nanosheets are considered as perspective materials exhibiting photocatalytic, catalytic, ferroelectric, and luminescent properties.

In the present work we report the results on the synthesis and characterization of organic-inorganic hybrids based on layered perovskite-like bismuth titanate $\text{H}_2\text{K}_{0.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13} \cdot \text{H}_2\text{O}$. $\text{H}_2\text{K}_{0.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13} \cdot \text{H}_2\text{O}$ could be prepared by simple ion exchange reaction from Ruddlesden-Popper phase $\text{K}_{2.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13}$. Organic-inorganic hybrids have been prepared by intercalation and grafting reactions. Intercalation reactions imply acid-base interaction between solid acid and organic bases (usually n-amines). Then, the preliminarily intercalated by amines compounds are used as starting materials for grafting reactions, which imply the covalent bonding between the grafting agents (usually alcohols) and inorganic matrix. In this work, we have used n-amines intercalated derivatives for reactions with n-alcohols. In particular, methylamine-intercalated hybrid was used for reactions with methanol, n-propanol and n-butanol. In case of n-butylamine intercalated compound we have added the reaction with n-hexanol, and n-octylamine intercalated derivative was used for reaction with n-decanol.

The characterization of the samples was carried out by XRD, TG, and C/H/N analyses, FTIR- spectroscopy and SEM.

References

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DIRECT WRITING OF THREE-DIMENSIONAL MICROSTRUCTURES USING FEMTOSECOND LASER PULSE-INDUCED REDUCTION

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Direct-writing technology has received attention for three-dimensional (3D) micro-additive manufacturing (μ-AM). AM techniques such as selective laser sintering (SLS) and selective laser melting (SLM) has been developed for metal bulk structures. However, just downscaling of those technique is difficult because the raw metal powders are easily oxidized by downsizing the metal powders. To overcome this problem, reductive sintering of metal oxide nanoparticles has been reported [1, 2]. We have also developed femtosecond laser reductive sintering of CuO nanoparticles to form metal Cu and semiconductor Cu2O microstructures selectively by controlling the laser irradiation conditions. In addition, 3D microflow sensors have been fabricated using the combination of femtosecond laser reductive sintering and 3D μ-AM techniques.

First we demonstrated the fabrication of a Cu-based micropyramid with 10 layers. The lamination was carried out using a dispenser and laser irradiation repeatedly. Figure 2 shows the fabricated flow sensor which consists of a micro bridge heater. The sensor successfully detected the flow rate in a range of 0–450 cc/min [3]. We will introduce the details about 3D μ-AM and its applications.

References
PDF METHOD APPLICATION TO THE STRUCTURAL STUDY OF CATALYSTS AND CATALYST SUPPORTS

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The synthesis and study of catalysts is currently an important scientific task which determines progress both in industrial development and in the field of chemistry. Structural characterization is a very important step in understanding catalysts’ action because the structure is one of the parameters that affect properties of these materials. However, when studying catalysts, one often encounters nanosized, defective materials, X-ray amorphous and close to them. Applying the usual X-ray diffraction methods based on the analysis of position and intensities of diffraction peaks to such systems can be difficult. Therefore, using special methods which take into account the specific features of X-ray scattering from small objects is required. The structure of such materials can be successfully studied by an X-ray diffraction method of the radial distribution of atoms or the radial electronic density distribution, also known as the analysis of atomic pair distribution function (PDF-analysis). This method allows us to obtain information about the short-range atomic arrangement and phase composition of materials whose coherent-scattering regions do not exceed 3 nm and even X-ray amorphous substances. The method is not widely used but is extremely relevant in connection with the development of nanotechnology and the growing interest in the structure and properties of nanoscale substances. PDF analysis is the recognized tool for studying nanoscale materials with different chemical compositions, solid amorphous materials, liquids, glasses, supported catalysts, etc. This report presents the capabilities of the PDF method and the results of the study of relevant and interesting from a structural point of view nanoscale catalysts and catalyst supports.

References

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Confinement and on-demand release of guest molecules is essential for using artificial host molecules as a molecular container. However, the strategies for the precise control of these kinetic processes have rarely been reported. We recently reported on-demand acceleration of guest exchange of a cationic cobalt(III) dinuclear macrocyclic metallohost by the replacement of the counteranion caps\cite{1}. We expected that intramolecular bridging of the two cobalt ions in the metallohost would retard the guest uptake/release behavior. Here we report dynamic structural conversion of a newly synthesized cobalt(III) metallohost that has four bifunctional ligands at the axial sites. In addition, we present the guest removal and guest exchange behavior of the two kinds of structural forms.

![Diagram](image.png)

Figure 1. Guest removal and guest exchange behavior of the two kinds of structural forms.

References
In recent years atomic layer deposition (ALD) has proved to be a successful method of fabrication and modification of electrodes for lithium-ion batteries. Tin oxide demonstrates considerable excellence over currently used materials for Li-ion battery anodes, however, lithiated tin oxides are expected to show even better performance. On the other hand layered lithium transition metal oxides (LiNiO$_2$, LiCoO$_2$) arguably represent the most successful materials for cathodes. In this research nanofilms of lithium oxide, lithiated tin oxide, lithiated nickel oxide and lithiated cobalt oxide were deposited by atomic layer deposition (ALD) using lithium hexamethyldisilylazide (LiHMDS), tetraethyl tin (TET), bis(cyclopentadienyl) nickel(II), bis(cyclopentadienyl) cobalt(II) as the metal-containing reagents and oxygen plasma as counter reagent. The temperature of deposition varied from 150 to 350°C. The monocrystalline silicon (100) and stainless steel (316SS) were used as supports. The thickness of the films was measured with spectral ellipsometry and x-ray reflectometry. The composition was studied by X-ray photoelectron spectroscopy, X-ray diffraction and time-of-flight secondary ion mass spectrometry. Morphology of the films was studied by scanning electron microscopy. It was found that layered structures of NiO-LiO$_x$ can be easily prepared by ALD, but nanolaminates of Li-Ni-O contain nickel in quantity by one order less than calculated on the basis of the average growth rate per ALD cycle. Nanolaminates of Li-Sn-O contain tin significantly larger quantities, but also lacking in comparison with the calculated data. Deposited Li-Ni-O and Li-Sn-O nanofilms contain significant amount of silicon and carbon as impurities of LiHMDS ligands. But impurities were not observed in pristine lithium oxide and probably are stabilized by tin and nickel oxide. Electrochemical study was carried out for the films deposited on the stainless steel. During cycling tests it was shown that lithiated tin oxide has a stable discharge capacity during 100 charge/discharge cycles, with efficiency above 99%.

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FABRICATION OF SnO₂ NANOPARTICLES WITH DIFFERENT MORPHOLOGICAL PARAMETERS AND THEIR IMPACT ON ORGANIC DYES DEGRADATION PROCESS

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Organic dyes from the textile, paper, cosmetic and pharmaceutical industries cause water and soil pollution worldwide. It is dangerous to the environment, the hydrosphere, people and living organisms. The most environmental friendly approach to contaminants elimination is photodegradation of using semiconductor nanoparticles (NPs) with high specific surface area. One of the promising materials is a wide band gap semiconductor SnO₂ (3.6 eV). There are a lot of works about application of SnO₂ NPs as a photocatalyst for different organic dyes photodegradation. However, to the best of our knowledge, the impact of photocatalyst shape and solution temperature on the organic dye photodegradation process is still under discussion.

Spherical NPs (SSA = 260 m²/g, d = 3 nm) were obtained by chemical precipitation method. Nanorods (SSA = 38 m²/g, l = 56 nm, d = 17 nm) were obtained using hydrothermal treatment (T = 260 °C, t = 5 hours) of as-prepared samples. All samples were characterized by XRD, TEM, FTIR-spectroscopy, and SSA estimation. The efficiency of the organic dyes (methylene blue, rhodamine 6G and Congo red as typical models of pollutant) photodegradation was studied using UV-Vis spectroscopy and electrospray ionization mass spectrometry (ESI).

It has been established that for all dyes the use of spherical nanoparticles and 60 °C are optimal in terms of the duration of the process. The impact of pH value of solution, NPs morphology and dye concentration on degradation was studied. The shortest degradation time was observed for pH=9 for all organic dyes: methylene blue – 15 minutes, rhodamine 6G – 23 minutes and Congo red – 20 minutes. Also the necessity of additional sample preparation for the Congo red dye is shown. In accordance to ESI, in optimal conditions the photodegradation processes result in the dyes full decomposition.

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STRUCTURE AND PROPERTIES OF NEW PEROVSKITES La₄Zn₂Me₂O₁₁

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The significant interest of perovskite-type oxides over the past few decades and even until now have stemmed from their piezoelectric, catalytic and/or ionic and/or mixed ionic-electronic transport properties [1]. Because of unique structure of perovskites to tolerate of various sizes of cations at both A and B cation sublattices it is possible to search for a new electrolytes with higher conductivity and chemical stability [2, 3].

This work is devoted to the complex investigation of physicochemical properties of new compounds obtained by substitution a half of position B-cations in known perovskites LaMe⁺³O₃ [4, 5] with zinc. Zinc oxide has been used for several reasons: the creation of oxygen deficiency; lower melting point and, accordingly, to improve the quality of ceramics; as non alkaline earth metal, that allows to increase the chemical stability.

In this work were obtained a new phases La₄Zn₂Me₂O₁₁ (Me=Al, In). The samples La₄Zn₂Me₂O₁₁ were synthesized using the solid-state reaction method. Synthesis was carried out with stepwise temperature increase to 100° increments in the range of 700–1400°C. Structure of these phases was investigated. Electrical properties of samples were studied by varying thermodynamic parameters (T, pH₂O, pO₂). The chemical stability of the samples with respect to carbon dioxide and water vapor was investigated.
Investigation of the systems with immobilized bifunctional organic molecules on inorganic core based on noble metal nanoparticles (NPs) cause a great interest due to their unique property known as localized surface plasmon resonance. Due to a high electromagnetic field concentrated in the interparticle gaps, such materials are characterized by enhanced optical performances [1-2]. In this work, we investigated the optical properties of gold and silver NPs modified by 4,4'-dimercaptostilbene (DMS) and 4,4'-disulfonylstilbene (DSS). The study of modified nanoparticles with adsorbed stilbene derivatives was carried out by the fluorescent and Raman spectroscopies together with UV-vis spectrophotometry. The different responses were revealed for NPs linked by DMS and single NPs covered by DSS. Fluorescent quenching corresponding to linear dependence on NPs concentration correlated with the Stern-Volmer equation was obtained for DSS only. Obtained Raman spectra revealed a rearrangement of adsorbed molecules when a surface coverage reaches a monolayer. Raman spectra deconvolution with Lorenz function allowed us to calculate the analytical enhancement factors for DMS.

Figure 1. Fluorescent spectra of DSS at various Au NPs concentrations.

References

Acknowledgements. This work was supported by the RSF (project № 17-73-10209). The authors acknowledge the Resources Centers of SPBU: the Center for Optical and Laser Materials Research and Center for Chemical Analysis and Materials Research.
SELF-ASSEMBLED SUPRAMOLECULAR COMPLEXES OF AZACROWN CONTAINING DIENONES WITH ALKANEDIAMMONIUM IONS

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In order to elucidate the possibility to construct photoactive supramolecular systems based on symmetrical dienones 1a-c substituted with two azacrown ether moieties were synthesized. The behavior of dienones in acetonitrile in the presence of alkanediammonium ions $+\text{NH}_3(\text{CH}_2)_n\text{NH}_3^+$ ($n = 1-12$) was studied by UV/vis absorption spectroscopy, fluorescence and NMR $^1$H spectroscopy.

\begin{scheme}
\begin{center}
\includegraphics[width=0.5\textwidth]{scheme1.png}
\end{center}
\end{scheme}

\textbf{Scheme 1.} Structure formulas of dienones 1a-c and salts 2
Spectra of the dienones undergo significant changes in the presence of alkanediammonium ions. The stoichiometry and stability constants of the formed complexes were determined. The dienones form 1:2 complexes with short alkanediammonium ions ($n = 1-7$) and high stable 1:1 complexes with long ions in diluted solutions.

The results of this study can be used for directional design of photoactive supramolecular assemblies and optical molecular sensors.

Acknowledgements. This work was supported by the Russian Science Foundation (project № 19-13-00020).
We present the new approach for plasmon assisted grafting of anisotropic AuNRs with spatial selectivity, which was used for creation of NPs with amphiphilic surface. The plasmon assisted activation of IS was performed under the illumination of AuNRs with wavelength corresponded to the longitudinal plasmon resonance of AuNRs and resulted in grafting of organic moieties (Ar-(CF3)2) to AuNRs edges. The AuNRs lateral sides remains unscreened and were further grafted with diazonium salt, ADT-COOH. As result of varying substituents in the chemical structures of iodonium and diazonium salts the amphiphilic NPs with spatially divided hydrophobic (grafted to AuNRs edges) and hydrophilic (grafted to AuNRs lateral sides) chemical groups were obtained (fig. 1). Proposed approach was realized in solution and does not require the surface assistance in the spatially selective modification of AuNRs. Thus, our experimental route is potentially highly scalable and provide the possibility for powered throughput creation of amphiphilic anisotropic NPs, with chemical moieties precisely located at desired place on NPs surface.

Figure 1. SERS spectra, measured with two probed wavelength on AuNRs grafted with Ar-(CF3)2 (AuNRs edges) and Ar-COOH (AuNRs lateral sides)
MoO$_3$(WO$_3$)/ZrO$_2$ systems how catalysts for butene coupling reaction (isobutane alkylation and butene oligomerization for production high octane-number components to fuel) are promising [1, 2]. For a deeper understanding of their properties, it was necessary to study their catalytic and physicochemical properties in a single study.

In this work MoO$_3$(WO$_3$)/ZrO$_2$ systems are investigated which were from ZrO$_2$· nH$_2$O and different MoO$_3$(WO$_3$)-precursors. Details of the syntheses and investigation methods are given in [2].

It was revealed the genesis of MoO$_3$/ZrO$_2$ and WO$_3$/ZrO$_2$ systems is in many ways similar to each other. This is manifested mainly in slowing the crystallization of amorphous ZrO$_2$, and further affects the change in the phase state of ZrO$_2$. The introduction of MoO$_3$(WO$_3$) by impregnation method from heteropolyacids strongly stretches the crystallization process by temperature. At the same time, the presence of amorphous ZrO$_2$ makes a significant contribution to the porous structure (an increase of surface area). The composition and temperature of treatment affect the properties of the resulting catalysts most significantly. Thus, an increase in the content of MoO$_3$ also contributes to a serious reorganization of the acid cover of the surface: the exponential growth the number of Brønsted acid sites and a non-monotonic change in the content of Lewis acid sites (LAS) with a sharp fall at 9% MoO$_3$.

The method of synthesis by impregnation makes it possible to obtain catalysts with the most developed porous structure and increased high LAS compared to the dry mixing method. The differences in catalytic properties are largely due to differences in the acidity of the surface. The high content of MoO$_3$ and a large supply of butenes contributes to the course of the oligomerization reaction. Reducing the supply of butenes and the introduction of MoO$_3$(WO$_3$) by impregnation contribute to the flow of alkylation of isobutane. Controlling the properties of MoO$_3$(WO$_3$)/ZrO$_2$ systems by varying the conditions of their preparation allows to regulate their physicochemical and catalytical properties.

References
Nowadays processing of renewable biomass as an alternative to conventional oil feed draws much attention. The main drawback of such feed is high content of oxygenates which are difficult to refine by existing paths. A perspective approach could be their catalytic cracking as an additive to hydrocarbon conventional feed yielding additional quantities of C$_2$-C$_4$ olefins.

The goal of this work is to research trends of hydrocarbon and model oxygen containing compound (acetone, glycerin) additives catalytic cracking in the presence of Y and ZSM-5 zeolite catalysts. In order to plan such experiments a central composite rotatable plan was designed. ZSM-5 content in the catalyst varied from 0 to 20 % (here and after %mass.) and composition of bio oxygenate additive to feed were chosen as independent variables. Oxygen containing feed additive consisted of acetone and glycerin binary mixtures, total content of oxygenates in the feed was fixed at 5 % in all experiments.

It was shown that in the presence of Y zeolite the highest yield of C$_2$-C$_4$ olefins (24,1 %) is achieved for acetone-rich additives to feed. Introduction of ZSM-5 as catalytic additive enables to achieve much higher yields of light olefins (28,5 %) for glycerin-rich feed additives. A synergistic effect was observed during catalytic cracking of hydrocarbon feed with oxygen containing additive of intermediate composition. This effect appears as a minimum in propylene and C$_4$ olefins yield depending on feed additive composition and a maximum of gasoline yield under same conditions. This is due to condensation reactions of oxygenates and/or their intermediates yielding heavier products of gasoline boiling range. Moreover a suppression of hydrogen transfer reactions catalyzed by Y and ZSM-5 combination was shown in the presence of oxygen containing compounds.

Acknowledgements. This work was carried out within the State Program of TIPS RAS.
Available thermodynamic data on composition of equilibrium vapor over metal iodides remains scanty despite numerous investigations of thermochemistry of metal halides. The vapor over binary systems of two different metal iodides is expected to include heterocomplexes and various dimer homocomplexes in addition to the monomers.

The vaporization of KI/FeI₂ and KI/AgI samples was investigated in the temperature ranges between 800 to 825 K and 721 to 964 K by using the mass spectrometric Knudsen effusion method. The ions M⁺, MI⁺, MI₂⁺, KMI⁺, KMI₂⁺ (M=Fe, Ag), FeI₃⁺, K⁺, KI⁺, K₂I⁺, KFeI₃⁺ have been registered. The silver iodide was synthesized in situ as the result of interaction of silver which was using as pressure standard with iron iodide. Neutral molecules corresponding to the aforementioned ions have been found. From their partial pressures, the equilibrium constants of gaseous phase reactions were determined:

\[
\begin{align*}
\text{KI (gas)} + \text{FeI}_2 \text{ (gas)} &= \text{KFeI}_3 \text{ (gas)} \\
\text{1/2K}_2\text{I}_2 \text{ (gas)} + \text{FeI}_2 \text{ (gas)} &= \text{KFeI}_3 \text{ (gas)} \\
\text{KI (gas)} + \text{AgI} \text{ (gas)} &= \text{KAgI}_2 \text{ (gas)}
\end{align*}
\]

From equilibrium constants the standard enthalpies of formation KFeI₃ and KAgI₂ were determined (KFeI₃, gas,298) = -213.9±1.2 kJ/mol and \(\Delta f\text{H}^\circ\) (KAgI₂, gas,298) = -166.3±7.1 kJ/mol.

The structures of KFeI₃ and KAgI₂ is presented on Figure 1. The barrier height between \(C_3\text{v}\) and \(C_2\text{v}\) structure for KFeI₃ is about 3 kJ/mol.
Lewis acids are widely used in organic catalysis to activate electron-excess molecules. Species with bulky substituents are of particular interest, since they can form frustrated Lewis pairs in combination with Lewis bases [1]. Also, when choosing a catalyst, it is important to estimate the strength of the Lewis acid and compare it with other compounds in order to choose the most suitable variant.

Tensimetric method allows to investigate the equilibrium between the gas and condensed phase in closed systems, thus it is possible to determine the composition of both the gas and condensed phases [2]. In this work we examined systems consisting of ionic oxophosphonium Lewis acid [(C_3H_2(NDipp)_2N)_2PO]^+[B(Ar(CF_3)_2)_4]^- (LA, Dipp = 2,6-diisopropylphenil) [3] and pyridine (Py) or acetonitrile (An). A series of tensimetric experiments were performed for this systems. From the data obtained, the gas- and condensed-phase compositions were calculated at different temperatures. It is shown that the acid forms 1:1 complex with pyridine and a solvate with acetonitrile.

A complex with pyridine is resistant towards dissociation up to 515 K, after which the irreversible autocatalitic pyrolysis began. The dissociation of solvate with acetonitrile begins at about 320 K and it is accompanied by a very small thermal effect, less than 10 kJ.

References:

Acknowledgements. This work was carried out in framework of RSF grant (grant № 18-13-00196). We thank Pawel Lowe (University of Munster, Germany) for the sample of Lewis acid.
OPTICAL PROPERTIES OF SURFACE MOLECULAR-IMPRINTED TITANIUM DIOXIDE NANOPARTICLES

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Perylenediimide (PDI) dyes - acceptors of well-known organic semiconductor systems [1]. They are often used in organic photovoltaic cells in which low values of the band gap are achieved, but PDI have a tendency to self-aggregate.

The method of surface molecular imprinting [2] to create films on the surface of TiO₂ nanoparticles with 1-H-pyrrol-N, N'-bis (3-pentyl) perylene-3,4,9,10-bis (dicarboximide)-5-hexyl-11-1H-1,2,3-triazol-1-yl-pentanoic acid (PDI-Taz-C₅OOH) imprints with acceptor properties (Fig. 1) was used. The band gap of the obtained material has reduced by 0.1–0.5 eV (Table 1), and the sorption capacity after template removal with ethanol has reached 0.75 µmol/g. At the same time, molecular imprinted (MIP) material can re-bind 2 times more PDI-Taz-C₅OOH than unimprinted (NIP).

Table 1. Band gap ($E_g$) of NIP and MIP samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor : template</th>
<th>$E_g \pm \delta$ (P=0.95, n=3), eV</th>
<th>$\Delta \lambda$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>3.09 ± 0.01</td>
<td>–</td>
</tr>
<tr>
<td>MIP</td>
<td>1:81</td>
<td>2.62 ± 0.10</td>
<td>72</td>
</tr>
<tr>
<td>NIP</td>
<td>–</td>
<td>2.98 ± 0.05</td>
<td>16</td>
</tr>
</tbody>
</table>

References

Acknowledgements. This work was supported by the Foundation for Assistance to Small Innovative Enterprises (Russian Federation) (project No 52562).
The improvement of existing and development of new technologies is impossible without creating new functional and structural materials. The potential application of these materials is diverse and constantly expanding. One of the most promising nanomaterials is single-walled carbon nanotubes. Research result indicated that the addition of nanotubes to the electrolyte as a dispersed phase has a positive effect on the properties and structure of the electrochemical coating. The deposition rate increases by 2 times, the adhesion of the coating to the base is improved, coating porosity decreases [1].

Figure 1. Electrochemical copper coating with nanotubes. Image was obtained with an atomic force microscope.

Electrochemical coatings withstood climatic-mechanical tests according to GOST RV 20.39.414.1-97 and GOST 23752-79.

Reference

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INFLUENCE OF TRANSITION METAL DOPING ON THE STRUCTURAL AND OPTICAL PROPERTIES OF SnO$_2$ NANOPARTICLES

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The development of new visible-light photocatalysts is a highly attractive area in nanotechnology. Their unique photocatalytic activity under solar irradiation make them potentially of great use for efficient environmental treatment. Tin dioxide (SnO$_2$) with a band gap of 3.6 eV and rutile crystal structure is an excellent and widely investigated semiconductor material that has been used in photocatalytic researches for their high photosensitivity and chemical stability. In view of a large number of studies, doping SnO$_2$ by 3d element is considered to be an easy way to decrease a band gap value, and consequently to increase the charge separation and spread the energy range of photoexcitation. Since the mechanism and impact of doping process on electronic structure and photodegradation effect is still under discussion, the objective of this research was to study the correlation between the structure of as-prepared nanoparticles (NPs) and their photocatalytic activity.

To clarify this aspect, we used 11-33 mol% Cu, Co, Cr as dopants for SnO$_2$ nanoparticles; the influence of pH values was also studied. Bare and doped SnO$_2$ NPs were obtained by the (co)precipitation method. As expected XRD data demonstrated only rutile SnO$_2$ peaks (ISDD 00-041-1445), the crystallite sizes increased for the higher pH values. According to TEM and SSA data, the nanoparticle size does not exceed 10 nm. The changes in lattice parameters indicate the success of the doping process.

Positions of dopant atoms in crystal cell, which determines the energy spectrum, as well as densities of states were calculated using abinitio calculations in ABINIT software package. UV-Vis absorption spectra show the difference between bare and doped SnO$_2$ nanoparticles. The obtained results were in good accordance with the photodegradation tests of Methylene blue (MB) under UV and Vis irradiation. After 15 min of Vis irradiation, the degradation rate of MB reached 38 % and 85 % for SnO$_2$ and Cu-doped SnO$_2$, respectively. It is shown that the nanoparticles under study a promising visible-light photocatalyst for efficient environmental photocatalysis.

Acknowledgments. Scientific research was performed at the Research Park of St. Petersburg State University Educational Resource Center of Chemistry: Center for Optical and Laser Materials Research, Chemical Analysis and Materials Research Centre.
CRYSTAL STRUCTURE, THERMAL STABILITY AND CONDUCTIVITY
OF (2E)-6-CHLORO-2-(6-CHLORO-4-METHYL-3-OXO-1-
BENZOTHIOPHEN-2-YLIDENE)-4-METHYL-
1-BENZOTHIOPHEN-3-ONE

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The crystal structures of Vat Red 1 (VD) crystal structures (monoclinic) derive from stacking of flat molecules arranged due to π-π interaction.¹ From the studies, the melting point of the Vat Red 1 is 409 °C and the optical band gap for VD is $E_{bg} = 2.30$ eV, and it has been calculated using powder diffuse reflectance UV–Vis spectra and the absorption edge of VD is at 539 nm. VD exhibited the highest occupied molecular orbital energies ($E_{HOMO}$), the lowest unoccupied molecular orbital energies ($E_{LUMO}$) values of $-0.21959$ eV and $-0.13635$ eV. The pristine thioindigo exhibits the $E_{HOMO}$ and $E_{LUMO}$ values of $-3.05$ eV and $-5.86$ eV.²

![Chemical structure of VD](image)

Fig. 1 Chemical structure of VD

Reference:
EFFECT OF ORGANIC ACID CONCENTRATION ON YTTRIUM OXIDE STRUCTURE FORMATION

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Studies in the synthesis of yttrium oxyhydroxides are relevant due to the high prospects for using these compounds as catalysts for removing organic contaminants from water, as well as the basis for nanoceramics and phosphors. The structure and particle size of materials have a significant impact on their properties and reactivity as catalysts. In this connection an important factor in synthesis of these compounds is the ability to control the structure, which allows controlling the reaction process and product quality. In the present study the samples were obtained by the sol-gel method with hydrothermal treatment. The sol-gel synthesis was carried out at final pH values (8, 9, 10) with the introduction of malic acid and citric acid of various concentrations (0.1 M and 0.5 M). The primary hydrothermal treatment lasted for 24 hours. After the primary hydrothermal treatment the solution was adjusted to pH = 12 and subjected to repeated hydrothermal treatment within 24 hours. A study was carried out as to the effect of malic acid concentration on the structure of the samples obtained. On addition of malic acid with 0.1 M concentration, particles looking like hollow tubes 5–10 µm long and about 1–2 µm wide are formed. The wall thickness is about 100 nm. When 0.5 M acid is used, particles of a clear hexagonal shape are formed, which are not hollow. The particle length is 8–10 µm, the width is 3–4 µm, with the formation of particles of similar size. Micrographs of a samples obtained with the addition of citric acid show hollow spheres, the surface of which is covered with pores. The pore diameter varies between 0.5–2 µm, the diameter of the spheres — 5–10 µm, the wall thickness is about 0.5–1 µm.

The analysis of the obtained diffractograms have shown that crystalline structures are formed only under the condition of repeated hydrothermal treatment with adjustment to high pH values. Analysis of the IR spectra suggests that malic acid is not included in the structure of the obtained samples, due to the absence of characteristic oscillations in the range of 1500–1750 cm\(^{-1}\). For the samples obtained with the introduction of malic acid, formation of compounds with non-associated OH groups has been observed.

Acknowledgements. South Ural State University is grateful for financial support of the Ministry of Science and Higher Education of the Russian Federation (grant No 4.9722.2017/8.9).
The formation of three-dimensional (3D) carbon structures remains one of the most important challenges in nanotechnology. We suggest that the covalent cross-linking of carbon nanotubes (CNT) by polyaromatic linker molecules will enhance CNT properties, e.g. solubility, conductivity, specific surface area, porosity, sensor response, etc. Molecules of pyrene, phenylcoumarin and phthalocyanine were chosen as three types of linkers due to their polyaromatic nature, different size of their core and good solubility in organic solvents.

3D-hybrid materials were obtained by azide-alkyne cycloaddition reaction via interaction of dialkyne-substituted polyaromatic derivatives with the surface of CNT modified by azide groups, according to the reaction:

\[ \text{N=N'N'} + \text{Si} \rightarrow \text{N=N'N'} \]

Figure 1. Scheme of 3D-materials synthesis via the reaction of azide-alkyne cycloaddition.

To compare the efficiency of functionalization method and properties of the obtained materials, hybrids with the same polyaromatic molecules were also obtained by non-covalent functionalization.

The structure of the obtained products was studied by TEM, SEM and Raman spectroscopy. Sensor responses of all hybrid materials toward NH\textsubscript{3}, H\textsubscript{2}S, H\textsubscript{2} and CO\textsubscript{2} were studied at different humidity. The responses of 3D-materials to ammonia were 10 times higher than those of pristine CNT and twice higher than in the case of hybrids non-covalently obtained. The possibility of selective detection of NH\textsubscript{3} in the presence of 50,000 ppm of CO\textsubscript{2} was demonstrated.

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PRODUCTION OF RECOMBINANT HUMAN TRANSFERRIN IN THE EUKARYOTIC EXPRESSION SYSTEM OF PICHIA PASTORIS

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Recombinant proteins in modern biotechnology and biopharmaceutics are of great interest in this industry. Today, protein production in recombinant expression systems has several advantages, in comparison with the available alternatives, such as the treatment of animal blood serum. It is important that the Pichia Pastoris expression system is less expensive than the expression in mammalian cells. The use of Pichia Pastoris ensures the correct folding of recombinant proteins, which is very important for the analysis of the final activity of the product. Transferrin (TFNG) is responsible for the receptor-mediated transport of iron ions into the cell. This protein is a promising object in medical therapies of various diseases, including cancer, conjugating TFNG with therapeutic agents and using as a targeted transport inside the pathogen. Also, TFNG is an important component of serum-free media for eukaryotic expression systems. To date, the majority of serum-free media will include albumin and transferrin, obtained from the blood of animals and humans. The use of these supplementary proteins significantly increases the risks of contamination with various infectious agents, including non-enveloped viruses such as hepatitis A virus and parvovirus B19 or agents causing Creutzfeldt-Jakob disease, because during their production, the detection or inactivation of such agents is not currently are effective. The replacement of TFNG in the serum-free nutrient media used to produce modern therapeutic drugs, their recombinant analogues will eliminate the risk of contamination with biologically active impurities. In our work, we were able to obtain a strain expressing 100 mg/L unrefined protein of culture fluid.

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The research is directed to synthesizing of novel hybrid Au-Ag@C nanostructure (called nanoflakes) with unique morphology, well-controlled geometric sizes, and multifunctional properties. The flakes are deposited on the substrate-solution interface illuminated with an CW laser beam ($\lambda = 325$ nm, $I = 0.5$ W/cm$^2$). The large interest of in-depth and detailed investigation of nanoflakes synthesis is determined by their following characteristics: (i) a linear birefringence caused by features of crystalline structure of carbonaceous matrix; (ii) plasmonic bimetallic clusters embedded to carbon phase and stimulating surface-enhanced Raman scattering (SERS), that can serve as efficient development for photonics, optics, and sensing technologies [1, 2].

The nanoflakes were obtained from solution of supramolecular complex (SMC) [$(\text{Au}_{13}\text{Ag}_{12}(\text{C}_2\text{Ph})_{20})(\text{PPh}_2(\text{C}_6\text{H}_4)_3\text{PPh}_2)_3)(\text{PF}_6)$] in aniline and acetophenone onto the different type of substrate (cover glass, quartz, polypropylene, and polyethyleneterephthalate). The flakes formation is the result of laser-induced decomposition of SMC. It was demonstrated that size and shape of nanoflakes depend on parameters of laser deposition and interaction between SMC and solvent with substrate surface. The deposited structures were characterized using a scanning electron microscope (SEM) and research optical system microscope with studying of nanoflakes in the polarization light (Figure 1).

Figure 1. The SEM and optical microscope images of obtained nanoflakes

References
NEW STATIONARY PHASE BASED ON A COPOLYMER OF STYRENE
AND DIVINYLBENZENE MODIFIED WITH GOLD NANOPARTICLES
FOR SEPARATION PROFENS AND β-BLOCKERS

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Nanomaterials have received much attention due to their novel chemical,
physical and electrical properties. Within separation science, gold nanoparticles
have found a promising home, because of their long-term stability, high surface
area-to-volume ratio, and ease of chemical modification. A new sorbent for
HPLC based on a styrene-divinylbenzene copolymer (CSD) was synthesized
by adsorption of gold nanoparticles on its surface, followed by modification
through the formation of self-assembled monolayers by the reaction between
gold and sulfur-containing reagent – lipoic acid with grafted lysine. Low-
temperature nitrogen adsorption, diffuse reflection spectroscopy, scanning
electron microscopy were used to examine physical and chemical properties of
obtained sorbent. The chromatographic behavior of profens and β-blockers was
studied on the sorbents depending on the composition of the mobile phase: the
nature of the buffer solution, its concentration and pH, the proportion
and nature of organic solvent. It was established that significant retention factors
for both groups of substances are observed using the mixture of acetonitrile and
buffer solution as the eluent. Herewith profens are kept longer with a lower
content of organic solvent, and β-blockers, on the contrary. Hydrophobic
interactions play a significant role in the retention of the studied compounds.
The order of elution of profens correlates with their hydrophobicity indices
logP, logD. This dependence is traced to a lesser extent for β-blockers, due to
the additional interactions. The separation of the six-component mixture of β-
blockers in 15 minutes and of the three-component mixture of profens in 20
minutes was carried out on the new sorbent.

Figure 1. CSD-Au-lipoic-acid-lysine

Acknowledgements. This work was supported by Russian Foundation for
Fundamental Research (№18-03-00742).
First isolated in 2004, graphene has sparked a great scientific interest thanks to its peculiar mechanical and electronic properties, which promise to upgrade many technologies, from microelectronics to biosensing and nano-medicine.[1] Among the many molecules that have been proposed as exfoliating agents of graphite, only a few ones successfully exfoliate and stabilize graphene in aqueous media.[2] Mechanochemistry has gained increasing importance in diverse fields of chemistry,[3] principally in the exfoliation and functionalization of nanomaterials like graphene, it has also many advantages such as shorter reaction times, higher product yields and the elimination of (harmful) organic solvents.

Here we report the development of an environmentally friendly, cheap and simple approach for the synthesis of aqueous soluble few-layer graphene, useful for biological purposes. From theoretical insight, state-of-the-art density functional theory (DFT) calculations within a super-cell slab periodic approach, and comparison with experimental result, we propose that different carbohydrates behave as melamine in a micro-solvation model where the interplay between non-covalent interactions, provides the necessary thermodynamic driving force to stabilize the graphene-water dispersions.[2] The prepared graphene have been characterized by TEM, X-ray diffraction, TGA, Raman spectroscopy. This study aims to use carbohydrates as exfoliating agents and open up new possibilities for preparing graphene materials, in large-scale, for biological applications.

References

Acknowledgements. Financial support from the EU Graphene-based disruptive technologies, Flagship project (no. 696656) and the Spanish Ministerio de Economía y Competitividad (project CTQ2014- 53600-R)
THERMAL PROPERTIES OF BIOCOMPATIBLE PIGMENTS BASED ON HAP NANOPARTICLES WITH VARIOUS MORPHOLOGIES


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These days biocompatible pigments are actively introduced into cosmetic industry to replace apparently toxic materials such as organic dyes and inorganic compounds. In addition, the multifunctional cosmetics with a skin care effects becomes more and more popular. The pigments must be thermally stable, as the technology of cosmetic production includes high temperature treatment. The range of appropriate materials is extremely low. In our opinion, hydroxyapatite (HAp), which is the main component of bone tissue, and widely used in cosmetic industry for induction of collagen production, appears to be a promising one. It is known that doping with 3d-elements possibly leads to the color change of initially white hosts, however, the amount of articles about doped-HAp remains low. Accordingly, the present work was dedicated to the synthesis of doped HAp nanoparticles and its thermal properties.

Nano-HAP samples doped with Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cr$^{3+}$ ions (concentration ratio 10:100) were synthesized hydrothermally at 180 °C for 2 hours in the presence of two different types of hydroxide source (NaOH and NH$_4$OH). Morphological characteristics were studied with XRD, TEM methods, SSA estimation, and FT-IR spectroscopy. TGA and DSC data were collected in temperature range from 20 to 1200 °C in air.

As a result, the HAp nanoparticles were doped with Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cr$^{3+}$ ions. According to XRD, the lattice parameters of each sample have changed, which confirms successful doping. All the samples obtained with NaOH (except Cr-HAp) are tricalciumphospate (TCP), while the others are HAp. The color of the as-prepared particles indicated as a typical for salts of injected ions. The study of thermal properties showed that all samples (except for Cu-HAp prepared using NaOH) remain stable to heating up to 900 °C. In addition, several samples demonstrated the changes from the starting crystal phase to TCP under high temperature.

Acknowledgements. Scientific research were performed at the research park of St. Petersburg State University educational resource center of chemistry: Centre for X-ray Diffraction Studies, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.
ROLE OF WATER IN THE FORMATION OF ORGANOGELS WITH CYCLO(LEUCYL-LEUCYL) DIPEPTIDE

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Supramolecular gels, formed through intermolecular interactions, are a class of soft materials with promising applications in the field of materials science. Cyclic dipeptides (CDP) or 2,5-diketopiperazines (2,5-DKP) are capable of gelation formation at concentrations below 1% w/v due to their structure of a molecule with two chiral centers which provides many opportunities for structural optimization through intermolecular interactions.

At the same time, the fundamental problem associated with determining the conditions for the formation of gels still remains unsolved. There are no approaches to predicting the type of solvent that can be gelled. The study of the role of solvents and their effect on the stabilization of a developing metastable material is an important topic for the development of supramolecular gels.

The present study was aimed at studying the ability of cyclic dipeptides to form gels on the example of cyclo(leucyl-leucyl) dipeptide. Solvents, including binary, were screened for their ability to induce gelation of cyclo(leucyl-leucyl). The conditions for obtaining stable organogels of cyclo(leucyl-leucyl) with a wide range of solvents were determined. The special role of water as an agent that forms intermolecular interactions for the preparation of stable gels has been established. The possibility of practical application of cyclo(leucyl-leucyl) for water purification was showed.

The results obtained in the course of research clarify the mechanism of the formation of organogels with cyclic dipeptides and can be used for preparation of new gels for solving problems of medicine, biotechnology and ecology.

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STUDYING THE ROLE OF MOLECULAR VIBRATIONS EXCITED BY UV PHOTODISSOCIATION OF OZONE MOLECULE ON POLARIZATION OF ANGULAR MOMENTA OF PRODUCING PHOTOFRAGMENTS

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Studying of a dissociation process deliver deep insight into many fundamental physical processes. Important information about dissociation dynamics, form of the potential curves, symmetry of excited states and the role of nonadiabatic interactions can be obtained from analysis of photodissociation’s cross section [1].

In this work was achieved cross section of photodissociation of molecule of prolate top type and was investigated effects of rotation and vibration of excited states. Computation was carried out using the known method of expansion over spherical irreducible tensors [2]. Angular momenta of photofragments can be oriented or aligned and it corresponds to first and second components of tensor’s rank. Usually wave function built up of spherical harmonics but in this work expansion over Wigner D-functions was proceed. Complex motion of the molecule of prolate top type was taken into account. Analysis of obtained results leads to the deep understanding of photodissociation process in the ozone molecule. Автор благодарит О.С. Васютинского за консультации и помощь при выполнении работы.

References

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LASER INDUCED MICRO-MODIFICATIONS OF OPTICAL PROPERTIES
IN OXIDE GLASSES

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Femtosecond (fs) laser induced modification of oxide glasses opens new routes for precise space-selective tuning of material properties and development of functional photonic devices including integrated waveguides, optical switches, phase plates, volume optical memory, etc. In this regard, glasses doped with photosensitive agents such as noble metals and semiconductors are of particular interest due to unique optical properties of nanoclusters, nanoparticles or quantum dots that can be precisely precipitated in the confined volume of glass. Hence fs modification could become a convenient alternative to conventional nanotechnology methods for the one-step development of 3D nanostructured materials with a wide set of functionalities in sensing, photonics and data storage devices and it is crucial to understand processes which take place during the fs modification including local chemical composition change, influence of glass matrix and laser parameters. We performed fs modifications of zinc phosphate and silicate glasses doped with Ag and CdS using high power near IR femtosecond laser system PHAROS SP coupled with Aerotech 3D translation stage. We showed the possibility of simultaneous formation of luminescent silver clusters and plasmonic silver nanoparticles in phosphate glasses as well as of luminescent CdS quantum dots in silicate glasses spatially confined in micron-sized pipe-shaped domains inside glass. Also we showed that laser treatment induces micro-modification of optical properties manifested in the appearance of luminescence and absorption in the visible spectral range and homogeneous birefringence in the laser-exposed domains. Using energy dispersive X-ray spectroscopy, we showed Ag ions migration process from center to the boundary of domains as well as migration of Zn to the center. Ability to form complex 3D shapes of luminescent, plasmonic and birefringent structures embedded in dielectric transparent glass materials will pave the way for the design of nanophotonic devices and multilevel optical memory.

References

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RHEOLOGICAL ADDITIVE FOR FIRE EXTINGUISHING POWDER

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Rheological additives are a necessary component in the manufacture of fire extinguishing powders (FEP), they increase flowability, prevent caking of components during storage and give the powder hydrophobic properties. The hydrophobic silica additive currently used in FEP has several disadvantages - nano-sized particles are stable agglomerates with irregular shape ($d_{\text{mid}}$ - 50 nm) ($S1$), which doesn’t provide uniform distribution of the additive over the surface of the fire extinguishing components and prevents free flow of the powder composition.

To increase the mobility of powder compositions, it has been proposed to use hydrophobic silicon dioxide in the form of spherical monodisperse particles of size 118 nm, were obtained by heterogeneous synthesis according to the method of Stober ($S2$).

Silicon dioxide Aerosil 380 with an average size of agglomerates of 90 nm ($S3$) was used together with $S2$, individual use of which in FEP is limited due to low tamped density ($\approx$ 50 g/l). For the study, rheological additives with different ratios of hydrophobic components $S2 / S3$ were added into a model FEP composition based on two-fractional ammonium phosphate salt with particle sizes of 200-315 $\mu$m (I) и 0-50 $\mu$m (II), where the average particle size is 280 $\mu$m and 35 $\mu$m, respectively. The ratio of the fractions were I / II = 60/40, the ratio of ammonium phosphate and the rheological additive was 95/5.

Research of the rheological and shear properties of the powder compositions were carried out using a Freeman Technology FT4 Powder Rheometer.

The use of non-agglomerated spherical silica particles $S2$ as rheological additive made possible to obtain more free-flow fire extinguishing powder compositions based on ammonium phosphate than using the $S1$ additive, keeping a high proportion of fire extinguishing component (about 95%). It has been established that the combined use of $S2$ and $S3$ silica in additive reduces the value of the flow energy of the powder composition. When the ratio of the components of the rheological additive is $S2 / S3$: 80/20, FEP has the lowest value of the flow energy, while the cohesion and flow function correspond to the composition with easy flowing properties.
Cubic tungsten carbide ($\text{WC}_{1-x}$) is a unique modification of tungsten carbide, which can be synthesized, according to the well-known phase diagram [1], only in an extremely narrow temperature range from ~2,700 to ~3,000 K. In addition, at slow cooling, it is extremely unstable and turns into the most common hexagonal tungsten carbides $\text{W}_2\text{C}$ and $\text{WC}$ [2]. Nonetheless, there are some reports, where its existence is shown at room temperature in the case of high-energy synthesis and superfast cooling rate of at least $10^8 \text{ K/s}$ [3]. Such conditions can be achieved by implementing a direct plasma dynamic synthesis in a system based on a coaxial magnetoplasma accelerator with graphite electrodes. When tungsten is laid in the plasma formation zone, the following initiation of the arc discharge in the interelectrode gap leads to the sublimation of the precursor and its acceleration in the graphite accelerating channel. Carbon enters the plasma structure due to the electroerosion. Thus, when the plasma containing tungsten and carbon is sprayed in an inert medium, an ultrafast crystallization and formation of tungsten carbide nanoparticles occurs. In this work, by means of X-ray diffractometry, X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy it is clearly confirmed the formation of cubic tungsten carbide in the aforementioned process, as well as the product purity can reach up to 95%. Using these products, the temperature stability of the $\text{WC}_{1-x}$ phase was studied under annealing conditions in air and in vacuum. It was found that due to the process peculiarities and the material structure (the presence of a carbon shell around the $\text{WC}_{1-x}$ particles), the resulting cubic tungsten carbide has a higher range of temperature stability in the air up to 700 °C compared with known data. Vacuum annealing made it possible to detect the presence of $\text{WC}_{1-x}$ phase in the product even at temperatures up to 1500 °C.

References

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Zirconium silicate materials based on plasma dissociated zircon

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Zircon-based vanadium Zr$_{1-x}$V$_x$SiO$_4$ ceramic pigments are a modern type of pigments used in ceramic industry. They are stable at high temperatures and melted glazes due to zircon properties: its refractoriness and chemical inertness. A perspective way to solve the problem of zircon pigments cost is to use the plasma dissociated zircon (PDZ) from natural mineral as a raw material [1]. PDZ is a spheroids which consist of crystalline monoclinic zirconia grains interconnected to each other by the amorphous silica glass. Ammonium hydrofluoride used for the chemical activation of PDZ. It reacts with components of PDZ with their partial destruction. This partial fluorination cause microdefects in the structure of PDZ for more intensive interactions between defective PDZ and vanadium ions to obtain more intensively colored pigments.

A phase composition of pigments consists of V-zircon and monoclinic zirconia. V-ZrSiO$_4$ formation was confirmed by the shift of zircon phase peaks on XRD patterns. The increase of calcination temperature led to higher yield of green color in materials because of the growth of vanadium solubility in zircon structure and a more crystallization degree of zircon. Brown color of pigments were formed because of formation of green V-zircon and orange V-zirconia [2]. The pigments had blue color in the presence of mineralizer (so-called Turkish blue). However, blue color yield reduces at higher calcination temperatures. It can be explained by the fact that the mineralizer promotes the formation of not only V-zircon, but also V-zirconia.

The use of the products of fluorine-ammonium treatment for plasma-activated zircon as the raw material in the V-ZrSiO$_4$ pigments technology allows to synthesize blue and green pigments with different color characteristics depending on the degree of fluoride activation of PDZ, the amount of chromophore, the calcination temperature and the presence of mineralizer.

References
A study of Lewis acidity is of both scientific and practical interest. Lewis acids are extensively used in organic synthesis as catalysts [1]. The question of a strength of Lewis acids remains controversial, since there is no uniform scale of Lewis acidity. The most common Lewis acidity scales are based on results of quantum chemical computations, for example, on the values of affinity energies for $\text{H}^-$, $\text{CH}_3^-$, $\text{F}^-$, $\text{Cl}^-$ anions in the gas phase [2]. Often, values obtained by different methods are not comparable. Therefore, it is important to find a parameter that can be determined by both computational and experimental methods.

In the present work the interaction between $(\text{C}_6\text{F}_5)_2\text{BC}_6\text{H}_2(\text{C}_6\text{F}_5)_3$ (Lewis acid, LA) and acetonitrile (Lewis base, LB) was studied by the static tensimetry method with membrane null-manometer [3]. Three experiments were carried out using different initial ratios of the LB and LA: 9.9:1, 5.6:1 and 2.3:1. In all experiments, the solid compound of 1.7:1 composition is formed at room temperature. Such composition may arise from additional acetonitrile incorporation into the crystal lattice after the complex formation due to the donor-acceptor interaction. Upon heating, the complex dissociates with the release of gaseous acetonitrile. Processes of desolvation and dissociation of the donor-acceptor bond occur as a single step, and therefore it is impossible to separate them. Quantum-chemical computations confirmed principal possibility of formation of both donor-acceptor complex and crystallosolvate. Computed dissociation enthalpies of complex and crystallosolvate are almost equal, in qualitative agreement with the results of tensimetry experiments.

References

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The development of catalysts for the reaction of partial oxidation of hydrocarbons is of great importance for the environmental safety and resource-saving technologies. Noble metals give the best effect as active component in this reaction. In this work, we prepared and characterised catalysts for the reaction of partial oxidation of hydrocarbons based on platinum supported on alumina of the bayerite series ($\theta$-Al$_2$O$_3$). Alumina compounds were obtained through the aluminate method from aluminum. We synthesized both granular and structured catalysts. The last ones are additionally supported on the FeCrAlloy mesh. The use of alumina and described structured supports provides number of advantages [1-2]. First of all, we characterized supports, their precursors and precursors of the active component. Then the catalyst samples were prepared by impregnating the support with solutions of different precursors. Since the catalysts are synthesized in a nanoscale state, we use special physicochemical methods to investigate these substances, the support form’s influence, the active component precursor’s nature: X-ray diffraction, transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and UV-Vis diffuse reflection spectroscopy.

References

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An advanced oxidation process has been implemented for detonation nanodiamond purification and surface chemical modification. The treatment intended for chemical oxidation of detonation nanodiamond surface through reactions with hydroxyl radicals (·OH).

A number of samples were processed: detonation carbon, purified industrial grade detonation nanodiamond[1] and single particle hydrosols of air oxidized[2] and hydrogen annealed[3] detonation nanodiamonds.

Comparative analysis of surface chemical composition provided by results of XPS and FTIR. Average size of primary nanodiamonds calculated by XRD data. Size distribution of detonation nanodiamond hydrosols measured by DLS. Elemental analysis provided by EDAX.

A method for obtaining uniform surface with oxygen-containing functional groups in spite of source of detonation nanodiamond was demonstrated. In some cases, advanced oxidation processing is more convenient than conventional gas-phase methods for surface modification.

References

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Zr$^{4+}$/F$^-$—SUBSTITUTED ANATASE TITANIUM DIOXIDE WITH ENHANCED ELECTROCHEMICAL PERFORMANCE

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Recently, anatase titanium dioxide is positioned as an anode material for high-rate lithium-ion batteries (LIBs). However, the sluggish transport of ions ($10^{-15}$ cm$^2$ s$^{-1}$) and electrons ($10^{-12}$ S cm$^{-1}$) serves a limiting factor. A promising method to modify the titania is a cationic (substitution of part of Ti$^{4+}$ with metal ions) and anionic (partial replacement of O$^{2-}$ with non-metals) doping. Within the scopes of the present work, the Ti$_{0.97}$Zr$_{0.03}$O$_{1.98}$F$_{0.02}$ solid solution with an anatase structure was synthesized by a template sol-gel method on a carbon fiber and investigated as an anode material for LIB. Through a wide range of physicochemical methods, it was established that Zr$^{4+}$ and F$^-$ ions incorporated uniformly in the Ti$^{4+}$ and O$^{2-}$ sites of TiO$_2$ lattice. The difference in the ionic radii of Ti$^{4+}$ (0.604 Å) and Zr$^{4+}$ (0.72 Å) leads to changes in TiO$_2$ unit cell. At the same time, replacement of O$^{2-}$ with F$^-$ contributes to the Ti$^{3+}$ generation into the crystal lattice and affects conductivity. In particular, the conductivity of Zr$^{4+}$/F$^-$ co-doped TiO$_2$ reached $1.7\times10^{-9}$ S cm$^{-1}$, that significantly higher than only Zr$^{4+}$-doped ($8.7\times10^{-12}$ S cm$^{-1}$) and undoped TiO$_2$ ($7.36\times10^{-13}$ S cm$^{-1}$) samples. The electrode from Ti$_{0.97}$Zr$_{0.03}$O$_{1.98}$F$_{0.02}$ was tested in half-cell with a lithium counter electrode in the voltage range of 1–3 V at a current density of 1C ($C = 335$ mA g$^{-1}$). After the 35th cycle of galvanostatic charge/discharge the reversible capacity of Ti$_{0.97}$Zr$_{0.03}$O$_{1.98}$F$_{0.02}$ was still equal to 163 mAh g$^{-1}$, whereas Ti$_{0.97}$Zr$_{0.03}$O$_2$ sample gave only 34 mAh g$^{-1}$. Additionally, Zr$^{4+}$/F$^-$ co-doped TiO$_2$ retains a capacity of 138 mAh g$^{-1}$ even upon testing at increased current density of 5C. Thus, it was established that co-doping with zirconium and fluorine of anatase titanium dioxide has a beneficial effect on its performance as an anode material for LIBs, including the operation under fast charge. The main reasons are as follows: i) unit cell volume increases due to the incorporation of zirconium; ii) conductivity improves after doping with fluorine.

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Bioactive and biocompatible coatings based on calcium phosphate (in particular hydroxyapatite \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \)) are relevant for developing new medical materials for bone implants [1].

In this work, polished titanium VT1-0 was used as a substrate. The template electrochemical synthesis was carried out using perforated coatings of xerogel titanium dioxide as a template. It was obtained by the sol-gel technology [2] and applied on a substrate by dip-coating. Depending on the synthesis conditions, various phases of calcium phosphate were obtained, including hydroxyapatite.

![Figure 1. The potential dependence of the ratio of the phases of hydroxyapatite and monetite.](image)

Under certain conditions, template synthesis of the composite has been realized, perspective for bone implantation due to its structure and composition [3].

References

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Nowadays, Langmuir-Blodgett (LB) films of functional organic compounds have been attracting much attention because LB technique helps in preparation of organic assemblies with planned structure and properties. Molecules with relatively large head groups compares to alkyl chains are often used in functionalized LB films [1].

An amphiphilic Schiff base complexes have been prepared in other to research physico-chemical properties. After preparation, compression isotherms were studied in order to determine the conditions under which it is possible to transfer it to a solid substrate (\( \pi = 20 \text{ mN/m} \) and \( \text{pH} \approx 5 \)).

![Figure 1 (left). Compression isotherms of LB films based on nickel complexes with Schiff bases.](image)

![Figure 2 (right). Microphotographs of monolayers containing nickel complexes with Schiff bases.](image)

The surface properties of monolayers were also studied by the method of Brewster angle microscopy. After a successful transfer to a solid substrate, the surface layer morphology was studied using a scanning electron microscope. The method of cyclic voltammetry was used to confirm the electrochemical properties of the substrate.

References
THE EFFECT OF PRECURSOR NATURE IN THE REACTION OF ASYMMETRIC HYDROGENATION OVER NANOSIZED PALLADIUM CATALYSTS

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In recent decades the attention of researchers has been devoted to the development of catalytic systems based on nanoparticles for using in stereo- and asymmetric catalysis\(^1\). It was established that the size, composition and shape of nanoparticles, electronic and steric properties of modifiers are important factors, which determining their catalytic characteristics. Therefore, methods for the formation of metal nanoparticles with desired sizes and shape based on using stabilizers and organic modifiers are being actively developed\(^2\).

It were investigated the catalytic systems palladium-based formed from various precursors in the presence of optically active (-)-cinchonidine in the enantioselective hydrogenation of acetophenone by molecular hydrogen. During the reaction 1-phenylethanol is formed, represented by two enantiomers: R-(+) and S-(−) - phenylethanol.

It has been established that the using of palladium bis-dibenzylidene acetone as a precursor allows to create a more active system than the using palladium bis acetylacetonate (the maximum hydrogenation rates in these systems are 13.8 \(mmol/(L*ht)\) and 1.4 \(mmol(L*ht)\), respectively). At the same time, the enantiomeric excess 45.4\% of the (S)-enantiomer was obtained with Pd(DBA)\(_2\) as a precursor, while Pd(acac)\(_2\) gave 14.8\% \(ee\). The additional stabilization of nanoparticles based on Pd(DBA)\(_2\) by the introduction of cross-linked polyvinylpyrrolidone leads to an increase in the operating time of the catalyst and simplifies its reuse without significantly reducing the catalytic properties of the system.

References:
SYNTHESIS AND STUDY OF SYMMETRICAL AND ASSYMMETRICAL CHROMOPHORES INCORPORATING THE 4H-pyran FRAGMENT

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Organic chromophores incorporating arylvinyl fragments are widely used in the organic electronics devices (OLEDs, OFETs). New sets of symmetrical and asymmetrical conjugated structures of D-π-A-π-D and D-π-A (A-π-D-A’-D’) types have been synthesized. Such spectral characteristics as quantum yields, optical bandgap values and Stokes shifts were determined. Stability towards electrochemical oxidation was also examined; simultaneously the values of HOMO/LUMO energies and electrochemical bandgaps were estimated.

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FABRICATION AND SWELLING BEHAVIOR OF GHRP-2 PEPTIDE LOADED POLYMER-INORGANIC HAP/AGAROSE COMPOSITE

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The composites based on hydrogels and inorganic components excitingly attract interest as potential material for tissue engineering such as bone defects fillers due to its swelling behavior. Nevertheless, it has some drawback because of the complex crosslinking procedure and inorganic component concentration restriction. This problem can be solved by using the hydroxyapatite nanoparticles modified by the organic molecules working as a crosslinking agent.

The present study is aimed to fabrication of growth hormone-releasing peptide - 2 (GHRP-2) loaded composites based on HAP NPs synthesized under different conditions and polysaccharide agarose. Moreover, the swelling behavior of obtained compositions and release of peptide were studied.

To produce composites three types of hydroxyapatite nanoparticles synthesized by co-precipitation method were used: bare HAP NPs \((HAp)\), HAP NPs synthesized in the presence of tartaric acid \((t-HAp)\) and bare HAP NPs modified by succinic anhydride \((m-HAp)\) for agarose and inorganic phase crosslinking. Synthesized HAP NPs were characterized by XRD, TEM methods, SSA estimation, and FTIR spectroscopy. It was shown that hydroxyapatite nanoparticles could extract peptide up to 94% from solution \((C_p = 250 \, \mu g /ml)\). The peptide loaded nanoparticles \((HAp@GHRP-2\) and \(t-HAp@GHRP-2)\) were combine with \(m-HAp\) in ratios 50 wt.% to 50 wt.%.

To fabrication composites the phase separation technique were used. The ratios of mixture \(HAp@GHRP-2/m-HAp\) or \(t-HAp@GHRP-2/m-HAp\) and polysaccharide agarose were 29 wt.%/71 wt.%, 44 wt.%/56 wt.% and 55 wt.%/45 wt.%. As expected, the composite’s swelling ratio decreased with HAP NPs mass increasing in citrate and phosphate buffers with \(pH=6.6\). It was shown that swelling ratio for all specimens increased rapidly for the first day and achieved more than 700 wt.%. After than it decreased and reached equilibrium state for the 40 day. It was demonstrated that the peptide release started in 10 days and amount of the released peptide in citrate buffer more than in phosphate one.
Nowadays, environmental pollution from automotive exhaust gases is one of the most important ecological problems. Over the past few decades, the use of three-way catalysts (TWC) providing simultaneous oxidation of CO and hydrocarbons along with reduction of NO\textsubscript{x} is a widespread method for neutralizing waste gases. The active components of TWC are noble metals (Pt, Pd, Rh), and various oxides (Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, La\textsubscript{2}O\textsubscript{3}, etc.) are used as a support [1]. The main problem of TWC remains their deactivation at high temperatures. The use of bimetallic alloy systems (for example, Pd-Rh) as an active component of catalyst makes it possible to reduce the impact of these negative effects due to the presence of metal-metal interaction [2].

The catalysts studied in the present work were prepared by an incipient wetness impregnation of Zr- and La-modified γ-Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} supports with aqueous solution of corresponding nitrates, simple and double complex salts (organic and inorganic) of Pd and Rh. The samples were characterized by a complex of physicochemical methods, such as TEM, XPS and other. The catalytic activity and stability of TWC were examined by a prompt thermal aging (PTA) method and in a test reaction of ethane hydrogenolysis (HGE) [2]. It was found that the catalysts based on La-doped Al\textsubscript{2}O\textsubscript{3} support and prepared from the nitrates are the most promising systems for further research. In this case, high-temperature reactivation of the catalyst was observed during the PTA tests. HGE results also confirm a presence of synergistic interaction between metals along with enhanced catalytic performance of the sample.

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Cyclometalated Ir(III) complexes have attracted particular attention as more stable analogs of Ru(II) dyes in dye-sensitized solar cells (DSSC). However, poor light-harvesting properties of Ir(III) photosensitizers prevent their widespread application in DSSC. Up to now, there have been 2 main approaches to improve properties of such complexes: varying cyclometalated (C^N or ‘antenna’) ligands or changing the substituents in 2,2’-bipyridine-based ‘anchoring’ ligands. Extending of conjugated π-system of antenna ligands might result in increase of molar absorbitivity coefficients in the visible region. Nevertheless, substantial improvements of photophysical characteristics might require some drastic ‘anchoring’ ligand changes. Specifically, aromatic β-diketones acting as negatively charged chelating ligands are anticipated to be very promising for constructing efficient Ir(III) dyes.

Herein, we present a comprehensive study (X-ray, NMR, MS, UV-Vis, CVA, LS) of several series of iridium (III) complexes with 2-arylphenantroimidazoles and different ‘anchoring’ ligands: dibenzoylmethane (dbm), and 1-(3-methoxycarbonylphenyl)-3-thiophene-propane-1,3-dione (mtpd) (Figure 1). The most promising complexes were successfully tested in DSSC.

**Figure 1.** Ligands and Ir(III) complexes studied in this work.

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SYNTHESIS AND STUDY OF YVO₄:Dy³⁺ NANOPIRATICLES

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We report systematic study of Dy³⁺-doped YVO₄ nanophosphors synthesized via modified Pechini technique. Effect of calcination temperature and doping concentration on structure and luminescence has been investigated. XRD and Raman spectroscopy revealed preparation of single-phase nanoparticles without any impurities. Synthesized nanopowders consisted of weakly agglomerated nanoparticles with average size about 50 nm. Photoluminescence spectra of YVO₄:Dy³⁺ nanoparticles consisted of the characteristic narrow lines attributed to the intraconfigurational 4f-4f transitions dominating by the hypersensitive ⁴F₉/2–⁶H₁₃/₂ transition. The calcination temperature variation did not affect ⁴F₉/2 lifetime, whereas increase of doping concentration resulted in its gradual decline. Potential application of YVO₄:Dy³⁺ 1 at.% and 2 at.% nanopowders as ratiometric luminescence thermometers within 298–673 K temperature range was tested. The main performances of thermometer including absolute and relative thermal sensitivities and temperature uncertainty were calculated. The maximum relative thermal sensitivity was determined to be 1.8 % K⁻¹@298 K, whereas the minimum temperature uncertainty was 2. Thermal cycling experiments showed good repeatability of studied thermometer.

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Due to their unique properties fullerenes have a large area of potential applications in various branches of industry and medicine [1-2]. At the same time, their real applications are limited significantly because of their low solubility in water. To overcome this problem one can use the chemical modification of fullerenes. Promising fullerene derivatives are fullerenols where fullerene cores are modified by hydroxyl groups. The surface properties of solutions of a fullerenol with a large number of hydroxyl groups C60(OH)X (X = 30 ±2) were investigated by the methods of dilational surface rheology, surface tensiometry, ellipsometry, Brewster angle microscopy, transmission electron and atomic force microscopies. The surface properties proved to be similar to the properties of dispersions of solid nanoparticles and differ from those of the solutions of conventional surfactants and amphiphilic macromolecules. Although the surface activity of fullerenols with a great number of hydroxyl groups is not high and these substances do not decrease significantly the surface tension, the fullerenol molecules form a macroscopically homogeneous adsorption layer at the solution surface with a high dynamic surface elasticity up to 170 mN/m. Atomic force microscopy shows that the adsorption layer is not homogeneous at the microscale and consists of interconnected surface micro-aggregates consisting of two – three layers of fullerenol molecules. The bonds between different aggregates are weak and can be broken even by slight mechanical perturbations.

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The steady interest in obtaining thin films of A\text{II}B\text{VI} semiconductors doped with optically and electrically active impurities is due to the prospects of their application in microelectronics and laser technology. Of particular interest are materials based on CdS and ZnS, used for the manufacture of fluorescent – including electroluminescent – devices [1].

Pyrolysis of aerosols or spray pyrolysis (SP) is one of the most promising method of film deposition. Its advantages are simplicity, reproducibility, and the ability to use a wide range of precursors to produce doped and undoped films.

The aim of the work is to deposit films based on cadmium and zinc sulfides by aerosol pyrolysis and to study their properties.

According to the results of thermodynamic analysis it was found that the optimal precursors for the production of CdS films (ZnS) are cadmium nitrate (Cd(NO$_3$)$_2$), zinc nitrate (Zn(NO$_3$)$_2$) and thiourea (CH$_4$N$_2$S). The optimal conditions of the process are determined in the thermodynamic approximation. Precipitation is preferably carried out in excess of thiourea (at a ratio of 1.8:1). The temperature range of CdS formation was 525 - 1200 K, for ZnS – 880 - 1400 K.

Films based on sulphides of zinc and cadmium doped with Mn and Fe ions were deposited by the SP method. The composition of the films was determined by the band gap determined by the edge of its own absorption and the X-ray microanalysis method. The correlation between the content of dopant in the precursor solution and in the film was shown. The structure and morphology of the films were studied by X-ray diffraction and scanning electron microscopy. The effect of doping on the structure and morphology of films is shown.

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PLATINUM(IV) NITRATOCOMPLEXES AS EFFICIENT PRECURSORS FOR PREPARATION OF PtₙOₘ/CeO₂ CATALYTIC SYSTEM

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Carbon monoxide is a highly toxic component of modern urban agglomerations air. Under inspiration, it blockades the tissues oxygen supplying in organism so even extremely low concentration of CO (<50 ppm) in air can lead to serious dysfunctions. Due to this, efficient catalytic systems of CO neutralization at low-temperature are required.

It was determined that PtₙOₘ particles strongly anchored on a CeO₂ surface is an excellent catalyst of CO oxidation reaction at low-temperature (50-100ºC). Additionally, it preserves activity at high temperature about 800ºC. A distinctive feature is that platinum, in such catalyst, incorporated into CeO₂ surface in ionic form and securely fastened by Ce-O-Pt connection. On the other side, employing nowadays starting reagents such as chloroplatinic acid are not “oriented” towards producing of PtₙOₘ/CeO₂ systems because to generate Pt-O groups harsh conditions are required that cause full or partial reduction of ionic platinum species to metallic Pt⁰ particles. Ultimately it leads to irregular distribution of Pt forms on CeO₂ surface and lowering activity of the catalysts.

In this work, we used nitratocomplexes of Pt(IV) as precursors for preparing PtₙOₘ/CeO₂ catalysts. Such complexes seem to be a perfect predecessor because of the whole number of essential advantages:
a) platinum atoms are already located in oxygen coordination environment;
b) labile terminal nitrato groups provide a facile way for grafting on ceria surface;
c) nitratocomplexes rearrange into PtₙOₘ species by heating in mild conditions. Moreover, platinum nitratocomplexes with various nuclearity can be prepared ([Pt(NO₃)₆]²⁻, [Pt(OH)₂(NO₃)₈]²⁻, [Pt₄(μ³-OH)₂(μ²-OH)₄(NO₃)₁₀], [Pt₆(μ³-OH)₄(μ²-OH)₆(NO₃)₁₂]²⁺), therefore, PtₙOₘ active sites with specified n can be constructed. Our first results show that catalysts prepared by sorption of dimeric [Pt₂(OH)₂(NO₃)₈]²⁻ complex on the ceria surface exhibit low-temperature activity (T₅₀% about 100ºC) for CO oxidation at a high gas hourly space velocity of 240000 h⁻¹.

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HALIDE AND POLYHALIDE TELLURIUM COMPLEXES: SYNTHESIS, STRUCTURE AND PROPERTIES

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Halide and polyhalide tellurium complexes attract great attention due to their intriguing physical properties. From the point of view of new materials, this area of research is very relevant, since such complexes can be used in perovskite-type semiconductors [1-2]. Anions of halide complexes can have both discrete and polymeric structure (figure 1). Currently, there is no theory to predict the structure of the product according to the initial reaction conditions.

Figure 1. Scheme of the formation of halide tellurium complexes.

In our work, we report, methods of synthesis, structural features, thermal stability and optical properties of new halide and polyhalide complex tellurium. The dependence of the structure on the reaction conditions is discussed.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-73-10040).
INVESTIGATION OF ETHANOL OXIDATION OVER COBALT CONTAINING ZEOLITE CATALYST

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Though there are many studies about the catalytic transformation of modern spirits, their work on conversion to zeolite catalysts in oxidizing environments is virtually significant. On the other hand, processes taking place over nanoparticles catalytic systems are great of interest. According to this presented paper is dedicated to development of synthesis methods of nanostructured catalytic systems, determination of their structure and morphology, and the identification of methods that can change the basic characteristics of the catalyst.

In view of this, nano complex catalyst samples were prepared by adding Co transition metal on the surface of NaX type of zeolith and their activity was studied in the process of ethanol oxidation.

The cobalt-nitrate solution on the NaX zeolite was impregnated to receive the crushed CoNaX catalyst, after that the sample was dried at 373 K and calcined at 523-573 K until full decomposition of cobalt nitrate. The obtained sample was calcined during 10 hours at 823 K. Thus, containing 1%, 2.5%, 5%, and 10% of cobalt were prepared zeolite based catalysts.

The activity of the obtained catalyst samples was studied in the reaction of ethanol oxidation by air oxygen. The process was carried out at a temperature range of 423-773K on a flow unit with a tubular reactor. The catalyst volume was 5 ml and the initial reaction volume was 2400 hours⁻¹. The ratio of initial gas reactants was taken at alcohol: air = 1:10. Analysis of primary substances and reaction products was carried out by chromatographic method.

References
The new type of composite materials based on polyaniline doped with metal-carbon nanoparticles (NPs) PANI/M@C, where NPs embedded in polymer matrix by method of laser-induced deposition, is under investigation. These objects attract the interest in field of electrochemistry thanks to efficient performance in electrocatalytical reactions provided by combination of polyaniline matrix conductivity and metal NPs catalytic properties. Moreover, the “in-situ” polymerization of polyaniline on substrates with different geometries gives additional way to increase the electrocatalytic efficiency of the system. The role of electrode geometry is discussed in [1]. Figure 1 demonstrates the possibility of obtaining PANI films (a) and nanotubes on anodic aluminum oxide nanomembranes (b,c).

Figure 1. Polyaniline films and nanotubes.

The composition of M@C NPs is predetermined by type organometallic complex used to laser-induced deposition process, which, in its turn, determines the type of catalyzed reaction.

References

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SYNTHESIS OF ULTRA DISPERSED GRAPHITE-LIKE MATERIALS IN DC ARC DISCHARGE PLASMA


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Synthesis of ultra dispersed carbon materials plays a significant role in the modern nanotechnologies. Nowadays the scientific community pays much attention to carbon and nitrogen compounds due to their outstanding properties [1]. There exist several methods to synthesis this material, such as CVD, laser ablation and arc discharge [2–4]. This work is focused on the synthesis of ultra dispersed graphite-like materials in DC arc discharge plasma in ambient air.

The mixture of melamine C₃H₆N₆ and graphite C in proportion of 2:1 was used as initial powder. The X-ray diffraction data obtained from the initial (a) and synthesized (b) powder are shown in Fig. 1. XRD pattern of synthesized powder (b) shows some peaks corresponding to the graphite-like structure reflections. Besides, the largest peak is wide, which indicates the presence of impurities. According to EDS analysis, the synthesized product contains carbon and nitrogen. TEM analysis also confirms the presence of graphene-like carbon structures doped with nitrogen.

Figure 1. Typical XRD patterns: a – initial powder, b – synthesized powder

References
THE EFFECT OF THE SYNTHESIS PARAMETERS ON THE PROPERTIES OF β-NaYxGdyF4:Yb,Tm UP-CONVERTING NANOPARTICLES

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Fluorescent nanoparticles β-NaYxGdyF4:Yb3+,Tm3+ due to their optical properties have a great potential for applications in bio-imaging as fluorescent labels and imaging probes. We have studied the effect of the hydrothermal synthesis parameters on the luminescent properties of NaYxGdyF4 nanoparticles co-doped with Yb3+ and Tm3+. The effect of the varied concentration of Y3+/Gd3+, the effect of different pH, the effect of time stirring and temperature control on the fluorescence intensity of β-NaYxGdyF4:Yb3+,Tm3+ nanoparticles have been studied in our work.

The nanoparticles with that were synthesized by hydrothermal method. The morphology of the obtained nanoparticles was studied by transmission electron microscopy. They have hexagonal structures and size of around 1000 nm. The up-conversion fluorescence of β-NaYxGdyF4:Yb3+, Tm3+ nanoparticles was measured at 980 nm excitation wavelength. The sample exhibited blue luminescence, which originated from

Acknowledgements. The measurements were performed in the “Centre for Optical and Laser materials research”, “Interdisciplinary Center for Nanotechnology”, “Centre for Molecular and Cell Technologies” and “Cryogenic department” of research park of Saint-Petersburg State University.
The processes of depositing and evaporating solution droplets underlie the method for producing electrodes of electrochemical devices. Unique conditions and effects appear when droplets of solutions of various substances evaporate. These effects lead to the structuring of the resulting products.

There is a specialty of our experiment in comparison to the previous experiment carried out by other authors. Before drying, the surface of the solution drop was treated with a gaseous reagent according to the gas–solution interface technique (GSIT) that was previously used by us to obtain nanocrystals [1], thin films and microtubes for a wide range of inorganic compounds. As the object of study, 8-40 mcL droplets of Mn(OAc)₂ solution applied on glass surface were selected. Ozone was a gaseous reagent. This material was chosen because manganese oxides have a great potential for practical use as electrode materials for chemical current sources, electrochemical sensors, catalysts for the oxidation of organic compounds, etc.

The first experiments showed that after treating a drop of Mn(OAc)₂ solution with a gaseous ozone, a light brown film forms on its surface. The observation after reaction showed that the film consists of separate “ribbons” with a width of 1-2 microns, some of which forming a network of honeycomb structures.

Figure 1. Optical (left) and scanning electron (right) microscope images of the samples obtained after drying the ozone-treated Mn(OAc)₂ solution drop.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-13-13018).
Protonated layered perovskite-like niobate HCa$_2$Nb$_3$O$_{10}$, relating to Dion-
Jacobson phases, is the solid crystalline semiconductor compound, in which
blocks with perovskite structure [Ca$_2$Nb$_3$O$_{10}$]$^-$ alternate with interlayer spaces,
containing protons. This niobate is well known as a heterogeneous photocatalyst for hydrogen evolution from water and water-organic media
under ultraviolet irradiation [1] that is of great importance for development of
environmentally friendly technologies. Being a solid acid, HCa$_2$Nb$_3$O$_{10}$ is able
to intercalate some organic bases into the interlayer space forming inorganic-
organic derivatives [2]. Since photocatalytic activity of layered perovskite-like
oxides strongly depends on structure and composition of the interlayer space,
intercalation of amines may significantly affect it and lead to the creation of
new highly efficient photocatalysts. Nevertheless, data on photocatalytic
properties of hybrid inorganic-organic perovskites are practically absent.
The present work is devoted to synthesis of amino derivatives
HCA$_2$Nb$_3$O$_{10}$$\times$RNH$_2$ (R = Me, Et, Bu, Oct) and investigation of their
photocatalytic activity in the reaction of ultraviolet light-driven hydrogen
production from the model water-methanol solution. The derivatives obtained
are characterized using modern physicochemical methods (X-ray powder
diffraction, Raman spectroscopy, thermogravimetry, elemental C,H,N-analysis,
scanning electronic microscopy). Measurements of photocatalytic activity are
performed using chromatographic hydrogen detection with and without
platinum addition as a cocatalyst. Possible reasons of the photocatalytic
activity dependence on the interlayer amine are discussed.

References

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03-00915). Authors are also grateful to Saint Petersburg State University Research Park:
Center for X-ray Diffraction Studies, Center for Optical and Laser Research, Center for
Thermal Analysis and Calorimetry, Center for Chemical Analysis and Materials
Research, Interdisciplinary Center for Nanotechnology.
Fischer–Tropsch synthesis (FTs) has proven its ability for the conversion of synthesis gas to high value hydrocarbons (e.g. gasoline, diesel and light olefins). Some of perovskite-type catalysts ABO₃, where A – Ln and B – 3d-elements, have been investigated for FTs, due to the flexibility in their design and preparation.

GdFe₁₋ₓMnₓO₃ (x = 0 – 1) ultrafine perovskite powder with grain size around 40-100 nm has been prepared by sol-gel method. The catalysts have been characterized by various physico-chemical methods. The crystallinity and phase purity of the perovskites were determined by XRD. The morphology and surface characteristics of the samples were investigated by SEM+EDS and TEM, specific surface area measurements were carried out by BET method. The oxidation states of Fe and Mn were identified by XPS.

The effect of Mn-substitution on the catalytic performance and the distribution of products of hydrogenation of CO in process FTs were investigated and presented in Figure. In case of GdFeO₃ the content of methane and light olefins was found to be 71% and 26%. While partial or fully substitution of Fe by Mn (x(Mn) = 0.5, 0.8, 1) results in methane decrease to 40%, olefins increase to 35% and increase the ratio of hydrocarbons C₅-C₆. Moreover it was found that GdMnO₃ catalyst provides better ethylene and butylene selectivity while GdFeO₃ exhibits the highest catalytic activity.

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HALOGENATION OF A MULTIPLE BOND IN A METAL-ORGANIC FRAMEWORK AS A WAY TO TUNE ITS SORPTION PROPERTIES

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Post-synthetic modification of metal-organic coordination polymers is a promising way to obtain materials that are difficult to synthesize directly. The presence of easily modifiable functional groups in the initial coordination polymer makes it perspective for the synthesis of derivatives with adjustable porosity, sorption selectivity, catalytic, luminescent and other properties.

We aimed to post-synthetically functionalize the organic ligand in the aluminum fumarate A520 [1] [Al(OH)(fum)] (1) with chlorine atoms and investigate the sorption characteristics for the resulting derivative. The quantitative chlorination of 1 at room temperature was confirmed by ¹H and ¹³C NMR spectra of digested samples, and PXRD demonstrated that overall crystal structure keeps intact. Thus, for the obtained compound the formula [Al(OH)(fumCl₂)] (2) can be reliably assigned.

Sorption measurements for 2 revealed a decrease in porosity according to low-temperature (77K) nitrogen adsorption, but a more than twofold increase in the selectivity of CO₂ adsorption respecting to CH₄ and N₂ at 273K and 298K compared to the aluminum fumarate 1. More, the preferential adsorption of acetylene over ethylene and ethane appears in the functionalized 2.

This fact can be explained by the appearance of new adsorption centers for molecules with high polarizability (CO₂ and C₂H₂) in the chlorinated derivative, as well as the partial blocking of channels in the porous structure by bulky chlorine atoms for substrates with larger particles.

The obtained results are the first example of direct chlorination of a multiple bond in a metal-organic framework, they also demonstrate the possibilities of post-synthetic modification of ligands in coordination polymers in the synthesis of highly efficient sorbents for the separation of gas mixtures.

References
As a result of the nuclear industry activities, a large amount of waste, especially radioactive, is generated. The composition of liquid waste may include any compounds, such as highly toxic chromium (III) salts. In view of the approaching era of decommissioning of nuclear power plants, the volume of waste will grow rapidly. To maintain a clean environment, it is necessary to develop materials that can minimize the effects of harmful substances.

A promising method for obtaining nanoparticles is hydrothermal synthesis, which allows for obtaining nanotube morphology. The resulting nanotubes have a number of properties that make it possible to use them as sorbents.

We have performed work on filling hydrosilicate nanotubes \((\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4)\) with the pecoraite structure. Sample nanotubes were placed in buksy and filled with aqueous solutions of chloride and nitrate chromium (III) with a concentration of 0.005 M to 0.5 M. When changing the temperature-time parameters, some solutions with nanotubes were mixed using a magnetic stirrer. The contents of the other packages were filled in static conditions, also with changes in temperature and time. After the experiments, the samples were washed with distilled water and dried.

The obtained samples were investigated by XRD, IR spectroscopy and TEM. The results of the analysis show that for the best filling of nanotubes it is necessary to increase the temperature, constant mixing and the optimal concentration of aqueous solutions of chromium.

Preservation of the nanoparticles structure in experiments under various conditions suggests the use of hydrosilicate nanotubes as a sorbent for wastewater treatment of chromium (III) compounds.

References
The development of new composite materials with specified properties such as high active surface area, small size, and high electrocatalytic activity is of great interest for many fields of science and technology, particularly, for fabrication of highly efficient gas sensors that are sensitive to concentrations of toxic and hazardous gases. The main advantages of composite sensors are their high reliability, sensitivity, and low cost [1]. The Laser-induced Chemical Liquid-phase deposition of compounds from solution (LCLD) method can be applied to receive nano-sized porous gas sensing material on the dielectric substrate. The sensing materials studied in this work are the nanostructured composites containing mixture of different molybdenum oxides. Molybdenum trioxide for instance is an important n-type semiconductor, and an effective gas sensor [2] due to its unique layered structure, where molybdenum atoms have different valences. There is a huge amount of active charge transfer centers in these structures making MoO₃ applicable in catalysis and photocatalysis as well.

In this particular study the manufacturing of nano-sized materials and testing their sensing properties was done. The composite nano-sized MoₓOᵧ materials were fabricated with LCLD method, based on the in situ laser-induced deposition of microcomposites containing molybdenum oxides with highly developed surface area from aqueous solutions on the surface of different dielectric substrates. The sensor activity of the deposits was determined for the group of reducing gases at different concentrations and temperature regions.

The regeneration temperature, time response and degeneration concentration were determined for a set of samples. The selectivity of the sample was tested in the presence of a mixture of gases (NH₃, NO). Nano-sized MoₓOᵧ samples show good properties for gas sensors thanks to large surface area and huge amount of active centers.

References

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Organic molecules with high-spin ground state are of interest as building blocks for multifunctional molecule-based magnets, sensitive spin probes and organic conductors [1–3]. In search for new types of stable high-spin organic structures, we for the first time synthesized diradicals 4–6 containing exchange-coupled 1,3,5-triphenyl-6-oxoverdazyl and nitronyl nitroxide moieties.

The synthesis of diradicals were effectively carried out by using a palladium-catalyzed cross-coupling reaction of iodoverdazyls 1–3 [4] with a nitronyl nitroxide-2-ide gold(I) complex in yields up to 82%. The molecular and crystal structures of 4–6 were solved by the single-crystal X-ray diffraction analysis. The obtained verdazyl-nitroxide diradicals were characterized by ESR, cyclic voltammetry (CVA), and HRMS techniques. DFT calculations revealed triplet ground state in diradicals 4 and 6, and singlet ground state in 5.

References
SYNTHESIS OF LAYERED PEROVSKITE-LIKE OXIDES $A_2Ln_2Ti_3O_{10}$ ($A = \text{Rb, K}; \ Ln = \text{La, Nd}$) AND THEIR ION-EXCHANGE PROPERTIES

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Layered perovskite-like oxides are crystalline compounds, which consist of alternating layers of perovskite structure and layers with another type of structure. They are of interest because of their properties, such as ionic conductivity, superconductivity, ferromagnetism and photocatalytic activity. Usually layered perovskite-like oxides are synthesized by high temperature ceramic method [1]. However, it demands high energy consumption and leads to large polycrystalline particles of the final products, which is not desirable for their practical use as catalysts. There are alternative methods, such as hydrothermal method and sol-gel synthesis, which allow to obtain smaller particles with uniform morphology at lower temperatures.

In this research layered perovskite-like titanates $A_2Ln_2Ti_3O_{10}$ ($A = \text{Rb, K}; \ Ln = \text{La, Nd}$) attributed to the Ruddlesden–Popper phases were synthesized by ceramic method according to [2]. Moreover, $K_2La_2Ti_3O_{10}$ was synthesized by sol-gel and hydrothermal methods under various conditions. The phase composition of each sample was investigated with XRD analysis. Ion-exchange properties were studied with regard to the substitution reaction of alkali cations for protons (protonation). These reactions were carried out in diluted HCl solutions with various pH and yielded three distinct phases with different substitution degree for each compound. Their cell parameters were determined by XRD analysis and the protonation degree was studied by TG analysis.

References

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2 section

POLYMER SCIENCE THE NEXT GENERATION
Among the membrane processes, pervaporation and ultrafiltration attracted the attention in the last century. Pervaporation is an applicable analytical tool for the separation of liquid mixtures containing an azeotropic, low-molecular weight and close-boiling components without additional chemicals and using less energy than conventional processes for liquid mixture separation that cannot separate these mixtures. Ultrafiltration membrane processes as alternatives to conventional methods are gaining wide attention in food processing industry; this is because it has several advantages over conventional method such as high selectivity, gentle product treatment, and lower energy consumption. One of the fastest and simplest ways to improve the properties of membrane polymeric materials is the creation of hybrid membrane. Membrane modification using Pluronic copolymers is usually performed via the introduction of Pluronic additive to the casting solution due to its amphiphilic nature, optimal hydrophilic/hydrophobic balance and high molecular weight. In this study, pluronic F127 was used to improve the transport properties of porous membrane based on PA and supported dense membrane based on PVA. Pluronic F127 was added into porous membrane matrix that were prepared by phase inversion method. Dense composite supported membrane based on PVA and pluronic F127 have been prepared by casting thin layer of PVA solution containing pluronic F127 in the required amount into modified polyamide porous membrane. The influence of pluronic F127 addition on the structure of porous and dense membrane was studied by IR, NMR and SEM. Transport properties of dense membrane were studied in pervaporation of azeotropic isopropanol/water mixture. Transport performance and antifouling properties of porous membrane were studied in ultrafiltration of water and solution.

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STUDY OF THE EFFECT OF TREATMENT CONDITIONS ON THE PROPERTIES OF IONIC LIQUID LIGNIN

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In this paper, the influence of processing conditions (temperature and time) on the molecular weight and elemental composition of spruce dioxanlignin was studied.

![Figure 1. Dependence of the average molecular weight of lignins reprecipitated from [bmim]Ac (left) and [bmim]MeSO\(_4\) (right) on the duration and temperature of treatment.](image)

For the reprecipitated dioxanlignins, an increase in the nitrogen content for all samples was observed with an increase in the varied parameters. It was found that during the reprecipitation of [bmim]MeSO\(_4\) there was an increase in the molecular weight of the lignins and decrease in the degree of polydispersity with the formation of highly condensed structures. For samples obtained by reprecipitation from [bmim]Ac, molecular weight values are reduced with a decrease in the degree of polydispersity, while high-molecular fractions are degraded. The results make it possible to obtain lignin with a given molecular mass distribution, which plays an important role in the creation of new technologies for the processing of vegetable raw materials.

The work was performed using the equipment of the core facility center "Arctic" Northern (Arctic) Federal University named after M. V. Lomonosov with the financial support of the Russian science Foundation (project No 18-73-00282).
Organic compounds, whose molecules have a conjugated system of bonds, attract special attention of researchers. These compounds are promising materials for modern technology [1, 2]. Prospects for the use of these materials are far from exhausted.

Based on the \( m \)-phenylenediamine and aldehydes obtained new benzylidenphenylenediamines (BFDA). Polymerization of BFDA in the presence of \((NH_4)_2S_2O_8\) produced polymers. The process of polymerization proceeds in a heterogeneous system with the formation in the first stage, the cation-radical. The resulting cation-radical recombination with the release of protons in the reaction system. Therefore, oxidative polymerization, BFDA flows through the slow (single-electron transfer).

\[
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\text{H}
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\end{align*}
\]

- Luminescent materials
- Luminescent mark
- Electrically conductive materials;
- Photoactive materials;
- Materials for bioanalytical systems;
- Anticorrosion coating;
- Polymeric antioxidant;
- etc.

Figure 1. Getting BFDA, polymers on their basis and their application.

References
Fluorotrifluoroacetometalates of alkali metals are analogues of the well-known class of oxocarboxylates 3d metals formed as a result of hydrolysis. The peculiarity of their crystal structure is symmetrical polynuclear frame. The octahedral environment of the metal atom consists of four carboxylic oxygen atoms, a bridging fluoride-ion and an axial neutral ligand [1].

The latter position is of particular interest, because when replacing it with a polydentate organic ligand, it is possible to obtain a polymer MOF with volumetric cavities.

In this work, the first step was taken to obtain polymer MOF based on trifluoroacetates of 3d metals. For the first time it was shown that it is possible to obtain compounds of the studied class with axial ligands other than the trifluoroacetic acid molecule present in all previously known compounds of this class, by controlling the synthesis conditions.

For example, under conditions of sharp cooling, a compound with axial water molecules was obtained. (Figure 1). K[Co₃(µ₃-F)(TFA)₆(H₂O)₃](HTFA)₄(H₂O) was synthesized by dramatically lowering the temperature of the solution. Crystal cell is monoclinic (P 2₁/n) with a = 13.1069(3) Å, b = 13.9789(2) Å, c = 20.9794(3) Å, β = 100.598(1)°, V = 3778.28(12) Å³, R = 5.07%, Rw = 8.90%.

In the future, it is planned to obtain and crystallographically study the crystallization products of the studied compounds with organic ligands.

Figure 1. A fragment of the crystal structure K[Co₃(µ₃-F)(TFA)₆(H₂O)₃](HTFA)₄(H₂O).

References
Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-03-01059).
NETWORK FORMATION OF DNA/POLYELECTROLYTE FIBROUS AGGREGATES AT THE AIR/WATER INTERFACE

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Polycations form soluble complexes with DNA in aqueous solution due to strong electrostatic attraction between the components and allow transfer of genetic material into cells [1]. Cationic polymers represent a class of nonviral carriers which can be designed to facilitate gene delivery into target cells. The corresponding biomedical interest resulted in extensive investigations of DNA-polyelectrolyte interactions in the bulk phase of aqueous solutions [2]. At the same time, the information on surface properties of these systems is scarce.

In the given work the dynamic surface properties of DNA/poly(methylalkyldiallylammonium chloride) (PMADAAC) aqueous solutions at the solution/air interface were studied by the surface tensiometry, dilational surface rheology, ellipsometry and atomic force microscopy. The deviations of the surface properties (surface elasticity, surface tension, ellipsometric angles) of DNA/poly(dimethylallylammonium chloride) from the values of water were close to the error limits. Measurements of the kinetic dependencies of the surface properties of DNA/poly(methylbutyldiallylammonium chloride) and DNA/poly(methylhexyldiallylammonium chloride) solutions discovered noticeable deviations from the results for solutions of individual components indicating thereby the adsorption of DNA/polyelectrolyte complexes. These deviations increased strongly at the approach to the isoelectric point. The atomic force microscopy allowed estimation of the morphology of the adsorption layer as a function of the molar ratio and total concentration of the two components.

References

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SYNTHESIS AND CROSS-LINKING OF FERROCENE-SUBSTITUTED POLYMETHYLHYDROSILOXANES

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Self-cross-linkable ferrocenyl-substituted polymethylhydrosiloxanes are synthesized for the first time. Karstedt’s catalyst and \( \text{cis-[PtCl}_2(\text{PhCH}_2\text{CN})_2] \) are used for self-cross-linking of the ferrocenyl-substituted polymethylhydrosiloxanes by the dehydrogenative reactions between Si-H groups [1,2] (Figure). cis-[PtCl\(_2\)(PhCH\(_2\)CN)]\(_2\) leads to cross-linked ferrocenyl-containing silicones (FSRs) without visible mechanical defects compared to Karstedt’s catalyst. The data reveals significant differences between FSRs and cross-linked unmodified polymethylhydrosiloxanes: FSRs have improved tensile properties (the tensile strength increased from 0.47 to 0.75 MPa) and 1.5–2.5 times lesser cross-linking degree. The surface resistivity of the FSRs is around \( 10^9 \, \Omega/\square \) that 10 times less than mechanical mixture of polymethylhydrosiloxane with 5 wt.% of ferrocene and 10000 times less than pure polymethylhydrosiloxane. The obtained FSRs can be potentially applied as flexible electroactive layers and antistatic surfaces for electronic and electrostatic-sensitive devices, interfaces and sensors.

Figure. Synthesis and cross-linking of the FSRs.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-20062_mol_a_ved). Measurements were performed at the Center for Magnetic Resonance, the Centre for Innovative Technologies of Composite Nanomaterials (all in Saint Petersburg State University).
Currently, one of the most important areas in modern society is the development of sustainable processes. Such processes include membrane separation processes due to the fact that these methods are environmentally friendly, use compact equipment and have low power consumption. The rapid development of membrane methods requires the search for new highly effective materials with an improved combination of physicochemical and transport properties. The obtaining novel membrane materials with improved characteristics can be easily achieved by the modification of the polymer matrix by inorganic filler that yields in developing the mixed matrix membranes (MMMs). In the present work water-soluble derivative of fullerene (polyhydroxylated fullerene or fullerenol) has been used as modifiers and cross-linking agents for sodium alginate.

The aim of this work was to develop and investigate the novel composite material based on sodium alginate modified by fullerenol for further preparation of novel environmentally friendly mixed matrix membranes with improved transport characteristics for pervaporation dehydration. The preparation methods and optimal conditions for nanocomposite were developed. Structural and physicochemical characteristics of nanocomposite material were studied by various physical and chemical methods of investigation (IR spectroscopy, scanning electron microscopy and sorption experiments).

Acknowledgements. This work was supported by Russian Science Foundation [project No 19-73-00105]. The experimental work was facilitated by equipment from Resource Centers: for Nano technology, Magnetic Resonance Research Centre, X-ray Diffraction Methods, Thermal Analysis and Calorimetry, Chemical Analysis and Materials Research Centre and GEOMODEL at St. Petersburg State University.
DEVELOPMENT OF PERVAPORATION POLYMERIC MEMBRANES WITH HIERARCHICAL STRUCTURE

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The rapid development of membrane technology requires the use of materials with desired properties to solve a specific technological separation problem. One of the most important ways to create membranes with optimal transport characteristics is their bulk and surface modification.

The aim of this work was to create new polymer membranes with a hierarchical structure, namely, the creation of composite membranes with several polymer layers of different chemical nature. The upper selective layer was applied by interfacial polymerization. As polymeric ultrafiltration substrates were used polyacrylonitrile, polyphenylene isophthalamide, and regenerated cellulose. As an intermediate polymer layer were used chitosan, polyallylamine hydrochloride, polyphenylene isophthalamide. It was shown that the creation of multi-layers leads to an increase in the efficiency of separation of organic and water-containing binary mixtures.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-58-04014) and Belarussian Republican Foundation for Fundamental Research (project No X19PM-052). The experimental work was facilitated by equipments from Interdisciplinary Resource Centre for Nanotechnology, Chemistry Educational Centre, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Magnetic Resonance Research Centre, Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Nanophotonics Centre and Centre for Geo-Environmental Research and Modelling (GEOMODEL) at St. Petersburg State University.
SYNTHESIS OF POLYMERIC GLYCOSILICONES VIA CUAAC AND HYDROSILYLATION REACTIONS

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Glycosilicones are new class of hybrid compounds, consisting of saccharide and siloxane fragments [1]. Possibilities for synthesis of glycosilicones are limited due to incompatible solubilities of sugars (hydrophilic) and polysiloxanes (hydrophobic). Protection-deprotection steps can be used to improve saccharide solubility, but it makes synthesis more complex and can lead to side reactions. Alternative method is to perform reaction heterogeneously. In this regard high-efficient reactions such as hydrosilylation [2] and azide-alkyne cycloaddition [3] must be used to obtain good conversion.

In this work cellulose-based glycosilicones were obtained via platinum and rhodium catalyzed hydrosilylation and copper catalyzed azide-alkyne cycloaddition with “grafting to” approach. Reagents with corresponding functional groups (alkyne, azide) were obtained from epoxy-terminated polydimethylsiloxane and hydroxyethyl cellulose. Choice of catalytic reaction and catalyst influences on reaction yield and degree of substitution. Resulting compounds are insoluble in water and organic solvents. Polysiloxane grafting increased hydrophobicity of obtained glycosilicones.

References

Acknowledgements. This work was supported by the Russian Ministry of Education and Science (State Contract 14.W03.31.0014, Megagrant). Measurements were performed at Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, Centre for Culture Collection of Microorganisms, Centre for Innovative Technologies of Composite Nanomaterials, Thermogravimetric and Calorimetric Research Centre.
MACROPOROUS HYDROPHILIC POLYMER LAYERS FOR APTAMER-BASED PROTEIN ANALYSIS

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Macroporous monolithic materials are solid-phase sorbents characterized by a system of interconnecting pores. Their structure can provide for proteins a hydrophilic environment similar to in solution conditions, the possibility of variation of the surface chemistry and high reproducibility of the synthesis. Moreover, the 3D-structure of the macroporous materials provides the higher probe loading and, consequently, the sensitivity of analysis. Due to such positive characteristics, this class of materials is widely used in such areas as gas and high-performance liquid chromatography, solid-phase extraction and flow-through heterogeneous biocatalysis. One of the new areas of application of macroporous materials is biological microanalysis using microarray [1-2]. Nowadays, more and more studies have been devoted to the development of diagnostic systems which are utilizing aptamers instead of antibodies as probes for molecular recognition of proteins and nucleic acids. Aptamers are a class of small oligonucleotide ligands increasingly growing in importance in the face of contemporary detection challenges. Compared with traditional ligands such as antibodies, aptamers have advantages including smaller sizes, lower manufacturing costs, none or low immunogenicity, versatile chemical modifications, extensive targets and batch-to-batch reproducibility.

In this work, a series of macroporous monolithic materials in the thin-layer form was obtained by the photoinitiative free radical polymerization. The influence of the polymerization mixture composition and polymerization conditions on the physico-chemical characteristics of obtained materials was investigated and material’s average pore size via the correct choice of porogen mixture was optimized. The developed materials were tested for the analysis of glycosylated hemoglobin using aptamer as a probe.

References
Molecular imprinted polymers (MIPs) represent the polymeric matrices bearing the artificial stereospecific recognition sites that are complementary to the template in shape, size and spatial position of the functional groups. Such site formation occurs in the process of copolymerization of functional and cross-linking monomers around the template, followed by the removal of latter from ready-to-use matrix. MIPs are very attractive for extraction of both low-molecular weight compounds and biological objects, such as viruses, proteins and cells.

The aim of this work was to synthesize molecular imprinted cryogels based on 2-hydroxyethyl methacrylate (HEMA) and poly(ethylene glycol) diacrylate (PEGDA) and to investigate the properties of materials obtained. Polymer nanoparticles (NPs) based on lactide-poly(ethylene glycol)-5000 copolymer, representing the experimental model of virus, were prepared by nanoprecipitation and then modified with α-chymotrypsin (NPs-CHTR). The particle size and ζ-potential were analyzed by dynamic light scattering (DLS). The HEMA-PEGDA matrices imprinted with NPs-CHTR were synthesized by cryo-copolymerization of monomers in the presence of these particles as templates. The process was carried out in water with application of ammonium persulfate/N,N,N′,N′-tetramethylethylenediamine as initiator system at 24 h and -13 ºC. Non-imprinted cryogels were synthesized at same condition for application as control materials (NIP). The effect of synthetic condition (molar ratio of functional monomers/cross-linking agent and concentration of monomers in the system) on mechanical characteristics of obtained materials was studied. The morphology of the matrices was investigated by SEM and X-ray microtomography. The cryogels were tested as the stationary phases for recognition of protein and nanoparticles.
The negative charged polyelectrolytes such as polyacrylic acid are able to form complexes with multifunctional counterions. They are used as carriers for the targeted drug and genes delivery, as medical imaging agents and antibacterial coatings. Currently, complexes of polyacids with inorganic ions and oppositely charged polymers are widespread in the literature; however, there is almost no information about low molecular weight organic compounds as counterions for polyelectrolyte complex formation.

In the present work the ionic complexes between polyacrylic acid with different molecular weight (Mn = 2000 and Mn = 26700) and multivalent organic counterions. Amines having fixed number of amino groups and different number of methylene groups were chosen as counterions. The possibility of the water-insoluble complex formation was determined by the turbidimetry, and the pH ranges within which such complexes are stable were studied. The influence of the different parameters on the characteristics of the forming complexes was investigated: the molecular weight of the polymer, the number of methylene groups in the amine, the ionic strength, the polarity of the medium. The stoichiometric composition of the complexes was equal to the reagent ratio in the starting mixture which was shown by NMR-spectroscopy. The size and ζ-potential of the complexes particles in the solution were estimated by the DLS method. Morphology of the complexes resulted from fast non-equilibrium adsorption on mica was studied by AFM and it was shown that the complex particles have vesicular structure. Moreover, SEM was used to investigate the morphology of the complexes in the form of solid precipitates and particles isolated from the colloidal solutions.

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RAFT-POLYMERIZATION OF 2,2,3,3-TETRAFLUOROPROPYL METHACRYLATE

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In recent years, control radical polymerization methods have been widely used to synthesize (co)polymers with a given architecture. Reversible addition-fragmentation chain transfer (RAFT) polymerization can be applied to a wide range of monomers unlike the rest of techniques; therefore, it is a more versatile technique for the synthesis of amphiphilic copolymers [1]. Fluorinated (co)polymers draw the attention of scientists due to some of their properties such as thermic and chemical resistance, atmospheric sustainability and low surface energy [2]. Controlled (co)polymerization of fluorine (meth)acrylates has not received proper attention in literature yet.

This work dwells on the issues of controlled synthesis of polymers based on 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA).

Polymerization of 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA) was carried out. Initially, the effectiveness of different chain transfer agents was investigated (AIBN was used as initiator, benzene was used as solvent). It was estimated through analyzing the curves of the molecular mass distribution of polymers at different conversions. It turned out that 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) and 4-cyano-4-[(dodecylsulfanyl-thiocarbonyl)sulfanyl]pentanoic acid (CDTPA) are more effective in RAFT polymerization of TFPMA which is confirmed by the linear increase of MW and the decrease of polydispersity with the rise of conversion. The chain transfer constants (C_{tr}) of CPDT and CDTPA were estimated by GPC measurement. End-groups of PTFPMA were defined by MALDI-TOF MS/MS. Further, polymerization of TFPMA in the presence of polymeric chain transfer agent PTFPMA was carried out. Then, amphiphilic block-copolymers were obtained using acrylic and methacrylic acid, and glycidyl methacrylate.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-03-00843).
INTERACTION OF REACTIVE OXYGEN DERIVARIVES WITH NITRIC OXIDE IN THE MODEL REACTION OF TRYPTOPHAN PHOTOOXIDATION

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The interest in short-lived biologically active simple molecules, in particular nitrogen oxide and active forms of oxygen (ROS), is due to the fact that such compounds act as regulators at various levels of the organization of living organisms. Nitric oxide is a multifunctional signaling molecule that controls intracellular and intercellular processes in organisms. ROS are a necessary component of the vital activity of the cells and the organism as a whole. The interaction of nitric oxide and its derivatives (such as dinitrosyl complexes of iron (DNIC) with active forms of oxygen leads to the formation of reactive metabolites of nitric oxide and its compounds - peroxynitrite, nitrogen dioxide, NO₂Cl and, which are important components of the immune response in humans and animals. Such interaction can lead to formation of NO and NO⁺ in biosystems and determine not only cytotoxic, but also regulatory and regenerative processes in living organisms.

The photogeneration of ROS is the basis of oxidative destruction of pathological cells and tissues (malignant neoplasms as well as infected wounds, burns, trophic ulcers) in the method of photodynamic therapy (PDT). In this work the influence of DNIC with thiol-containing ligands and dimethylglucamine salt of chlorin e6 (photoditazine, PD) on the rate of photosensitized oxidation of organic substrate, tryptophan. Also, the DNIC-PD system was investigated in the presence of the amphiphilic polymer-Pluronic F-127. It is shown that in the presence of DNIC, the rate of photodegradation of PD is increased, but the introduction of Pluronic F-127 into the system the rate constant of photodegradation of PD is decreased. It is the fact opens up the possibility of simultaneous use in the treatment of wounds of photodynamic therapy and DNIC without losing the effectiveness of PDT.

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SYNTHESIS OF SUPRAMOLECULAR COMPLEXES OF (CO)POLYSILOXANE WITH Fe(III), Co(II) AND Ni(II)

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Synthesis of new supramolecular (co)polysiloxanes with electroactive centers and creation on their basis materials with the most important properties (self-healing, electrical conductivity, flexibility, bioinertness, etc.) is challenging task.\(^1\,^2\)

In the study new supramolecular complexes of (co)polysiloxane with Fe(III), Co(II) and Ni(II) were synthesized. The PDMS oligomer with 2,6-pyridinedicarboxamide groups was prepared by condensation reaction between bis(3-aminopropyl)-terminated poly(dimethylsiloxane) (Mn = 850) and 2,6-pyridinedicarbonyl dichloride to give a colourless viscous liquid. The obtained copolysiloxane was subsequently crosslinked into solid by Fe(III), Co(II) and Ni(II) chlorides.

The structures of the synthesized copolysiloxane were studied by NMR spectroscopy. Molecular mass characteristics of the copolysiloxane were determined by gel permeation chromatography (Mw=48000, Mn=32500).

The redox-active properties of supramolecular complexes of copolysiloxane with Fe (III) and Ni(II) using cyclic voltammetry have been established. Electrophysical characteristics of the synthesized supramolecular complexes of copolysiloxane with Fe(III) and Ni(II) were investigated using high-frequency impedance (conductivity \(10^{-10}\)Sm/cm at 1kHz).

References

Acknowledgements
This work was supported by the Russian Foundation for Basic Research (project No 18-33-20062_mol_a_ved). Measurements were performed at the Center for Magnetic Resonance, the Centre for Innovative Technologies of Composite Nanomaterials (all in Saint Petersburg State University).
Complication of the architecture of amphiphilic copolymers by introducing additional blocks and branching into the structure of macromolecules expands the possibilities for creating on their basis wide range of nanostructures of different morphology that cannot be achieved in the case of linear diblock copolymers. In this respect, molecular brushes – graft copolymers with densely grafted side chains – are of particular interest.

In this study the well-defined amphiphilic molecular polyimide (PI) brushes with hydrophilic polymethacrylic acid (PMAA) side chains and amphiphilic block-copolymer poly(methacrylic acid)-block-poly(methyl methacrylate) (PMAA-block-PMMA) side chains were synthesized by the “grafting from” approach in combination with ATRP method. For that, PI brushes with poly(tert-butyl methacrylate) (PTBMA) side chains were obtained initially. PI brushes with block-copolymer side chains were synthesized by chain extension of MMA from living chain ends of PI-g-PTBMA. At the last step, the target amphiphilic PI brushes with hydrophilic PMAA blocks in side chains of various composition were obtained by acidic hydrolysis of TBMA units.

Conditions of the controlled synthesis making it possible to adjust grafting density, length and distribution of side chains were determined.

It was found by TEM and DLS that depending on the composition, size and distribution of side chains the amphiphilic molecular PI brushes possess different self-assembly behaviour in selective solvents.

Acknowledgements. This work was supported by the Russian Ministry of Education and Science [grant number 14.W03.31.0022 (Megagrant of the Government of the Russian Federation)].
Adsorption of liposomes, spherical particles composed of a lipid bilayer, on a microgel particle is an example of a multiliposomal system potent for drug delivery applications (Figure 1). Such constructs have been proposed in the literature as a versatile platforms for a combination therapy of different types of diseases ranging from tumors to infections and auto-immune deficiencies. Liposomes have been previously immobilized on polymer stars, inorganic colloids, polycationic brushes. These and similar systems either do not concentrate a large enough amount of liposomes or contain toxic components and have, thus, only theoretical significance.

In the present study liposomes were adsorbed on biodegradable biocompatible microgels synthesized by RAFT copolymerization of N-vinylcaprolactam and N-vinylformamide with consequent hydrolysis of amide groups in the copolymer. Thus obtained macromolecules were cross-linked with poly(ethylene glycol) diacrylate to yield microgels of effective diameter 200 nm [1].

Liposomes were then adsorbed on these microgel particles and the complexes were characterized with DLS and laser microelectrophoresis. The composition of a saturated complex was estimated. Effect of adsorption on the permeability of the lipid bilayer was studied with use of doxorubicin-loaded liposomes. As the last step, effect of ionic strength on the interaction was investigated.

References

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One of the important objects of application of fibrous nanomaterials obtained by electroforming (EF) are chemical current sources, where they can be used as interelectrode separators [1, 2].

The aim of our work was to study the effect of the properties of polymer solutions on the process of EF and the porous structure of the resulting fibrous material for use as a separator in a sealed lead-acid battery.

For the formation of fibrous materials, the following polymers were selected: polyvinylidene fluoride (F-2M, company "Galopolymer Kirovo-Chepetsk", TU 2213-012-13693708-2004) and polystyrene (PS, company "Nizhnekamskneftekhim" TU 2214-126-05766801-2003). The solubility of polymers f-2M, PS and their mixture in a solvent based on dimethylformamide (DMFA) and butyl acetate (BA) in different ratios was estimated using computational and experimental methods [3]. Physicochemical properties of the obtained polymer solutions, such as viscosity, electrical conductivity, and surface tension, are investigated. The fibrous material was obtained by capillary-free EF method at the NSLAB 200S plant. The influence of physical and chemical properties of polymer solutions and technological parameters of electroforming on the porous structure, air permeability, surface density and thickness of the obtained materials was estimated. It was found that an increase in the pore size leads to an increase in the viscosity of polymer solutions. The resulting fibrous materials have been tested in models of lead-acid batteries (SKA) as separation materials such as "sandwich". It is shown that the use of the proposed separation materials increases the efficiency of oxygen ionization in a sealed SKA.

References
NOVEL FLUORINE-CONTAINING NORBORNENE-TYPE POLYMERS FOR MEMBRANE GAS SEPARATION

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One of the promising approaches to obtain thermally and chemically stable materials for efficient gas separation is the synthesis of polymers based on fluorine-containing norbornene derivatives. In order to reveal new correlations between polymer structure and membrane properties the synthesis of a series of novel fluorine-containing tricyclononenes was executed [1]. A series of exo-tricyclononenes was synthesized via stereo- and regio-specific thermal [2σ+2σ+2π]-condensation of the quadricyclane with fluoroalkenes. The synthesized monomers were then successfully subjected to ROMP in the presence of 1st generation Grubbs catalyst.

Figure 1. Novel fluorine-containing metathesis polytricyclononenes

Gas separation properties of new polymers were studied and influence of different fluorine-containing substituents on gas-transport parameters was estimated. Membranes based on the new polymers showed increased selectivity of gas separation for different CH₄-containing gas mixtures.

References

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MULTIBLOCK COPOLYMERS WITH MIXED LINEAR-BRUSH TOPOLOGY WITH BRUSH-TYPE CENTRAL BLOCK

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Multicomponent copolymers containing more than three thermodynamically incompatible blocks attract increased attention due to the possibility of formation of microstructures in films and selective solvents. An important task of modern polymer chemistry is the synthesis of multiblock copolymers with controlled length and architecture of each of the blocks. Currently, approaches based on the combination of several methods of controlled polymerization are often used in the synthesis of such copolymers. Combination of blocks with radically different structure, such as aromatic and aliphatic blocks, is especially of great interest, since it opens up the possibility of varying the properties of copolymers.

Figure. 1. Synthesis of multiblock copolymers PMMA-block-PCL-block-(PI-graft-PMMA)-block-PCL-block-PMMA.

In the present work we synthesized new three-component pentablock copolymers PMMA-block-PCL-block-(PI-graft-PMMA)-block-PCL-block-PMMA with mixed linear-brush topology with central block of grafted polyimide with PMMA side chains. Targeted block copolymers were synthesized using a combination of ROP and ATRP. Obtained copolymers were analyzed using 1H NMR and IR spectroscopy, SEC with triple detection and sedimentation-diffusion analysis.

Acknowledgements. This work was supported by the Russian Ministry of Education and Science [grant number 14.W03.31.0022 (Megagrant of the Government of the Russian Federation)].
ARENEDIAZONIUM TRIFLATES FOR POLYLACTIC ACID SURFACE MODIFICATION

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Polylactic acid (PLA) is a biodegradable, biocompatible and eco-friendly biopolymer which nowadays is widely used in different medical applications as surgical sutures, bone screws, scaffolds, and thin coatings for implants [1]. However, such materials have significant limitations due to hydrophobic behavior of PLA surface and a lack of reactive side-chain groups [2].

We proposed an effective and simple method for PLA surface modification by arenediazonium triflates which allows to control surface wettability. The proposed approach includes treatment of thin PLA films surface with water or water with ethanol solutions of arenediazonium triflates under ultraviolet irradiation (254 nm). We obtained a range of previously unknown arenediazonium triflates ArN₂⁺TfO⁻ and investigated its structure and properties by IR, NMR, TGA/DTA/DSC [3]. Modified films were investigated by optic goniometry to determine the effect of different functional groups of arenediazonium triflates on PLA surface hydrophilicity/hydrophobicity. We have found that treatment with 4-carboxyarenediazonium triflate increases surface hydrophilicity up to 45.6° and [1,1'-biphenyl]-4-diazonium triflate increase surface hydrophobicity up to 100.9° in comparison with pristine PLA surface – 74.1°. Scanning electron microscopy was used for morphology survey of modified films surface. Chemical composition of coatings formed onto PLA surface was examined by X-ray photoelectron spectroscopy to assume the coating formation mechanism.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No. 17-03-01097).
The processing of UHMWPE is complicated due to its high melt viscosity and is usually conducted by solution method. Another opportunity to process UHMWPE is solvent-free method developed by Smith\(^1\),\(^2\) and modified by Rastogi\(^3\). In this work, we report catalytic systems based on titanium (III/IV) tetrahydrofuranates that are able to produce UHMWPE, suitable for solvent-free processing techniques.

![Catalytic system I](image1)

![Catalytic system II](image2)

These systems catalyze ethylene polymerization with activities up to 1840 kg PE/mol Ti\(^{-1}\)·h\(^{-1}\)·atm\(^{-1}\). The obtained UHMWPE reaches \(M_w\) up to \(7.9 \times 10^6\) Da and has very low bulk density, less than 0.1 g/cm\(^3\). That is one of the crucial prerequisites for solid-state formation of tapes from UHMWPE nascent powder. All UHMWPE powders with \(M_w\) higher than \(2 \times 10^6\) Da were transformed into tapes by solid-state method described by Ozerin\(^4\). For the resulting tapes, the highest breaking strength of 2.1 GPa has been achieved.

References

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STIMULI-RESPONSIVE POLYMERS BASED ON (DIALKYLAMINO)ALKYL-(MET)HACRYLAMIDES. VARIETY OF PROPERTIES AT PH, CONCENTRATION AND STRUCTURE OF MONOMER UNITS

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Thermo- and pH-responsive poly-(dialkylamino)alkyl(met)acrylamides differing in the structure of the monomer (Figure 1) were synthesized using method of radical polymerization at 70°C. Molecular masses and hydrodynamic radii of scattering objects were determined in chloroform solutions by static and dynamic light scattering. The buffer solutions of polymer were studied using light scattering and turbidity methods. Acidity of solutions changed from pH = 7.00 to 13.00. Temperature dependences of optical transmission, intensity of scattered light and hydrodynamic radii of scattering species and their fraction in solutions were obtained in temperature interval from 15 to 70 °C.

![Figure 1. Structures of monomers.](image)

Table 1. Phase separation temperatures $T_1 / T_2$, °C at $c = 0.800$ g/dl for studied polymers.

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<td>29/32</td>
<td>44/50</td>
<td>51/66</td>
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Acknowledgements. This work was supported by Russian Foundation for Basic Research (project № 18-33-00576 mol_a).
HIGHLY EFFICIENT METHOD FOR PRODUCING TRANSPARENT AND HYDROPHOBIC SILICA AEROGELS

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In recent years, there has been an increased interest in porous materials, which is related to their applicability in different areas of science, medicine and technology. Aerogels, silica aerogels in particular, have special abilities: (1) high specific surface area and porosity, with a low density; (2) high insulation and soundproof rates; (3) optical transparency; (4) low permittivity; (5) low Young's modulus; (6) thermostability and other.

There are several successive stages that are carried out when obtaining silica aerogels: (1) sol–gel synthesis - wet gel forming; (2) aging and the formation of a lasting gel; (3) workup - preparing the gel for drying (including replacement one solvent with another, the catalyst and byproducts removal etc.); (4) drying - manufacturing an aerogel from the wet gel.

At the same time, we can highlight a number of critical technological problems, that are cost- and time-consuming, in the production of silica aerogels: duration of formation (1) and aging (2) of the gel (one to several days); use of excess amounts of acidic and/or alkaline catalysts/reagents; need to change one solvent in the gel pores to another and other stages of drying preparation (3); duration and high cost of the drying stage.

![Figure 1](https://example.com/figure1.png)

Figure 1. Transparent (a, b) and fluorescent (c, d) aerogels.

This work is aimed to solving these problems - developing a new method for obtaining aerogels, based on highly efficient, simple, commercially available and cheap catalytic system. This system will reduce the number and duration of technological stages of the process and will allow for preparing aerogels with tunable transparency, hydrophobicity and mechanical strength (Figure 1).

Acknowledgements. This work was supported by the Ministry for Science and Higher Education of the Russian Federation, Grant of the Government of the Russian Federation No. 14.W03.31.0018.
Thermoresponsive star-shaped eight-arms (poly-2-isopropyl-2-oxazoline)–
block-(poly-3-(2-oxazoline) propionic acid) (Fig. 1) was synthesized using a
“grafting from” approach. Molar mass of sample was about $M_w = 22000 \text{ Da}$.
The aqueous solutions of polymer were studied using light scattering and
turbidity methods. The solution concentration was equal to $0.005 \text{ g} \cdot \text{cm}^{-1}$.
Acidity of solutions changed from pH = 2.2 to 12.4. The temperature
dependences of optical transmission, intensity of scattered light and
hydrodynamic radii of scattering species and their fraction in solutions were
obtained in temperature interval from 15 to 55 °C.

![Figure 1. Structure of star-shaped polymers.](image1)

![Figure 2. Dependences of phase separation temperature on pH.](image2)

It is shown that at pH > 5, the phase separation temperature does not depend on
medium acidity (Fig.2). At pH < 5, the sharp decrease in phase separation
temperatures were observed with reduction of pH.

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Research (project No 18-03-00356).
Primary amino group is very suitable functionality for chemical modification of natural polysaccharides in comparison with OH-group. The most common way to introduce primary amino group in macromolecule of sodium hyaluronate is partial deacetylation of sodium hyaluronate. However, this approach requires hard conditions and leads to partial depolymerization of the hyaluronic chain [1]. Herein, we report new one-pot route to introduce amino functionality into macromolecule of sodium hyaluronate (Scheme 1). The first stage consists in preparation of cetyltrimethyl ammonium (CTA) salt of hyaluronic acid, which is soluble in DMSO. The salt interacts with Boc-protected amino acid in the presence of DCC and NHS, followed by deprotection of amino functionality. The change of cetyltrimethyl ammonium cation (CTA) to Na⁺ proceeds by dialysis of the prepared polymer against sodium chloride solution. Then, after dialysis against water to remove excess of sodium chloride, the obtained polymer was freeze-dried.

![Scheme 1. Introduction amino functionality into macromolecule of sodium hyaluronate.](image)

The obtained polymer was characterized by ¹H NMR and infrared spectroscopies and also by elemental (C, H, N) analysis.

References

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USAGE OF DISPERGATORS-MONOMERS TO INCREASE AGGREGATIVE STABILITY OF SYNTHETIC LATEXES

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It is showed that one of the reasons of synthetic latexes coagulation and coagulum formation is destabilizing influence of stable macroradicals on polymer-monomer particles [1]. Electron density of macroradicals leads destabilization of hydrate adsorption layer and to latex coagulation during storage period if adsorption layer protection is insufficient and monomer conversion rate is high [2]. Full termination of macroradicals by inhibitors of radical polymerization increases latex stability. EPR research showed reaction between stable radicals of EPR marker and living macroradicals inside polymer-monomer particle.

Stabilizing ability and surface activity of naphthalene dispersing agents lowers with increase of its polycondensation rate. Naphthalene dispersing agents lower critical micelle concentration of surfactant, prolong micellar stage of polymerization, increase emulsifier saturation of adsorption layer and macroradicals termination rate in polymer-monomer particles during polymerization.

Dispersing agents-monomers we synthesized showed similar effect and are able to built-in polymeric chain thus reducing concentration of no biodegradable naphthalene compounds in waste waters. Dispergators monomer are proposed as a replacement of existing dispersive agents.

References
TITANIUM (III) AS AN ACTIVE PARTICLE IN THE POLYMERIZATION OF ETHYLENE AND VARIOUS METHODS OF ACTIVATION OF TITANIUM (III/IV) POST-METALLOCENE COMPLEXES TO OBTAIN UHMWPE

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As a result of this work, the catalytic activity of non-metallocene complexes of titanium (III) and (IV) (Figure 1) was compared during the polymerization of ethylene. Also the oxidation state of the transition metal in these complexes before and after their activation by aluminum (Et₂AlCl, Et₃AlCl₃, EtAlCl₂, Et₃Al) and magnesium (Bu₂Mg) organic compounds or their binary mixtures was determined. The activation process for both complexes was studied by EPR, NMR, and UF-Vis spectroscopy.

![Figure 1. structure of complex Ti (III) and Ti (IV).](image)

Both systems, Ti (III) and Ti (IV), catalyze ethylene polymerization with activities up to 4500 kg PE/mol Ti⁻¹·h⁻¹·atm⁻¹. It was found that the complexes of titanium (III), are two times more active than ones of Ti (IV). Obtained UHMWPE reaches Mₘ up to 7.2·10⁶ Da and has very low bulk density, less then 0.1 g/cm³. That is one of the crucial prerequisites for solid-state formation of tapes from UHMWPE nascent powder. All UHMWPE powders with Mₘ higher than 1,6*10⁶ Da were transformed into tapes by solid-state method described by Ozerin [1]. The highest breaking strength of 2.9 GPa has been achieved for the resulting tapes.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No. 16-03-10502) and Russian Foundation for Basic Research (Project No. 17-03-00234).
Pervaporation is a promising method for the separation of liquids in the bioprocessing, petrochemical and pharmaceutical industries. This method allows to separate closely boiling and thermally unstable components, as well as azeotropic mixtures and mixtures of isomers. Pervaporation is an environmentally-friendly method of separation, for its implementation does not require expensive equipment and high energy consumption. The rapid development of pervaporation requires the search for new high-performance membrane materials with desired properties.

In the present work the novel membranes based on polyvinyl alcohol were prepared by bulk modification. Bulk modification was carried out by introducing the metal-organic framework UiO-66(NH$_2$)$_2$-EDTA into the PVA matrix. The improvement of the transport properties of polymer membranes occurs due to the porous structure of the metal-organic frameworks.

The study of the physicochemical properties of the membranes was carried out by scanning electron microscopy, IR spectroscopy and thermogravimetric analysis. Contact angle was using for study of the surface properties of the membranes, the degree of swelling was study by the gravimetric method.

The transport properties of the developed membranes were studied by pervaporation separation of the azeotropic mixture of isopropanol - water (88/12 wt.%). All developed membranes were highly selective for water (more than 95 wt.% water in the permeate). The introduction of UiO-66(NH$_2$)$_2$-EDTA into the PVA matrix leads to significant changes in both the physicochemical and transport properties of polyvinyl alcohol membranes.

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Currently, one of the most important areas in modern society is the development of sustainable processes. Membrane separation methods are related to such processes due to the fact that these methods are environmentally friendly, use compact equipment and have low power consumption. One of the most popular membrane processes for the separation of low molecular weight components is the pervaporation, which allows the separation of azeotropic mixtures, mixtures of isomers and thermally unstable mixtures. The rapid development of this method requires the search for new high-performance membrane materials with desired properties.

In the present work the novel membranes based on polyphenylene isophthalamide (PA) were prepared by bulk modification. Bulk modification was carried out by introducing the metal–organic framework UiO-66(NH2)-EDTA into the PA matrix. The improvement of the transport properties of polymer membranes occurs due to the porous structure of the metal–organic frameworks.

The study of the physicochemical properties of the membranes was carried out by scanning electron microscopy, IR spectroscopy, NMR spectroscopy. Also contact angle and swelling degree of the membranes were measuring.

The transport properties of the developed membranes were studied by pervaporation separation of the azeotropic mixture of methanol – toluene (72/28 wt.%). All developed membranes were highly selective for methanol. The introduction of UiO-66(NH2)-EDTA into the PA matrix leads to significant changes in both the physicochemical and transport properties of polyvinyl alcohol membranes.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-73-20060). The experimental work was facilitated by equipments from Interdisciplinary Resource Centre for Nanotechnology, Chemistry Educational Centre, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Magnetic Resonance Research Centre, Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Nanophotonics Centre and Centre for Geo-Environmental Research and Modelling (GEOMODEL) at St. Petersburg State University.
Nowadays, the essential improvement of the transport properties of polymer membranes can be achieved by the modification of the polymer matrix by inorganic filler that yields in developing the mixed – matrix membranes (MMMs). The introduction of inorganic filler in the polymer matrix of the membrane allows getting tailoring properties. MMMs combine the simplicity of processing polymer membranes with the superior transport properties of inorganic particles.

In the present work the novel membranes based on polyvinyl alcohol were prepared by bulk modification. Bulk modification was carried out by introducing the metal-organic framework FeBTC into the PVA matrix. The improvement of the transport properties of polymer membranes occurs due to the porous structure of the metal-organic frameworks.

The study of the physicochemical properties of the membranes was carried out by scanning electron microscopy, IR spectroscopy, and thermogravimetric analysis. Contact angle was using for study of the surface properties of the membranes, the degree of swelling was study by the gravimetric method.

The transport properties of the developed membranes were studied by pervaporation separation of the azeotropic mixture of isopropanol - water (88/12 wt.%). All developed membranes were highly selective for water (more than 95 wt.% water in the permeate). The introduction of FeBTC into the PVA matrix leads to significant changes in both the physicochemical and transport properties of polyvinyl alcohol membranes.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-73-20060). The experimental work was facilitated by equipments from Interdisciplinary Resource Centre for Nanotechnology, Chemistry Educational Centre, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, Magnetic Resonance Research Centre, Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Nanophotonics Centre and Centre for Geo-Environmental Research and Modelling (GEOMODEL) at St. Petersburg State University.
SYNTHESIS OF ELECTRICALLY CONDUCTIVE CORE/ SHELL POLYMER MICROSPHERES

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Today, biosensors are increasingly used in medicine by which wide range of relevant biological molecules can be conveniently detected or quantified. The desire for miniaturization of devices makes researchers to look for new materials. One of solutions was to use organic semiconductors as biological sensors. Such materials have properties that could be interested from the point of view of flexibility, ease of processing, biocompatibility and mixed ionic and electronic conductivity.

Thus, the aim of the work was to create electrically conductive core/shell particles that are promising for creating sensory films on their basis.

For the polymerization of the electrically conductive layer from 3,4-ethylenedioxythiophene (EDOT), it is necessary to obtain stable particles with a diameter of 5-10 μm with a surface layer enriched in sulfo groups. The paper shows several ways of forming the polymer core such as copolymerization of styrene with sodium 4-vinylbenzenesulfonate by emulsion and dispersion polymerization, as well as inverse suspension polymerization of sodium 4-vinylbenzenesulfonate.

As a result, particles with a diameter range of 250-650 nm were synthesized by emulsion polymerization, 300-650 nm by dispersive polymerization, 5-10 μm by inverse suspension polymerization. At the same time, the concentration of sulfo groups in the surface layer of particles obtained by inverse polymerization was 145-300 μmol/m², which is 1000 times greater than that for particles obtained by emulsion and dispersion polymerizations. Therefore, such particles are of the greatest interest for further research.

The forming of electrically conductive shell was carried out by polymerization of EDOT in the presence of various initiators: K₂S₂O₈ and FeCl₃. As a result, it turned out that the initiating system has a strong effect on the system, for example, particles aggregated and formed a flake-like precipitate in the presence of FeCl₃, but during polymerization in milder conditions, in the presence of K₂S₂O₈, the particles saved their spherical shape.
Platinum (0) and (II) complexes, notably cis-$[\text{PtCl}_2(\text{BnCN})_2]$ and Karstedt’s catalyst, are used for self-cross-linking of the polymethylhydrosiloxanes by the dehydrogenative reactions between Si-H groups$^1$. The cross-linking is carried out using a one-component system at RT in air. Karstedt’s catalyst leads to the formation of Si–Si cross-links, obviously, by dehydrogenative coupling and Si–O–Si cross-links by oxygenation or autoxidation of Si–Si bonds. The cis-$[\text{PtCl}_2(\text{BnCN})_2]$ results in predominantly Si–O–Si cross-links. The cis-$[\text{PtCl}_2(\text{BnCN})_2]$ allows creating high-quality silicone rubbers without visible mechanical defects (bubbles and cracks) in comparison with hyperactive Karstedt’s catalyst. Swelling measurements and SSNMR demonstrated that cis-$[\text{PtCl}_2(\text{BnCN})_2]$ forms silicone rubbers with a 1.5–2 times lower cross-linking degree than in the case of Karstedt’s catalyst. This cross-linking approach can be used to obtain new Si–H-containing silicone materials, in particular, for creation heterogeneous reducing agents.

References

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INFLUENCE OF THE TYPE OF CROSSLINKING AGENT ON THE HYDRODYNAMIC AND SORPTION PROPERTIES OF SUPERRMACROPOROUS SORBENTS BASED ON POLYETHYLENIMINE


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The influence of crosslinking conditions and the type of crosslinking agent from a series of diglycidyl ethers of glycols (1,4-butanediol, ethylene glycol, glycerol and polyethylene glycol) on the morphology, swelling degree, hydrodynamic characteristics and sorption capacity of supermacroporous monolithic materials (cryogels) based on polyethylenimine (PEI) have been investigated. We have found that diglycidyl ether of 1,4-butanediol (DGE-1,4-BD) with a ratio of crosslinking agent (CA): PEI 1:4 is the most effective crosslinking agent at -20 °C. Using confocal scanning microscopy, it was shown that the cryogel has a homogeneous pore structure with an average size of 106 µm (Fig.1A). Static sorption capacity of the sorbent for copper (II) ions was 2.21 mmol/g.

Breakthrough curves of copper (II) ions sorption on PEI cryogels were obtained at a flow rates 120-300 bed volume (b.v.)/h. The monolithic sorbents provided removal of copper down to the lowest acceptable limit (<1.0 mg/l) with effective dynamic sorption capacity of 1.5 mmol/g at flow rate up to 250 b.v./h (Fig.1B).

Acknowledgements. This work was supported by the Russian Science Foundation (project № 18-79-00093).
Poly(dopamine) has attracted interest recently as a universal surface modification agent in a broad range of biotechnological, electrochemical and nanotechnological applications [1]. One of the most common way of the polydopamine synthesis is dopamine oxidation in its aqueous solution. Dopamine hydrochloride is easily oxidized and undergoes spontaneous polymerization in a slightly alkaline environment. Oxygen from the air acts as an oxidant. The reaction proceeds spontaneously under mild conditions. Polymerization leads to changes of the solution color from almost colorless via light brown to dark brown. The polymer film is formed on the surface and polymer grains are formed in the bulk. The dynamic surface properties of polymer film at the air-water interface during formation were studied by dilatational surface rheology, ellipsometry and Brewster angle microscopy (BAM). The dynamic surface elasticity was measured as function of time and concentration by the oscillation ring method. It was shown that there is a significant increase of the elasticity for solutions with concentration from 0.75 g/l to 2 g/l. The highest values of the dynamic surface elasticity (~ 60 mN/m) were obtained for solutions with a concentration of 1 g/l. These values are comparable with those for solutions of globular proteins [2] indicating that the film consists of separate domains. The high surface elasticity is due to the interactions of relatively rigid domains of the polymer film. This assumption is supported by BAM images. Different steps of the growth of the film are observed. At first, the heterogeneity of the film increases gradually at the approach to equilibrium. The higher the initial concentration is, the faster the polymerization takes place and the thicker is the formed film. The dynamic surface elasticity decreases for dopamine solutions of 2 g/l and 5 g/l. For these solutions, the thickness of the polymer film reaches about 80 nm. In this case the film could break under its own weight. The cracks in the film lead to weakening of the mechanical properties of the layer.

References

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SYNTHESIS AND MACROMOLECULAR REACTIONS OF SILICON-CONTAINING POLYENES

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Organosilicon polymers are widely used as precursors of ceramics, photocurable polymers, crosslinking agents, membrane materials, etc. This study aimed at the synthesis of new silicon-containing multiblock copolymers, which could be of potential interest for gas separation. New copolymers built from glassy norbornene blocks and amorphous blocks of organosilicon olefins were synthesized using the cross-metathesis macromolecular reaction between polyenes [1]. The parent polynorbornene (PNB) and poly(1,1-dimethylsilapentene-3) (PSiP) were prepared by ROMP of norbornene and 1,1-dimethylsilacyclopentene-3 (SiP) in the presence of Grubbs’ Ru-catalysts of 1st (G1) or 2nd (G2) generation. Poly(1,1,3,3,5,5-hexamethyltrisiloxanyl-5-decenylene) (PSiO) was obtained by ADMET polymerization of bis(5-hexenyl)-1,1,3,3,5,5-hexamethyltrisiloxane) (SiO). The cross-metathesis between PNB and PSiP or PSiO was carried out in the presence of G1 and G2.

\[
\text{PNB} + \text{PSiP / PSiO} \xrightarrow{G1/G2} \text{multiblock-copolymer}
\]

Figure 1. Macromolecular cross-metathesis reaction

New NB-SiP and NB-3SiO copolymers with various degrees of blockiness were obtained and characterized by \(^1\text{H}, ^{13}\text{C}, \text{and } ^{29}\text{Si NMR, DSC, IR, and GPC. It was shown that their thermal properties depend on the composition and average block length and can be regulated by adjusting the cross-metathesis conditions.}

References

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PHYSICO-MECHANICAL PROPERTIES OF POLYSTYRENE COMPOSITES FILLED WITH DIFFERENT TYPES OF PARTICLES

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Rapidly growing applications of composite materials in industry stimulate analysis of various aspects of their mechanical behavior. The aim of this work was the study of the influence of various types of (nano)fillers on physico-mechanical properties of polystyrene (PS) based composites. Block samples of composites filled with different types of particles (MMT, HNT, SiO2, Al2O3, CB, CNT, Mica) were obtained by melt technology. The concentration of particles amounted to 0, 5, 10, and 20 wt%.

Rheological characteristics of composite melts were determined using the rheometer Physica MCR 301 (Anton Paar), the influence of the particles concentration on the mechanical properties of composites in tension was studied on Instron system. The dispersion of particles in the polymer matrix was estimated from the micrographs of cryo-cleavage surfaces of the composite samples, taken using a Carl Zeiss Supra-55 scanning electron microscope. The mechanical properties were studied in uniaxial tension and three-point bending tests. Basing on the data obtained, the strength at break, strain at break and elastic modulus of composites were determined.

It was shown that the introduction of MMT, CNT, and Al2O3 cause an increase in material viscosity by an average of 2 to 5 orders of magnitude over the pure PS. This increase is indicative of the formation of a network structure between the polymer and filler particles. The introduction of more rigid particles were shown to provide an increase in the elastic modulus of composites. HNTs were shown to be most promising among the considered aluminosilicate inclusions demonstrating substantial increase of elastic modulus with concentration along with acceptable aggregation even at 15% concentration. The best results though were obtained with carbon nanoparticles (CNT and CB). At the same time, it should be noted that composites containing CB demonstrate higher strength than pure PS.

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The beam deflector device is a necessary part of the holographic display system and LIDARs. One of the fastest approaches to modulate optical phase shift in time is based on the use of nematic liquid crystals (LC). Under the action of the electric field, the Fréedericksz transition from the planar state to the homeotropic state is observed (Fig. 1), giving rise to the phase shift between the ordinary and extraordinary rays.

The main problem of these systems is relatively slow relaxation time. One possible solution is the stabilization of the nematic by a polymer network, which allows increasing Frank's elastic constants, thereby reducing the relaxation time. In this work mesogenic (capable of LC phase formation) or non-mesogenic monomers (1.5-5.0%) and UV photoinitiator are introduced into the highly birefringent LC-mixture and polymerized, resulting network stabilized liquid crystal.

The series of monomers were studied, with variable concentration of monomers and initiator and different conditions of UV-irradiation. The samples were characterized by polarization microscopy and by the electro-optical setup (the turn-off time was determined).

Some regularities for monomers and irradiation condition are established. It is shown, that for the polymer-stabilized system, it is possible to obtain relaxation time, which is four times better (10 ms) than in pure LC.

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COMPOSITES ON THE PLATFORM OF THERMALLY STABLE POLYMERS DOPED WITH CeO₂ NANOPARTICLES: THERMAL AND MECHANICAL PROPERTIES

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Aromatic polyimides (PIs) have an excellent combination of thermal and mechanical properties and cater for numerous applications. However, current demand for PI materials requires an ongoing improvement of the said properties. Incorporation of nano-components into polymer matrices has been proved to enhance functional properties of the resulting composite. Recently, nanocomposites based on the PI matrices have been being under intensive study. Nevertheless, there are still many issues in the design of such nanocomposites, not solely in processing, but also in understanding interactions between the polymer matrix and nanoparticles and the functional response of the final material.

In this work, we tackled these issues. We have prepared nanocomposite films based on a number of aromatic PIs doped with CeO₂ nanospecies. The latter have a fascinating feature of changes in charge-states Ce⁴⁺ to Ce³⁺, thereby affecting the properties of the composite. The thermal analysis of the nanocomposites under study in air and in inert atmospheres reveals that ceria nanoparticles enhance thermal properties of the composites based on only such PIs which contain SO₂-group in the elementary units of their chains. The reason behind this enhancement is suggested. The mechanical and thermomechanical properties of the nanocomposite films are also reported. Results obtained provide new options for the design of polyimide nanocomposite materials with enhanced thermal stability.

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Age-related macular degeneration and diabetic retinopathy are among the most common ocular diseases that lead to vision loss. These pathologies are characterized by proliferation and migration of epithelial cells and increase in vascular permeability and inflammation. [1]. A key role in the regulation of these processes plays vascular endothelial growth factor (VEGF).

In the last decade, a great number of studies were focused on the development and testing of anti-VEGF therapy in vitro and in vivo. One of the most promising approaches is an intracellular delivery of small interfering RNA, which is capable of knocking down the VEGF gene. [2] The major obstacles for RNA delivery are poor cellular uptake, insufficient targeting of RNA molecules and their instability under physiological conditions. To overcome these problems polymer particles can be applied as nanocarriers for siRNA.

This work is devoted to the creation of biocompatible polypeptide nanoparticles based on lysine, glutamic acid, phenylalanine and isoleucine. The target copolymers were obtained using ring-opening polymerization of corresponding N-carboxyanhydrides. The obtained nanoparticles were characterized by nanoparticle tracking analysis and dynamic light scattering and their morphology was studied by a transmission electron microscopy. Transfection and cell cytotoxicity of the nanoparticles were studied in vitro.

The experiment of intracellular delivery of siRNA encapsulated in polymer particles was carried out and the VEGF gene knockdown was successful.

References

Acknowledgements. This work was supported by Mega-Grant of Russian Government (No 14.W.03.31.0025).
Coordination polymers have been a subject of intensive research in the past decades. A wide variety of organic spacers have been utilized to link coordinating functions together, including adamantane. Adamantane derivatives attract the attention of researchers for the construction of coordination polymers because of their conformational rigidity and thermal stability, but most of the works are related to 1,3-adamantane dicarboxylic acid as a dicarboxylate linker. Here we prepared an orthogonally substituted adamantane derivates 3-(triazol-1-yl) or 3-(tetrazol-1-yl) adamantane carboxylic acids. Several coordination polymers were prepared and their a range of their properties was studied. One of the polymers was found to act as a catalyst in Chan-Evans-Lam arylation of imidazoles with boronic acids. Influence of the reaction conditions on the geometry of complexes is also observed.

Figure 1. Reaction of the ligand formation and two examples of obtained complexes.

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CHROMATOGRAPHIC EVALUATION OF THERMAL STABILITY OF POLY (3-TRIBUTOXYSILYLTRICYCLONONENE-7)

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Thermal stability is one of the most important parameters of the stationary phases in gas chromatography. However, there are no common procedures for determination of this characteristic for the newly developed polymers being the candidates for utilization in GC as the stationary phases. The present work is devoted to the evaluation of process of thermal ageing of poly (3-tributoxysilyltricyclononene-7) (See Figure. 1) using chromatographic method.

![Figure 1. The structure of the metathesis poly(3-tributoxysilyltricyclononene-7)](image)

The polymer was placed into the quartz capillary and then the following procedures were performed:
1) efficiency and selectivity of the native polymer used as a stationary phase were determined;
2) the accelerated thermal ageing of the polymer was performed at 200°C for 7 h;
3) efficiency and selectivity of the aged polymer used were evaluated.

The efficiency of the original polymer was more than 15 000 theoretical plates per column for the best chromatograms. This value practically did not change after column heating, meaning that poly(3-tributoxysilyltricyclononene-7) might be used as a stationary phase in GC at temperatures up to 200°C.
NOVEL MUCOADHESIVE GRAFT-COPOLYMERS FOR THE TREATMENT OF ANTERIOR SEGMENT OCULAR DISEASES

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Topical administration, mostly in the form of eye drops, is employed to treat anterior segment diseases. Upon administration, precorneal factors and anatomical barriers negatively affect the bioavailability of topical formulations. Mucin present in the tear film plays a protective role by forming a hydrophilic layer that moves over the glycocalyx of the ocular surface and clears debris and pathogens [1]. Tear film displays a rapid restoration time of 2–3 min, and most of the topically administered solutions are washed away within just 15–30 s after instillation. Thus, the colloidal nanosized carriers have been widely explored to overcome various static and dynamic ocular barriers.

Novel drug delivery strategies such as bioadhesive particles and gels were developed to sustain drug levels at the target site. In this work we aim to develop novel mucoadhesive thermo-responsive hybrid polymer carriers for topical non-invasive application to improve drug delivery to the anterior segment of the eye. The polymers based on natural polysaccharides and thermo-responsive pNIPAAm chains were obtained via RAFT polymerization. Physico-chemical properties were widely studied. Nanoparticles and polymer gels were successfully obtained using thiol-chemistry approaches. The encapsulation and release of dexamethasone and 3H-propranolol were studied and optimized for ocular delivery. Finally, the in vitro retention study of polymers on the corneal epithelium was done using mucin binding affinity assay.

References

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KINETICS AND DYNAMICS OF FLUOROQUINOLONES SORPTION BY METAL-AFFINE SORBENTS BASED ON CARBOXYALKIL CHITOSAN DERIVATIVES.

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The uncontrolled release of antibiotics into the environment with wastewaters of pharmaceutical production, hospitals, livestock and poultry farms has been recently recognized as a serious danger to human health. Due to the low efficiency of municipal wastewater treatment facilities towards many classes of antibiotics, the search for new approaches and materials for efficient removal of antibiotics from wastewaters of pharmaceutical plants and drinking water is the urgent problem.

Fluoroquinolones are widely used antibiotics, having high chelating ability with respect to ions of divalent and trivalent metals. Earlier, we have developed a method of fabrication of metal-affine sorbents based on carboxyalkyl chitosan cryogels crosslinked with hexamethylene diisocyanate [1].

In this work, the kinetics and dynamics of ciprofloxacin sorption, as the most common fluoroquinolone, by metal-affine sorbents based on cross-linked carboxyethylchitosan (CEC) containing Cu (II) and Al (III) ions have been studied. Using kinetics data, we have shown that the sorption of ciprofloxacin on the CEC-Cu (II) cryogels takes place in the external diffusion mode that is determined by the highly developed porous structure of the sorbents and good accessibility of all active sorption centers. The dynamics of ciprofloxacin sorption was investigated on Cu(II)-containing metal-affine sorbents at flow rates up to 40 bed volumes per hour (b.v./h). Effective dynamic sorption capacity was calculated from breakthrough curves assuming that sorption was efficient if 99% of ciprofloxacin was recovered. We have shown that effective dynamic sorption capacity of CEC-Cu (II), crosslinked with epichlorohydrin, reaches 0.42 mmol/g at a flow rate of 10 b.v./h and pH 7.5 for initial ciprofloxacin concentration 2·10⁻⁴ mol/l.

References

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PREPARATION AND PERVAPORATION PERFORMANCE OF SULFONATED COPOLYIMIDE.

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Polyimides containing high-polar groups, especially sulfonated polyimides, recently became an object of interest due to their potential application as a material for diffusion membranes \cite{1}. Usually, they are being considered as a suitable material for proton exchange membranes. The presence of mobile hydrogen atoms in sulfonic groups of a polymer ensures the availability of proton-conductivity when the polymer is swollen in a protonic solvent. However, there are only a few articles where the transport properties of sulfonated polyimides in the processes of membrane liquid or gas separation were studied \cite{2,3}.

A novel sulfonated copolyimide was synthesised via polycondensation of 4,4’-Diaminobiphenyl-2-2'-disulfuric acid (BDSA), 4,4’ oxydianiline (ODA) and 5,5’-[1,3-Phenylenebis(oxy)]bis(2-benzofuran-1,3-dione) in m-cresol. The chemical structure of the obtained polymer was confirmed with NMR spectroscopy. Thermodynamical properties of obtained films were characterised by the methods of differential scanning calorimetry and thermal gravimetric analysis.

For the investigation of transport properties of obtained copolymer dense films were prepared and tested in the process of pervaporation of methanol/toluene mixtures at 20, 40 and 60 °C. Obtained films showed great values of permeability and selectivity in the wide range of mixture compositions and are considered as a potential pervaporation membranes material for effective methanol/toluene mixtures separation.

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ETHYLENE POLYMERIZATION AND COPOLYMERIZATION WITH HEXENE-1 ON CATALYTIC SYSTEMS BASED ON Ti (IV) FLUORINATED SALEGININ COMPLEXES

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Earlier we have reported catalytic systems based on Ti (IV) complexes with OO-type ligands that are effective both in polymerization and copolymerization of olefins [1,2]. These systems were further tested in tandem catalysis to yield LLDPE. In this work, we report new Ti (IV) complexes with fluorinated ligands that can form effective catalysts for olefin polymerization and copolymerization.

Figure 1. Catalytic systems.

The best results in ethylene polymerization have been shown by the catalytic system 1/Et2AlCl/Bu2Mg. The activity reached 1600 kg PE/mol Ti-1·h-1·atm-1 and the resulting polymer (UHMWPE) was formed into tapes with breaking strengths up to 2.6 GPa. However, the catalytic system 3/Et2AlCl/Bu2Mg was superior to other systems in ethylene copolymerization with hexene-1 (activity up to 4500 kg/mol Ti-1·h-1·atm-1). The studies of copolymers properties are in progress.

References

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THE NEW WAY OF CREATING WATER-SWELLABLE POLYMER COMPOSITES

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Water-swellable polymer composites combine remarkable mechanical characteristics with the ability of swelling in water [1]. The ability of the composite to swell in water is provided by water-absorbing components (WAC). One of the main drawbacks of such composites is the insufficient interfacial interaction of particles of the hydrophilic WAC and the hydrophobic elastomer matrix. This leads to the leaching of the WAC from the matrix of the composite and the reduction of its mechanical characteristics. In this regard, it is important to find a way to enhance the interfacial interaction in water-swellable polymer composites to improve the integrity of the material.

A possible solution to this problem may be the creation of water-swellable composites using chlorosulfonated polyethylene, due to its reactivity [2, 3]. Thus, the purpose of this work is to study the possibility of enhancing interfacial interactions in water-swellable polymer composites based on chlorosulfonated polyethylene, as well as to study their properties.

Chlorosulfonated polyethylene, high-pressure polyethylene, ethylene-vinyl acetate copolymer, and Na-carboxymethylcellulose as a WAC were used as components of the composite. The composite was obtained in a two-rotor mixer for 10 minutes, under conditions of high shear rates (100 rpm) and at 190 °C providing an increased value of the decay rate constant of sulfonyl chloride groups in chlorosulfonated polyethylene.

As a result of the study of the sample surface by scanning electron microscopy, the best interaction of the particles of the WAC with the polymer matrix was found. This is reflected in a decrease in the leaching of the WAC after exposure to water. These compositions have high mechanical characteristics (6-8 MPa) in combination with the possibility of achieving high degrees of swelling.

References:

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Laser 3D printing is the technology of additive manufacturing of models, prototypes and products from liquid photo-curing compositions. The method is based on the irradiation of a liquid photopolymer mixture with a laser or other optical radiation to create digital models.

Organosilicon compounds are used as objects of study, their advantage is that the objects obtained from them with the help of 3D printing are bioinert and can be turned into ceramic by pyrolysis [1]. In the work using IR-Fourier, NMR spectroscopy, solubility and swelling tests, thermogravimetric analysis were investigated photocuring of polydimethylsiloxanes with terminal acryloxy and methacryloxy groups, as well as photo curing of 3-glycidoxypropyltrimethylsilane. Possible mechanisms of their photocuring are proposed.

Composites based on these compounds with nanostructured fillers, such as silicon dioxide, yttrium oxide doped dysprosium and carbon nanotubes, were obtained. These composites were studied using Raman scattering and scanning electron microscopy. The formation of new chemical bonds for a composite based on photocured 3-glycidoxypropyltrimethylsilane and oxide nanoparticles has been found.

References
COPOLYIMIDE BRUSHES AS MODIFIER OF PERVAPORATION MEMBRANES

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Modification of known polymers by incorporation of different fillers is a perspective method to create new materials with improved characteristics. Nowadays branched polymers are actively studied, particularly polymer brushes. Incorporation of polymer brushes not only changes the matrix polymer structure but also allows varying of polymer composition properties. The objects of the present work are composite materials based on poly(m-phenylene-iso-phthalamide) (PA) and copolyimide brush that is regularly grafted polyimide with side poly(methyl methacrylate) chains (PI-PMMA). The aim of the work is to study influence of PI-PMMA as filler on a structure, physical, mechanical, thermal properties of composite materials PA/PI-PMMA. Morphology of test composite films was studied by scanning electron microscopy. Interactions between polymers were defined using viscometry, dynamic light scattering and IR-spectroscopy. Length of the side PMMA chains influences significantly on interactions between the matrix and polymer brush and mechanical properties of the composite films. Particular attention was paid to stable microphase separation in the compositions. It was revealed that the film compositions have microphase separation with uniform distribution of polymer brush there but dense durable films containing polymer brush with concentration up to 30 wt% were obtained. Membranes based on compositions PA/PI-PMMA were prepared for pervaporation of methanol-hexane mixture and gas separation. It was found that the test membranes are effective materials for pervaporation and gas separation.

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THE EFFECT OF COMPLEX FILLING ON THE PROPERTIES OF POLYTETRAFLUOROETHYLENE

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Due to its uniquely low coefficient of friction, as well as its ability to maintain its value over a wide temperature range, polytetrafluoroethylene (PTFE) attracts the attention of tribologists around the world. Interest as a tribological material does not subside due to the fact that the matrix easily responds to all sorts of modifications by introducing a variety of fillers.

The aim of the work is to study the complex of various types of fillers on the physicomechanical and tribological characteristics of composites based on PTFE.

The objects of study were PTFE and composites based on it, containing as fillers carbon fibers (CF) or basalt fibers (BF) with functional additives, FORUM® nano-dispersed powder and activated aluminium oxide (Al2O3). FORUM® was used as a functional additive to reduce the friction coefficient, and Al2O3 - to improve the adhesion interaction at the interface. Characteristics of the shape and size of the particles, and the chemical composition of the filler significantly affect the properties of the mixture. CF improve compressive strength, making it more resistant to wear. Test samples were obtained by dry mixing the components, followed by cold pressing to form them, after which they were sintered in a muffle furnace at a temperature of 375 °C and calibrated to correct the shape of the samples and eliminate the effects of thermal shrinkage during sintering. Mechanical activation technology was used in a planetary mill Activator-2S (Russia). The main technical characteristics were obtained by standard methods: "Compression test method" (GOST 4651-2014), "Method of determining the friction coefficient" (GOST 11629-2017), "Elastic modulus" (GOST 9550-81).

The results of the study showed that the use of complex filling in a certain combination leads to a significant improvement in the properties of composites based on PTFE: the compressive strength increases by 40-80%, a high degree of crystallinity is observed in the composite with 18 wt.% BF and 0.5 wt.% Al2O3, the wear resistance increases up to 1500 times in contrast to the initial PTFE. Thus, new promising formulations of polymer composite materials (PCM) based on PTFE for tribological purposes with enhanced performance characteristics have been obtained.
Segmented polyurethanes are block-type copolymers with \([A-(B)_k]\) structure, where \(A\) is a hard block, and \((B)_k\) is a soft one. The role of soft blocks can act as aliphatic glycols, which have ether and ester groups in their structure, while hard blocks are usually represented by aromatic diisocyanates with diols or diamines. The resulting urethane and/or urea groups contribute to microphase separation and the formation of a domain structure in multiblock copolymers. Currently, materials based on segmented polyurethanes are widely used as rigid and flexible foams, elastomers, functional coatings, adhesives and sealants.

In this work, the synthesis was carried out and the structure and properties of segmented polyurethanes were investigated. A combination of 4,4'-methylene diphenyl diisocyanate (MDI), 2,4-diisocyanato-1-methylbenzene (TDI), 1,3-phenylendiamine (MF) and bis[4-(4-aminophenoxy) phenyl] sulfone (BAPS) was used as hard aromatic segments. The soft segments were polycaprolactone (PCL) with a molecular weight of 530 g/mol and 2000 g/mol. The synthesis was carried out according to a two-stage scheme. The first stage of the process was accompanied by the formation of urethane. The second one was urea formation as a result of the interaction between isocyanate and amine groups.

The structure of the obtained multiblock copolymers was confirmed by IR and NMR spectroscopy. The deformation-strength properties and the effect of changes in the system of hydrogen bonds with an increase in the molecular weight of the flexible segment were studied. It was shown that polyurethanes (MDI-PCL2000-MDI) BAPS and (MDI-PCL530-MDI) BAPS are thermoplastic elastomers: the flow stress reaches 50 MPa, the elongation at break is up to 900%. The thermal properties of the obtained materials were studied by TGA, DSC and DMA methods. The values of the glass transition temperature in copolymers range from -52°C to 66°C, the destruction temperature is 256-298°C.

References
The progress in electrical transportation systems and an increasing number of electronic devices leads to the intensive search of new effective and environment friendly materials for construction of power sources. One of the important directions in this field is the elaboration of solid polymer electrolytes (SPEs), in particular, based on the natural polymers (such as chitosan or cellulose) [1]. In the last decade, ionic liquids and their particular type - deep eutectic solvents (DESs) have been actively studied due to their unique physicochemical properties such as relatively high conductivity, thermal stability and wide working potential window and natural origin [2]. Combining of the natural DESs and natural polymers into one system is a promising way to obtain renewable low toxic SPEs.

This research focuses on the investigation of the relationship between the structure and electrical properties of the chitosan-DES films. The choline chloride and the raw of dibasic acids (oxalic (OA), malonic (MA) and succinic (SA)) were used for obtaining of DESs. The films with various DESs were prepared by solution casting method and final films contained 50 wt% of DES. Electrical impedance spectroscopy at various temperatures was performed and specific conductivity (\(\sigma\)) was calculated. It was found that values \(\sigma\) for OA and SA were significantly higher than ones for samples prepared with MA. This allows to suggest the formation of enriched DES network of ionic conducting channels inside the film prepared with OA and SA. This leads to the significant enhancing of the ionic conductivity at ambient temperature from \(7.2\times10^{-8}\) S/cm for film with MA up to \(6.3\times10^{-5}\) S/cm and \(7.2\times10^{-5}\) S/cm for ones containing SA and OA respectively.

References

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Recent reviews on drug delivery systems outline that further development of such systems should result in embedding stimuli-sensitivity and ability to carry several therapeutic agents simultaneously. These requirements can be satisfied with the system composed of liposomes bound to a thermosensitive microgel. Microgels of certain composition may undergo significant decrease in size upon heating which may lead to release of encapsulated drug. Investigation of complex behavior in media with different pH and ionic strength values is important for complete understanding of the system’s properties.

We have experimentally demonstrated that anionic liposomes made of egg lecithin and 30 mass % phosphatidylserine can be adsorbed on the surface of cationic thermosensitive microgel synthesized from 3-((N,N-dimethylamino)propylmethacrylamide, N-isopropylacrylamide and N,N-methylenebisacrylamide. Liposomes stay intact upon adsorption and for complex properties description liposome-to-microgel mass ratio is used. The process of complex formation was investigated in media with different ionic strength values. It was shown that with an increase of ionic strength the rate of aggregation in liposome-microgel mixtures slows down until it stops completely at 120 mM indicating that no interaction between oppositely charged particles occurs at this value of ionic strength. Interestingly, the same trend was observed in the range of pH = 4.75 – 7.2 when the microgel’s protonation degree changes from 1 to 0.7. To study the role of liposome composition, a series of liposomes composed of variable mass ratio of egg lecithin and cardiolipin were used. With all the samples, the above-described procedures were performed including complex formation at different liposome-to-microgel ratios and in the media with different values of ionic strength using the relevant ratio chosen. It was shown that the quantity of cardiolipin in the lipid bilayer determines the maximum value of ionic strength at which liposome-microgel complexes can be formed.

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SYNTHESIS AND VISUALIZATION OF NOVEL HELICAL BOTTLEBRUSH POLY(PHENYLACETYLENE)S

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The precise design of structurally complex polymers is increasingly important for their unique physical properties in recent years. In particular, various kinds of topologies based on helical polymers have recently drawn great attention from not only academia but also industry because of their valuable potential application, such as chiral separation and asymmetric synthesis for pharmaceuticals [1]. Recently, we have developed a novel catalytic system capable of inducing living polymerization of various phenylacetylene derivatives. This finding opened new fields of synthesizing structurally complex helical polymers.

Here, we report the formation of the structurally complex polymers based on helical polymers. We have synthesized poly(phenylacetylene)-based bottlebrush polymers by a “grafting from” method, which were obtained quantitatively and their molecular weight distributions were very low. AFM analysis revealed that the polymers have well-controlled bottlebrush structures (Figure 1). We also describe the chiroptical properties of bottlebrush polymers bearing chiral groups on the side brush chain.

This is the first example of bottlebrush poly(phenylacetylene)s. We are convinced that these complex structures might allow the development of new functional chiral materials.

Figure 1. AFM image of bottlebrush polymers.

References
SELF-ASSEMBLED NANOPARTICLES AS POLYMYXIN DELIVERY SYSTEMS

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Polymyxins represent a group of peptide antibiotics. The limiting side effects of polymyxin’s administration are their nephrotoxicity and neurotoxicity due to the increased dosage required for the achievement of therapeutic action. In turn, the reason for higher dosage application is a fast inactivation of the peptide drug in the bloodstream [1]. To overcome the aforementioned disadvantages, the use of polymeric drug delivery systems can be a matter of choice. This work proposes the creation of delivery systems for polymyxins based on self-assembled biodegradable particles from amphiphilic copolymers of amino acids. Currently, this class of nanoparticles attracts increased attention of the scientific world, both in terms of basic research and in terms of commercial application [2]. A series of the random amphiphilic copolymers based on aspartic/glutamic acid and isoleucine were synthesized by ring-opening polymerization of α-amino acid N-carboxyanhydrides. Molecular weight characteristics and composition of copolymers were determined using gel permeation chromatography and quantitative HPLC-MS analysis of amino acids. According to the data of transmission electron microscopy, the obtained amphiphilic copolymers formed spherical particles. The characteristics of particles were determined by the method of dynamic and electrophoretic light scattering. The cytotoxicity of the obtained particles was evaluated in a wide range of concentrations and the stability of the particles was studied in the model and culture media. A technique for HPLC analysis of polymyxins B and E was developed, and the features of antibiotic’s encapsulation into the obtained polymer particles were studied. Such important parameters as encapsulation efficiency and maximum drug loading were determined. The release profile of polymyxins in a model solution was also studied.

The study was supported by Russian Science Foundation (project № 19-73-20157).

References
In recent years, optical research methods are widely used in pharmacology, medicine and biotechnology to characterize new materials and objects. AFM and laser interferometry has become the most common and successfully used tools for the study of surface properties in tissue engineering to repair damaged tissues of a living organism [1]. Directed growth and controlled development of mesenchymal stem cells are realized using matrices and scaffolds capable of supporting cell proliferation [2].

The aim of the work is to study the characteristics of the structure and biological properties of biodegradable polymer matrices with anti-inflammatory activity, created on the basis of chitosan in combination with polypeptides secreted by mesenchymal stem cells, and promising for the development of materials for biomedical purposes. The optimal conditions for the production of thin-film biopolymer matrices by the method of irrigation with acetic acid solution of chitosan, cross-linked by genipin onto an aluminum plate and further use of spin-coating, are determined. A non-invasive assessment of structural features (surface topography, microrelief character, heterogeneity of polymer structure) and biological properties (biocompatibility, adhesiveness, immunogenicity, thrombogenicity, etc.) of the obtained thin-film matrices using super-resolving laser modulation microscopy and AFM was carried out. The phase images of biopolymer samples were obtained which could be interpreted as a two-dimensional projection of their three-dimensional structure.

References

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REGULAR SILICON ORGANIC COPOLYMERS - PRECURSORS FOR MATERIALS WITH SPECIFIED PROPERTIES

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Silicone resins are three-dimensional polymers with residual functional groups \cite{1}. They are widely used as varnishes, paints and electrical insulation coatings due to a complex of unique properties: high thermal and thermal oxidative stability, resistance to ultraviolet radiation, a wide range of operating temperatures, bio-inertness, manufacturability, etc.

The traditional method of resin production is hydrolytic co-polycondensation of trifunctional and difunctional organochlorosilanes, where trifunctional create a three-dimensional net, and difunctional improve mechanical properties. However, such methods of production have drawbacks: compositional heterogeneity, complexity of control of material properties and poor reproducibility.

This paper presents regular copolymers (i.e. with a regular arrangement of functional and non-functional fragments). The functional fragment \cite{2} contains functional groups and is responsible for the formation of a three-dimensional polymer net; the non-functional fragment provides the product with the necessary set of physicochemical properties (Fig 1).

Thus, the properties of the polymer are set by its chemical composition, and not by an empirical selection of the conditions of the hydrolytic co-condensation reaction, as in the case of the traditional method.

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3 section

NEW SYNTHETIC METHODOLOGIES IN ORGANIC AND BIOMEDICAL CHEMISTRY
SUSTAINABLE PATHWAYS TO AMINES VIA COUPLING AND HYDROGEN BORROWING REACTIONS

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The development of efficient and selective methodologies is of prime importance to achieve the goals of green chemistry. Hydrogen borrowing (hydrogen auto-transfer) reactions are considered to be eco-friendly, atom economic alternatives to conventional synthesis methods since they result in only water as a side product. Moreover, they allow for the utilization of widely available alcohols as substrates that can also be derived from renewable resources. These catalytic methods received huge attention in the last decades, employing noble[1] and earth-abundant metals.[2]

Herein, we show our recent developments in the N-alkylation of amines with alcohols using Ni, Fe and Ru based catalytic systems via the hydrogen borrowing approach. More specifically, we have developed a highly active and easy-to-prepare Ni based catalyst system[3], that is in situ generated from Ni(COD)$_2$ and KOH under ligand-free conditions. Moreover, novel methodologies using Ru and Fe complexes for the synthesis of β-amino acid esters and N-substituted heterocycles will be presented.[4]

Additionally, we demonstrate our recent achievements regarding the use of doped porous metal oxides as catalysts in catalytic conversion of lignocellulose and lignocellulose derived chemicals to higher-value building blocks including amines via cross-coupling and hydrogen borrowing reactions.[5]

![Chemical Reaction](attachment:image)

R$^1$, R$^2$, R$^3$ = benzyl, alkyl

References
L-Alpha glycercylphosphorylcholine (alpha-GPC) is part of the nootropic drug group. It is used to treat cognitive impairments of various etiologies. One of the main methods for the synthesis of choline alfoscerate is the catalytic transesterification of 95% lecithin with methanol, using 1-propylamine as a catalyst [1].

In this paper, we studied the catalytic activity of diethylamine for the transesterification of a 35% solution of lecithin in soybean oil while changing various reaction conditions. The determination of the completeness of the conversion of lecithin (Rf = 0.43) and the authenticity of α-GPC (Rf = 0.05) is carried out by thin layer chromatography in eluent chloroform: methanol: acetic acid: water in a volume ratio of 5: 2.5: 0.8: 0.4 respectively. The results showed that at room temperature and the same mole ratios, diethylamine and 1-propylamine exhibit similar catalytic activity. The reaction rate was slightly increased by the influence of ultrasound with a frequency of 45 kHz. Heating to the boiling point (water bath temperature 80 °C) leads to a significant increase in the reaction rate. In addition, it was found that when methanol contains more than 5% water, is observed a decrease in the reaction rate and the formation of an insoluble precipitate — a mixture of carboxylic acid amides.

References
Ketoacetylenes are useful intermediates in the synthesis of diverse heterocycles through dipolar cycloaddition or nucleophilic addition-elimination mechanisms. However, there are no literature data on the biological activity of the molecules composed of these fragments. Assuming that ynone fragment could be involved in hydrogen bonding with nucleobases, the aim of this work is to evaluate cytotoxicity of calixarene tetraketooctylcylens with variable arrangement of ynone units and their DNA binding ability.
Surface pressure–area isotherms of ynone 1 on water (C = 0.1 mg/mL in CHCl₃) without and with DNA (5–50 mg/L) and A375 lung cell viability in the presence of ynone 1.

In this work, ketoacetylene derivatives of calix[4]arene on the lower rim in 1,3-alternate (1) and partial cone (2) stereoisomeric forms have been synthesized and characterized. DNA binding studies at the air–water interface have shown that the monolayer of calix[4]arene 1 is expanded in the presence of 5 mg/mL of calf thymus DNA, which indicates incorporation of the nucleotide. Furthermore, no cytotoxicity of calixarenes 1 and 2 towards human lung cell line (A375) has been detected, which is a promising result from the viewpoint of DNA detection using ketoacetylene units preorganized on a calixarene scaffold.

The work was supported by the Russian Foundation for Basic Research (project no. 17-53-10016-KO-A).
Despite the physiological function of the cytokines of the IL-17 family in innate and adaptive immunity, dysregulated production of these cytokine has been shown to play a role in developing autoimmune and inflammatory conditions. The IL-17 family of cytokines contains 6 structurally related cytokines. IL-17A, the most extensively studied member of this family, has been implicated in the pathogenesis of autoimmune and inflammatory diseases such as psoriasis and rheumatoid arthritis. As a result, blocking the interaction of IL-17A with its receptor, IL-17RA, has emerged as an effective strategy in the treatment of diseases of this nature [1].

Inhibition of protein-protein interactions with small molecules presents many difficulties for medicinal chemist and IL-17A with a very large protein-protein interaction interface and no distinct small-molecule pocket, has certainly proved one of the most difficult targets in small-molecule drug discovery.

Monoclonal antibodies targeting IL-17A or its receptor have shown remarkable efficacy in autoimmune disorders. Secukinumab, a monoclonal antibody interacting with IL-17A, for instance, has been approved for the treatment of psoriasis and the search for finding more monoclonal antibodies is still ongoing. However, so far no small-molecule inhibitor of IL-17A has made it to the pharmaceutical market [2].

Here, we report the computer-aided development of small-molecule inhibitors of IL-17A. Biophysical assays of these compounds revealed the outstandingly high affinity of some of the compounds synthesized. Moreover, we could unambiguously define the binding site by a cocrystal structure of one of our small molecule binding to IL17A.

References


Acknowledgements:
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One of the most important problems of pharmaceutical and supramolecular chemistry is design of new, non-toxic macrocyclic structures to stabilize and prolong the action of proteins with antitumor activity. New generations of water-soluble amphiphilic nanocontainers (capsules) can act as encapsulation systems. The use of amphiphilic macrocycles that promote the formation of self-associates will contribute to the encapsulation, compaction, and metered release of the drug. This will significantly reduce drug toxicity, as well as lead to a prolonged action of a therapeutic agent to slow its release.

Functionalization of structure of macrocycles by terpenoid fragments will increase biocompatibility and increase the efficiency of interaction with tumor cells. The structure of the obtained compounds was characterized by a complex of physical methods – $^1$H, $^{13}$C, NMR and IR spectroscopy, mass spectrometry, individuality was confirmed by TLC. The ability of the compounds to form self-associates was studied by the DLS method. It was shown that the compounds obtained in water form nanoscale aggregates.

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A NEW STEREOSELECTIVE SYNTHESIS OF BIOLOGICALLY ACTIVE NATURAL 5Z,9Z,13Z-EICOSATRIENIOIC ACID

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Unsaturated carboxylic acids attract chemists’ and pharmacologists’ attention owing to the broad spectrum of biological properties they exhibit. For example, it was found that di-, tri-, and polyenoic acids containing a 1Z,5Z-diene moiety in the molecule, which are isolated in micro quantities from sea sponges and gymnosperm seeds, exhibit antiviral, antimicrobial, antitumor, antimalarial, and antituberculosis activities, and are also used as biologically active additives to reduce appetite in the treatment of obesity [1-3].

We developed an original procedure for preparation of natural 5Z,9Z,13Z-eicosatrienoic acid (20:3) (5) using the new reaction that we developed, namely, Ti-catalyzed cross-cyclomagnesiation of oxygenated and aliphatic 1,2-dienes induced by Grignard reagents, in the key stage of the synthesis.

Scheme 1.

Using flow cytometry, the new molecules were shown for the first time to be efficient apoptosis inducers in the HeLa, U937, Jurkat, and K562 cell cultures and to have dose-dependent effect on the S and G2 phases of the cell cycle.

References

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SELECTIVE MULTICOMPONENT APPROACH TO THE NEW 5-(4-HYDROXY-6-METHYL-2-OXO-2H-PYRAN-3-YL)-CHROMENO[2,3-B]-PYRIDINE SCAFFOLD

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Cyano-functionalized chromeno[2,3-b]pyridines inhibit mitogen-activated protein kinase-activated protein kinase 2 (MK-2) and suppress the expression of TNFα in U937 cells [1], and also increase the level of phosphorylated cofillin in HCA2 cells, making chromeno[2,3-b]pyridines possible therapeutic option in the treatment of Werner syndrome [2].

In the present study we found multicomponent synthesis of 5-C substituted chromeno[2,3-b]pyridines from salicylaldehydes 1a-i, 2-aminoprop-1-ene-1,1,3-tricarbonitrile and 4-hydroxy-6-methyl-2H-pyran-2-one (Fig. 1). In small amount pyridine–ethanol catalyst/solvent system chromeno[2,3-b]pyridines 2a-i was obtained in 45-85% yields (4h, reflux).

Figure 1. Multicomponent assembling of salicylaldehydes 1a–i, 2-aminoprop-1-ene-1,1,3-tricarbonitrile, and 4-hydroxy-6-methyl-2H-pyran-2-one into chromeno[2,3-b]pyridines 2a–i.

This new facile and efficient procedure found by us utilizes simple equipment; it is easily carried out, final compounds do not require additional purification and isolation step consists only from filtration followed by washing with a small amount of ethanol.

References

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SYNTHESIS OF 2-AMINO-6-METHYLPYRIMIDIN-4(3H)-THION DERIVATIVES AND THEIR PLANT GROWTH STIMULANT ACTIVITY

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The pyrimidine derivatives exhibit a wide diversity of biological activity. The pyrimidine nucleus is a part of natural compounds – nucleic acids, vitamins, strong poisons (tetrodotoxin), coenzymes, as well as a number of medicines (barbiturates, antitumor agents, pyrimidine sulfamides, antibiotics) [1]. A series of pesticides that are widely used in agriculture have been synthesized on the basis of pyrimidine [2]. At the same time, judging by the literature data, compounds with a combination of the pyrimidine ring with other pharmacophor heterocycles, in particular, with azoles and azines, have been poorly studied. The purpose of this work was to develop accessible and effective methods for the synthesis of novel pyrimidine derivatives, as well as compounds with combination of pyrimidine withazole and azine rings in the molecule and study their biological activity in terms of searching for new environmentally friendly pesticides or plant growth regulators.

A large number of new compounds were synthesized by the functionalization of 2-amino-6-methylpyrimidine-4(3H)-thion at the expense of 2-amino group and the exocyclic sulfur atom of the pyrimidine cycle.

![Chemical structures](image)

All synthesized compounds demonstrated a stimulating effect on plant growth. The substances that in the experiment showed the activity higher than 80% (compared to heteroauxin) were selected for additional study and further field trials.

References
PHOSPHORYLATION OF 2-THIOPYRIMIDINE DERIVATIVES

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As the object of the study, we chose compounds of a number of 2-thiopyrimidines, since representatives of this class are well known as biologically active compounds. The initial pyrimidines were obtained by us in the course of a three-component one-pot reaction (Figure 1):

![Figure 1. Synthesis of 2-thiopyrimidine derivatives.](image1)

We found that in the course of further functionalization of the obtained 2-thiopyrimidines with chloroethynephosphonate (Figure 2), the corresponding 3-phosphorylated thiazolopyrimidines are formed as final products. The formation of the final phosphonates proceeds with high chemo- and regioselectivity with high yields. The structure of the obtained products of bicyclic structure was established by \(^1\)H, \(^{13}\)C, \(^{31}\)P nucleus NMR spectroscopy, and also proved by X-ray structural analysis.

![Figure 2. Reaction of chloroethynephosphonates with obtained 2-thiopyrimidines.](image2)

Acknowledgements. This work was supported by Ministry of Education (project No 4.5554.2017/8.9) with using the resources of Engineering Centre of SPbSIT (TU). The reported study was funded by RFBR according to the research project № 18-33-00430.
ZINC TRIFLATE IS A CATALYST FOR THE SYNTHESIS OF NEW AMINO-IMIDAZOLES
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Aminoimidazoles have a remarkably broad utility in medicinal chemistry: anti-inflammatory, antiviral, antimicrobial, anesthetics and can be used as antidepressants and analgesics. Recent new drug developments from imidazole derivatives show better effects and less toxicity. Therefore, the search for new biologically active heterocyclic analogs of imidazole is an important task in the field of medical chemistry [1].

The reaction of the synthesis of imidazole derivatives consists in the aminating of propargylamides and their cyclization catalyzed by zinc triflate [2]. We obtained compounds with various aromatic and aliphatic substituents both in the amine and imidazole fragments (Fig. 1).

![Figure 1. Reaction.](image)

In order to minimize the imidazolidine derivatives formed during the reaction, we carried out a selection of the catalyst, as well as the ratio of the reactants. The highest yield was achieved with a ratio of urea to amine of 3:1 and using zinc triflate as a catalyst. On aromatic ureas, ZnCl also showed a good yield, but the desired product was not formed with aliphatic ureas using ZnCl. The structures of the synthesized compounds were confirmed using $^1$H, $^{13}$C NMR spectroscopy and HRMS.

References
In this study we have developed a practically convenient, three-component approach to $N$-hydroxytetrahydroisoquinolonic (THIQ) acids via a variant of the Castagnoli-Cushman reaction involving in situ cyclodehydration of homophthalic acid with concomitant formation of an oxime in refluxing toluene with azeotropic removal of water. Using hydroxylamine acetate or $O$-benzylhydroxylamine in lieu of the hydroxylamine hydrochloride typically employed to prepare oximes was key to the success of the reaction.

For prepared $N$-benzyloxy THIQ acids decarboxylation and debenzylation reactions were additionally investigated. Five selected cyclic hydroxamic acid compounds produced in the course of this study have been profiled and confirmed as ligands for Fe$^{3+}$. Thus, a new, practically simple and flexible approach to potential iron overload disease treatments or analogs of bacterial siderophores for antibiotic delivery has been validated[1].

References


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META-FUNCTIONALIZATION OF NAPHTALENE PROTON SPONGE VIA THE USE OF SCHLOSSER’S SUPERBASE

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Lithiation of 1,8-bis(dimethylamino)naphthalene (DMAN) with Schlosser’s superbase (n-BuLi–t-BuOK) in the presence of TMEDA in hexane was examined (Scheme 1). It has been shown that, compared with previously studied n-BuLi–TMEDA or t-BuLi–TMEDA mixtures, this reagent provides much more selective meta-lithiation. A variety of 3-substituted and 3,6-disubstituted derivatives of DMAN has been prepared in a good to reasonable yield after quenching the reaction mass with different electrophiles. A possibility of further functionalization of thus introduced meta-substituents to synthesize more complex 3-substituted derivatives of DMAN is also demonstrated.

Scheme 1.

The influence of bulky trimethylsilyl substituent on the selectivity of metalation of dimethylaniline and anisole is studied. Neighboring SiMe₃ group forces dimethylamino and methoxy groups to occupy conformation with unshared electron pair turned towards silicon atom. This forced conformation prevents NMe₂ groups from providing DOM-effect, facilitating meta metallation, while OMe group demonstrates more rotation freedom supporting ortho-metallation.

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Octahedral rhenium cluster complexes $[\{\text{Re}_6\text{Q}_8\}\text{L}_6]^n$ ($\text{Q} = \text{S, Se, L} = \text{organic or inorganic ligand}$) possess promising properties such as X-ray contrast due to high local concentration of heavy elements, luminescence in NIR region and redox activity. Usually such complexes are not soluble in water or not stable in water solution. One of known water-soluble rhenium cluster complexes are compounds containing 1H-benzotriazole as a terminal ligand. Moreover, these clusters are stable in water solution at physiological pH, which in combination with physicochemical properties is promising for biomedical applications. Thus, it was suggested to obtain new octahedral rhenium cluster complexes with typical triazoles, namely 1,2,3-triazole (1,2,3-trzH) and 1,2,4-triazole (1,2,4-trzH) and investigate their physicochemical and biological properties.

In this work, we studied the interaction of the hydroxide octahedral rhenium cluster complexes $\text{K}_4[\{\text{Re}_6\text{Q}_8\}(\text{OH})_6]$ ($\text{Q} = \text{S, Se}$) with 1,2,3-triazole and 1,2,4-triazole. Reactions were carried out in the melt of pro-ligands in sealed glass tube at 200 ºC. During this study, anionic cluster complexes $[\{\text{Re}_6\text{Q}_8\}(1,2,3\text{-trz})_6]^+$ and $[\{\text{Re}_6\text{Q}_8\}(1,2,4\text{-trz})_6]^+$ were obtained, which are easily soluble in water and in many organic solvents. All obtained compounds were investigated by a set of physicochemical methods ( multinuclear NMR- and IR-spectroscopy, elemental analysis, mass-spectrometry, etc.). Furthermore, their luminescence and redox properties were studied, as well as biological effects using MTT test, flow cytometry and confocal microscopy.

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UNSMMETRICAL BACTERIOCHLORINS WITH PERFLUOROCARBON SUBSTITUTEnts: SYNTHESIS AND PROPERTIES

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Bacteriochlorins belongs to the novel generation photosensitizers (PS) for photodynamic therapy of cancer with effective NIR absorption (range 700-800 nm). The application of bacteriochlorins with fluorocarbon emulsions – delivery system of oxygen and PS - requires their modification to impart solubility in the fluorocarbon phase. We used the approach previously developed on the example of porphyrin and chlorin structures [1, 2].

![Bacteriochlorin synthesis](image)

Figure 1. Bacteriochlorin synthesis
In the report will be considered the design of fluorinated bacteriochlorins, its synthesis and properties.

References

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PREPARATION AND CATALYTIC ACTIVITY OF RHODIUM (III) HYDROXOCOMPLEXES FOR REARRANGEMENT OF ALDOXIMES TO PRIMARY AMIDES

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Rhodium (III) hydroxocomplexes prepared by treating of the rhodium chlorocomplexes by alkali water solution exhibits catalytic activity in a number of organic and inorganic reactions. The polycondensation of the hydroxocomplexes which accelerates with the increasing of temperature, rhodium concentration and decreasing of alkali concentration may influence the catalytic activity. The technique allowing the reproducible production of various mixtures of rhodium (III) hydroxocomplexes is developed and used for catalysts preparation. For this, a solution of K\textsubscript{3}RhCl\textsubscript{6} (0.005M) in NaOH (2M) is kept at room temperature for 20 min to produce exclusively [Rh(OH)\textsubscript{6}]\textsuperscript{3-} ions which undergoes a polycondensation reaction at 60°C for 30 min giving a mixture of hydroxocomplexes with a number of rhodium atoms from 1 to 4.

The deposition of complexes to the surface of Al\textsubscript{2}O\textsubscript{3} is carried out by dropwise addition of Ca(NO\textsubscript{3})\textsubscript{2} which saves the distribution of species obtained at the previous step. The catalysts consisting of highly dispersed Ca\textsubscript{x}[Rh(OH)\textsubscript{y}] salt mixture deposited from two abovementioned solutions were tested for activity in benzaldoxime to benzamide rearrangement at 140°C in water. The experiments show that polynuclear species are at least 3 times more active than [Rh(OH)\textsubscript{6}]\textsuperscript{3-} but they are degrade in progress of the reaction.
SYNTHESIS AND CYTOTOXIC ACTIVITY OF Sn (IV) CARBOXYLATES BASED ON CHOLIC ACID


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Organotin compounds demonstrate wide range of their biological activity including anticancer properties.

The aim of the work is the synthesis of Sn (IV) carboxylates based on bile acids and the study of their cytotoxic activity. Organotin carboxylates of the general formula $\text{R}_3\text{Sn(LCOO)}$ and $\text{R}_2\text{Sn(LCOO)}_2$ were synthesized (where $\text{R} = \text{Me, Ph}$; $\text{L}$ is fragments of cholic ($\text{L}_1$), deoxycholic ($\text{L}_2$), lithocholic acid ($\text{L}_3$)). Compounds were characterized by $^1\text{H}$ and $^{13}\text{C}$ NMR and elemental analyzes. Cytotoxicity activity in vitro of the compounds was studied on A549, WI38, MCF-7, SW480, and HCT-116 cancer cell lines in the MTT test. It was shown that all compounds possess high cytotoxicity, $\text{IC}_{50}$ values in the range of 0.2 - 8 $\mu$M were found. The toxicity of $\text{R}_2\text{Sn(L}_2\text{COO)}_2$ is one order lower than that of $\text{R}_3\text{Sn(L}_2\text{COO)}$ (1.3 and 0.3 $\mu$M, respectively). The study of the cell cycle and by flow cytometry showed that the compounds block the cell cycle in the G2/M phase. Analysis of the apoptotic profile showed that diphenyltin derivatives induce apoptosis more intensively than triphenyl derivatives (the number of apoptotic cells was 25% and 21%, respectively) (Fig. 1).

Fig. 1. Apoptotic profile of cancer cells HCT 116 after treatment with $\text{R}_2\text{Sn(L}_2\text{COO)}_2$ (a) and $\text{R}_3\text{Sn(L}_2\text{COO)}$ (b) at 2 and 0.4 $\mu$M respectively after 24 h.

References


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TWO-PHOTON FLUORESCENCE ANISOTROPY INVESTIGATION OF TRYPTOPHAN DISSOLVED IN SOLUTIONS WITH DIFFERENT VISCOSITY

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Tryptophan is an amino acid naturally existing in proteins which are now widely used as a fluorescent probe for investigation of proteins in solutions and cells [1]. We present an experimental study of two-photon excited polarized fluorescence in tryptophan in water-propylene glycol solutions with different viscosity and polarity. The fluorescence was excited within a two-photon absorption scheme. The excitation wavelength was varied in the range of 385–510 nm and the fluorescence was detected by a time-correlated single photon counting (TCSP) system by two independent detectors. Fluorescence decay signals were described by a bi-exponential model [1-2]. The fluorescence decay parameters: fluorescence lifetimes \(\tau_1, \tau_2\), weight coefficients, rotational correlation time \(\tau_{rot}\), anisotropy parameter \(r_0\), and total intensity were extracted from experimental data by means of the computer code based on Python 3. The results obtained demonstrate the dependence of these parameters on the viscosity of the solvents and wavelength of the absorbed radiation.

References
ZrO$_2$/NiO: A RECYCLABLE CATALYST FOR 4-COMPONENT FUSION TO PRODUCE NOVEL 1,4-DIHYDROPYRIDINES AND THE MECHANISTIC STUDY

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Among the heterocyclic compounds, N-heterocyclics scaffolds in general acquired more prominence in the medicinal and pharmaceutical chemistry [1]. In particular, 1,4-dihydropyridines (1,4-DHPs) are the privileged scaffolds of biological importance[2]. In this we are presenting Nickle oxide loaded on zirconia (NiO/ZrO$_2$) as an expedient catalyst for the synthesis of ten novel unsymmetrical 1,4-dihydropyridine derivatives at room temperature is studied. The Lewis acidic nature of the catalyst proved excellent for the one-pot four-component reaction with excellent yields of 93-98% in 20 minutes. Mechanistic studies show that that enamine and imine are the two possible pathways for the formation of 1,4-dihydropyridines with high selectivity. Catalyst reusability up to 6 cycles and reaction at room temperature (RT) makes this protocol green and economical. The single crystal structure of 5-methyle derivative observed as a single colorless block-shaped crystals, corresponds to a triclinic cell. This is the first report of using NiO/ZrO$_2$ as a catalyst in the multicomponent fusion in one-pot reaction system.

![Synthesis of novel 1,4 dihydropyridines.](image)

Figure 1. Synthesis of novel 1,4 dihydropyridines.

References

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In the past two decades, the issue of polymorphism has become acute in the drug market. It was shown that solubility and, as a consequence, biological activity largely depend on the polymorphic modification for many substances. In accordance with the rules governing the requirements for the production and use of food and drugs for each medicinal substance should be necessarily contain the information about all the available polymorphs. This makes it all studies on finding polymorphic modifications, deciphering their structure, studying thermal stability, as well as possible transformations during storage and at different stages of the processing chain very important.

Polymorphic modifications can be obtained by different ways: by changing the conditions of crystallization or storage, by varying temperature and pressure, by various solid-phase transformations – phase transitions and chemical reactions, and also by mechanical action. Thus, we can conclude that the problem of controlling the polymorphism of medicinal substances is one of the most popular areas of modern pharmaceutical science. It should be noted that most of the works describing the polymorphism of drugs is devoted to the identification of various polymorphic forms, their mutual transitions and biological activity. At the same time, the development of methods for stabilizing certain thermodynamically unstable modifications is practically neglected, which makes this work relevant.

Thus, this work is devoted to studying the influence of the method of preparation of polymorphic modifications on the kinetic parameters of polymorphic transitions. In the present work, metastable β-glycine polymorph was obtained by a method of rapid removal of the solvent, as well as by crystallization with various co-crystallizators, such as glucose, sodium chloride and potassium iodide. Polymorphic phases and their time stability were investigated by X-ray powder diffractometry. It was found that β-glycine obtained by co-crystallization with glucose is more stable form than simple β-glycine. It was shown that β-form of glycine has bigger dissolution rate than α-form by dissolution kinetics studies.

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1.2-ZWITTERIONIC REACTIVITY OF DONOR-ACCEPTOR CYCLOPROPANES IN REACTIONS WITH ACETYLENES


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Donor-acceptor cyclopropanes 1 (DACs) are a broad class of substituted three-membered carbocycles. They are known for their capability to undergo small ring opening to act as 1,3-zwitterionic synthons. Our group developed a quiet different type of reactivity of DAC – the use of 2-arylcyclopropane-1,1-dicarboxylates (ACDC, 1) as sources for generation of 1,2-zwitterions 2 in the presence of GaCl₃ [1].

Now we demonstrate a new approach for using ACDC 1 in reactions with acetylenes in the presence of GaX₃. We have been developed a new strategy for assembly of substituted (3-haloallyl)malonates 3, dihydronaphtalenes 4 and lactones 5 [2]. As the result all discovered processes proceed with a high regio- and diastereoselectivity and good yields of products obtained. Reaction conditions and features of these processes will be discussed.

References

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1,2-ZWITTERIONIC REACTIVITY OF DONOR-ACCEPTOR CYCLOPROPANES IN REACTIONS WITH NITRONES, AZIDES AND DIAZOCOMPOUNDS


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Donor-acceptor cyclopropanes (DACs) are remarkable building blocks widely used in contemporary organic synthesis. Most commonly, DACs are used as sources of 1,3-zwitterion intermediates, which are then used in reactions with a broad range of substrates, including 1,3-dipoles, for example organic azides [1]. Recently, we discovered a new type of reactivity of DACs 1, which consists in generating 1,2-zwitterionic intermediates 2 under the action of Lewis acids, in particular, gallium halides [2]. It was interesting to study the reactions of these intermediates with 1,3-dipoles, in particular with nitrones, azides and diazocompounds.

It was found the interaction of 1,2-zwitterion with benzylazide and methyldiazoacetate lead to products 3 and 5 respectively. Nitrones does not react with compound 2, however, it participates as a ligand in the dimerization of zwitterionic intermediates giving unknown dimer 4a. As the result all discovered processes proceed with a good yields of products obtained. Reaction conditions and features of these processes will be discussed.


This work was supported by the Russian Foundation for Basic Research (project No 18-33-01000).
Adamantylcontaining compounds with cumulated double bonds, such as isocyanates, isothiocyanates and isoselenocyanates, are frequently used in the synthesis of biologically active compounds. We developed new and enhanced known methods for the preparation of adamantylcontaining heterocumulenes of the following structure A:

One-pot method for the preparation of isocyanates from carbon acids based on the Curtius reaction was developed, which allows to increase yield and decrease the potential explosiveness of the process. New one-stage syntheses of adamantylcontaining isocyanates and isothiocyanates based on the reaction with 1,3-dehydroadamantane were introduced [1]. New reaction of adamantylcontaining amines with phenylisothiocyanate leading to corresponding adamantylcontaining isothiocyanates was discovered [2]. New 1,3-disubstituted ureas and diureas B – potent soluble epoxide hydrolase (sEH, E.C. 3.3.2.10) inhibitors were synthesized based on heterocumulenes A. The effect of substituents in adamantyl moiety on the properties on inhibitors was investigated. Inhibitory activity of the most potent compounds reaches IC$_{50}$ = 0.4 nM [3]. For the most potent inhibitors the affinity constants and microsomal stability were evaluated.

References

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The Castagnoli-Cushman reaction (CCR) is a reaction of cyclic anhydrides of dicarboxylic acids with imines 1 (fig. 1). At this moment succinic (2), glutaric (3) and homophthalic (4, HPA) anhydrides are the most popular substrates for CCR. HPA is the most reactive in CCR from all known anhydrides.

We have developed a group of new azole-annulated anhydrides as substrates for CCR (fig. 2). It was suggested to name this group «azole-including» anhydrides [1]. Results of the CCR with anhydrides 8-11 explained the influence of electronic effects of azole heterocycles to reactivity of anhydrides [1,2]. For «indole-including» anhydrides 11-13 the influence of the position of the electron withdrawing substituents in indole ring to reactivity of anhydrides was shown [3].

References

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DEVELOPMENT OF METHODS FOR THE PREPARATION OF NEW ELECTROCHROMIC COMPOUNDS BASED ON CYCLOADDITION OF 1,2-BIS (4-PYRIDINYL) ETHYLENE AND 1,2-BIS (4-PYRIDINYL) ACETYLENE DERIVATIVES TO 1,3-DIPOLES


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A new class of electrochromic compounds 9 containing conjugated pyridinium fragments was synthesized by 1,3-dipolar cycloaddition. Their electrochemical characteristics were studied by CVA, electrochromic cells were made, and their spectral properties were studied from 0 to 2 V. All compounds colored from colorless to brown at 1.5 V.

Figure 1. Synthesis of target compounds, pictures of electrochromic device, CVA curve of 9c.

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The development of new chemosensors is an actual problem, since the rapid identification of organic structures of various structures is an urgent task of modern organic chemistry.

We have proposed an approach to the synthesis of novel polytargeted chemosensor 1 based on 4-(trifluoromethyl)pyridine, containing an acceptor tricyanobutadiene fragment (TCPy). These structures were obtained by trifluoropentane-2,4-dione heterocyclization with dimer of malononitrile. Synthesized TCPy 1 can form salts with various organic bases. As a result, compounds 2 are obtained, possessing solid-state fluorescence. Photoluminiscence maximum of salts can be varied by the used organic base. This can be observed using toluidine isomers as example (Fig.1).

Figure 1. Synthesis, and solid state fluorescence of toluidine salts of TCPy.

It has been found that the application of TCPy 1 as chemosensors is quite wide, since these structures form fluorescent salts with one-, two-, three-, and four-substituted amines, with various biomolecules, as well as with metals.

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1,3,4-oxadiazoles based on arylidenesulfonamides: the new class of potent and isoform-selective monoamine oxidase inhibitors


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Good potency inhibitors of human monoamine oxidase (hMAO) isoforms may be useful for the treatment of depression and Parkinson’s disease. The series of 1,3,4-oxadiazole benzenesulfonamides 4 have been synthesized by cyclization of N,N’-diacylhydrazines 3, which consists in the reaction of dehydration [1-2]. Also the compounds 4 were obtained by cyclocondensation of the sulfonyl chlorides 7.

Figure 1. Reaction of synthesis of benzenesulfonamides 4.

The obtained compounds 4 were evaluated as potential inhibitors of hMAO-A and B. The most potent MAO-B inhibitors of these compounds have value IC50 = 0.00272; 0.04841 and 0.07943 μM. These potencies are in the same range as those of reference MAO inhibitors used in the clinic.

References
Pyrrole and indole fragments are an important structural parts of a wide range of natural compounds and biologically active substances. N-Vinylpyrroles are one of the universal types of reactive carriers of the pyrrole moiety. We investigated the reactions of N-vinylpyrroles and indoles with various 1,3-dipoles: nitrones, azomethine imines, nitrileoxides. [1, 2]

It was found that for the considered reactions different pathways are possible, depending on the conditions of conduction and the structure of the initial compounds. This makes it possible to obtain both (3+2)-cycloaddition products, and polycyclic products of formal (3+3)-cycloaddition then Lewis acids are used as catalysts.

References

Acknowledgments. NMR, HRMS and XRD studies were performed at the Saint Petersburg State University Center for Magnetic Resonance, Center for Chemical analysis and materials research and X-Ray Diffraction Center, respectively.
EXPLORATION OF S_N-F-APPROACH TOWARD FUNCTIONALIZED NITROXIDES AND NITRONYL NITROXIDES

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An actively using of conjugated nitroxides in the molecular design of magnets, spin labels, and redox active materials stimulates the development of ways of their preparing. In this work we demonstrated the possibility of obtaining functionalized nitronyl nitroxides by regiospecific substitution of fluorine in polyfluorinated arenes by a 4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl lithium derivative [1–3].

It was shown that the interaction of tert-BuNH₂ with perfluoroarenes and the subsequent oxidation of the resulting arylamines by m-CPBA leads to formation of new nitroxide radicals. The complexation reaction of Cu(hfac)₂ with the synthesized paramagnets gives complexes with ferromagnetically coupled spins.

References

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3-Aza[bicyclo[3.1.0]hexanes] and related nitrogen heterocycles with a cyclopropane moiety are of great importance for organic and medicinal chemistry. As a result, it is not surprising that many efforts have been made to develop new protocols for the synthesis of these heterocycles.

In the past two years, our research group has demonstrated that 1,3-dipolar cycloaddition methodology can be extended to the synthesis of complex spiro[cyclopropa[a]pyrrolizines] and 3-azaspiro[bicyclo[3.1.0]hexanes] [1,2,3].

In this work, we aimed to explore expandability of this method by utilizing ninhydrin-derived azomethine ylides in cyclopropene 1,3-dipolar cycloadditions. Differently substituted cyclopropenes, including unstable substrates, were found to be highly reactive in these reactions affording the corresponding 1,3-dipolar cycloadducts with full regio- and stereoselectivity in impressive yields (up to 96%). The studied reactions are IED-controlled processes in which high regio- and stereoselectivity result from orbital control and second-orbital interactions as it has been disclosed by DFT calculations.

![Figure 1. 1,3-DC reactions of ninhydrin-derived ylides to cyclopropenes.](image)

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Project No 18-33-00464).
Functionalized 2-azabuta-1,3-dienes are attractive organic substrates for the synthesis of nitrogen-containing heterocycles (1,3- and 1,4-oxazine, dihydropyrazine and dihydropyrimidine derivatives), which can be formed by 1,4-electrocyclization or various 1,6-electrocyclizations involving azabutadiene fragment [1]. To study 1,6-electrocyclization of azabutadienes with participation of C=N bond of the aromatic pyridine cycle, we choose 1-(pyridine-2-yl)-2-azabuta-1,3-diene 3, which were supposed to be obtained by Rh(II)-catalyzed reaction of [1,2,3]-triazolo[1,5-a]pyridine derivatives 1 with 2H-azirines 2.

![Reaction scheme](image)

It was found that properties of the 1-(pyridine-2-yl)-2-azabuta-1,3-dienes 3 are very different and depend on its substitution pattern. Some derivatives 3 (R1 = CO2Me) are stable and do not undergo any cyclizations. On the contrary, in the presence of a cyano group in the azabutadiene (R' = CN) or a methyl group (R1 = Me) 1,6-electrocyclization into 4H-pyrido[1,2-a]pyrazines 4 is the main direction of cyclization. In some cases, the 1,6-electrocyclization is reversible (R1 = Ar) (Fig. 1).

References.

Acknowledgements: we gratefully acknowledge the financial support of the Russian Science Foundation (Grant No. 19-73-10090). This research used resources of ‘Magnetic Resonance Research Centre’, ‘Chemical Analysis and Materials Research Centre’, ‘Centre for X-ray Diffraction Studies’ and ‘Chemistry Educational Centre’ of St. Petersburg State University.
SYNTHESIS OF AMIDES OF CARBOXYLIC ACIDS WITH AN IMIDE AND ALICYCLIC FRAGMENTS

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A search for new compounds capable of improving the properties of seeding material, increasing the productivity, and enhancing the resistance of crops to phytopathogens, drought, and cold is currently a topical problem in the optimization of agriculture. It is known that compounds containing an amide fragment possess a high biological activity and constitute a wide spectrum of fungicidal, insecticidal, and herbicidal preparations [1, 2]. However, at present, there are problems associated with the stable resistance of pathogens to available preparations, large amounts of wastes during their production, and, as a consequence, harmful effects on the environment. Thus, the search for, and the creation of, compounds free from these shortcomings is a timely task in the chemistry of pesticides [3]. Some compounds containing an imide fragment that are known to possess biological activity and low cytotoxicity have found application as growth-regulating reagents [4].

Our work is devoted to the synthesis of amides of carboxylic acids containing an imide and cycloalkenyl fragments. We synthesized several potentially bioactive compounds in which we combined the active structure of an amide with imide and cycloalkenyl fragments.

\[ \text{O} \quad \text{N} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{NH} \quad \text{R} \quad \text{1} \]  

1. DMSO, K\(_2\)CO\(_3\), amino acids
2. DMSO, K\(_2\)CO\(_3\), amine

\( \text{R} = \text{H, iPr, iBu, -CH}_2\text{Ph} \)

\( \text{R}^1 = \text{morpholine, cyclohexylamine, aromatic amine} \)

Figure 1. Reaction

\( N\)-Substituted imides of alicyclic dicarboxylic acids were obtained in the in situ reaction of the corresponding amines with the products of the reaction of anhydrides (I) and (II) with natural amino acids in the equimolar ratio in the presence of a 1% solution of K2CO3 in DMSO. This method makes it possible
to obtain target compounds with high yields over a short time without intermediate isolation and with the use of readily available reagents.

References
Oxido complexes containing the $V^{IV}=O$ and $V^{V}=O$ moieties are ubiquitous in the coordination chemistry of vanadium. They demonstrate efficient catalytic oxidase reactivity in various transformations. [1-2].

This work is devoted to the study of reactions of $VX_3$ ($X = Cl, Br$) or $VCl_3$(thf)$_3$ with diimine ligands, such as 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen), 4,4'-di-tert-butyl-2,2'-dipyridyl (dbbpy), bis(imino)acenaphthene (dpp-bian) in acetonitrile in air, which lead to the formation of molecular complexes $[VOCl_2(dpp-bian)]$ (1), $[VOCl_2(H_2O)(dbbpy)]$ (2), and polymeric compounds $[VOX_2(L_{NN})]$ ($X = Cl, Br; L_{NN} = bpy, phen$) (3). Magnetic and redox properties were investigated for the obtained compounds. Complexes 1-3 exhibit high catalytic activity in alkane oxidation reactions, and complex 2 catalyzes cyclooctene oxidation [1-2].

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-03-00155).
A novel class of heterogeneous catalysts with an uniform distribution of Brønsted acidic centers was easily created by simple mixing of aqueous solutions of the tetrahydrochlorate of tetrakis(4-aminophenyl)methane and disodium 2,6-naphthalenedisulfonate acid salt in a ratio of 1:2, respectively (Figure 1). The structure of the formed salt was established by X-ray diffraction analysis.

According to the local X-ray spectral analysis the distribution of functional groups within the samples of CAHOC is uniform. CAHOC catalyzed epoxide ring opening reactions with MeOH, t-BuOH, H2O and Diels-Alder reactions (Scheme 3). In all the reactions CAHOC functioned as a heterogeneous catalyst and could be easily recovered from the reaction mixture and reused several times.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-53-05004 Арм_a).
ISOXAZOLE STRATEGY FOR THE SYNTHESIS OF UNSYMMETRICAL 2,2''-BI- AND 2,2':6',2''-TERPYRIDINE LIGANDS

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One-pot Fe(II)/Au(I)-catalyzed protocol for the 4-propargylisoxazoles to methyl nicotinates derivatives transformation have been developed in our research group few years ago [1]. Further extension of this approach yielding symmetrical and unsymmetrical 2,2'-bipyridines have been reported by us recently [2]; later bipyridines turned out to be quite interesting as the ligands for luminescent complexes based on transition metals.

Little is known about properties of the same complexes of terpyridines, but in terms of chemical logic and minor accumulated evidences, one could suppose these substances to possess higher QY and other interesting optical properties. Here we wish to present the latest results of our investigation giving a way to titled compounds.

![Scheme of proposed approaches to 2,2'-bi/2,2':6',2''-terpyridines synthesis](image)

Figure 1. Schematic representation of proposed approaches to 2,2'-bi/2,2':6',2''-terpyridines synthesis

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-33-00182).
Carbometallation is an efficient method of regio- and stereocontrolled synthesis of olefins. This work demonstrates that carbozincation of \(N,N,N',N'\)-tetramethyldeca-2,8-diyne-1,10-diamine results in the selective formation of a bis-alkyldiene cyclohexane derivative. Previously, we have shown that Zr-catalyzed cycloalumination of \(\alpha,\omega\)-bis(aminomethyl)alkadiynes results in the selective formation of a bis-alkyldiene cyclohexane derivative [1]. Similarly, the reaction of \(N,N,N',N'\)-tetramethyldeca-2,8-diyne-1,10-diamine with 2.5 equiv. of \(\text{Et}_2\text{Zn}\) in the presence of 10 mol. % \(\text{Ti(O-iPr)}_4\) and 20 mol. % \(\text{EtMgBr}\) carried out in diethyl ether at room temperature for 18 h and followed by deuterolysis or hydrolysis affords bis-alkyldiene cyclohexane 1 and 2 derivative (Figure 1).

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-73-20128) and Russian Foundation for Basic Research (project No 18-03-00817).
UNEXPECTED POLYMORPHIC BEHAVIOR OF FOUR RACEMIC 3-PYRROLIN-2-ONE DERIVATIVES

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Polymorphism of organic, especially chiral, compounds is of great interest and value for modern crystallography, physical chemistry, process, and patent law. Since the free energy of different polymorphs of the same substance is different, all their physicochemical properties are different, that is, melting point, solubility, stability, hygroscopicity, pharmacodynamic and pharmacokinetic properties, and so on. Therefore, bioactive substances are particular attractive from the point of view of guided polymorph search. In this abstract, we reported crystallization and heterogeneous equilibria and transitions of four racemic N-substituted 4-arylsulfanyl-3-chloro-5-hydroxy-3-pyrroline-2-ones consisting an unsaturated γ-lactam ring that is an important pharmacophore group. As a result, in this series of compounds, a unique “conglomerate-conglomerate” polymorphic pair and a pair of packing polymorphs were found. All individual crystalline phases were studied by means of single crystal and powder X-ray diffractions. Their phase behavior was carefully investigated using heat flux differential scanning calorimetry, temperature-resolved solid-state vibration spectroscopy and hot-stage microscopy.

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SYNTHESIS OF N-PYRIDYLUREA COPPER (II) COMPLEXES

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Complexes of copper (II) are widely used substances, especially in medicine as antimicrobial, antiviral, anti-inflammatory, as well as antitumor agents. Moreover, they are catalysts for several organic reactions. One of frequently used ligand motif in such complexes is pyridine and its substituted analogues. Our group has recently developed a mild method of $N$-pyridinyl substituted ureas synthesis, using pyridine-$N$-oxides and dialkylcyanamides [1]. These substances can be used as bidentate ligands for copper (II) complexes. We have synthesized several kinds of such complexes depending from CuCl$_2$ amount: i) square planar, with only one urea ligand; ii) octahedral, with two urea ligands and two chlorides; iii) square pyramidal cationic with two urea ligands and one chloride. They were characterized by IR spectroscopy and HRMS as well as single crystal X-ray diffraction data.

![Synthesis of N-pyridylureas and their complexing.](image)

Figure 1. Preparation of $N$-pyridylureas and they complexing.

References

Acknowledgements. Physicochemical studies were performed at the Research park of Saint Petersburg State University.
Organic boronic acids have wide application in C,C and C,X- cross-coupling reactions and in medicinal chemistry [1]. However, many of them have limited stability, which complicates their usage in organic synthesis. Here, we have developed novel three-component condensation reaction between boronic acids, tris-oximes 1 and primary halides under mild conditions, leading to ate complexes 2. This is very unusual process in the chemistry of oximes, which rarely undergo cyclotrimerization reaction (Scheme). Heterocage complexes 2 have thermal stability up to 250°C, they are resistant to air-moisture and do not undergo hydrolysis in neutral and alkaline media. Thus, boradamantanes 2 may be considered as protective groups for unstable boronic acids.

Furthermore, the developed boronate-triol condensation was efficiently used in the design of fluorophore-labeled natural molecules (peptides, steroids), supramolecular assemblies, modified polymers, boronic acid scavengers, solid-supported organocatalysts, and biodegradable COF-like materials [2-3].

References

Acknowledgements. This work was supported by RFBR (Grant № 18-33-00647).
Highly functionalized pyrroles have found various applications in organic synthesis, pharmaceutics and material science. Last year, highly substituted β-hydroxypyrroles have unexpectedly become very accessible compounds due to the new method for their preparation that appeared [1]. However, chemistry of these compounds remains poorly studied, and their synthetic potential is not clear.

In the present work we report three highly selective transformations of synthetically accessible β-hydroxylated pyrrole-3-carboxylates 1 and pyrrole-2,4-dicarboxylates 2, which proceed under mild conditions to afford high yields new pyrrolin-3-one or pyrrole derivatives in high yields. Thus, a variety of pyrrol-3-yl sulfonates 3 and 2-aminopyrrolin-3-ones 4 were prepared using appropriate sulfonylating agent and “amine/halogenation agent” mixture respectively. The base-mediated reaction of pyrroles 1,2 with triflyl chloride provides the oxidative homocoupling products, bipyrrolinones 5. The conditions which enable the control of the diastereoselectivity of the reaction in favor of one or the other of the two isomers were found. The mechanism of this new reaction is discussed.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project № 17-13-01078). This research used resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies, and Chemistry Educational Centre of the Research Park of St. Petersburg State University.
The tandem Ugi/Diels-Alder reaction is one of a myriad of post-condensational modifications of the classic Ugi reaction. First reported in 1999, the UDA reaction provides a simple route to complex bridged tricyclic products [1]. In the present study we expanded the scope of the UDA methodology by incorporation of the dienophile in the amine and not in the acid counterpart. These UDA reactions proceeded smoothly to provide compounds 1 as nearly equimolar (the diastereomeric ratio being 1:<2) mixtures in good combined yields. These compounds can be involved in further modifications such as dehydrative aromatization to provide isoindolines 2 or intramolecular alkylation [2] to provide fused piperazinediones 3. These reactions are currently under investigation in our laboratories.

References

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Ru(II)-ARENE OXALATE COMPLEXES WITH BEXAROTENE AND LOMIDAMINE LIGANDS

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A significant sector of the anticancer drugs market is occupied by platinum-based compounds — cisplatin and its analogues. Ruthenium compounds, as the most promising alternative to platinum complexes, have a number of advances over classical platinum drugs, such as reduced general toxicity and different major targets. Ru(II)-arene compounds can be modified using biologically active ligand to achieve selective targeting of a cancer cell, selective accumulation or preparation of dual action drug.

The use of anionic chelating ligand, such as oxalate ligand instead of halide, has already been used to overcome solubility and stability problems, in the case of platinum-based compounds and titanocene analogues. For example, replacing two chloride ligands in RAPTA-C compound by oxalate ligand yielding complex that resistant to hydrolysis. This modification has a significant effect on the chemical and biological properties of the compound.

In our study new Ru(II)-arene oxalate compounds with lonidamine and bexarotene moiety were prepared. All complexes were characterized by NMR, ESI-MS and elemental analysis. Compounds were found to be stable in aqua and DMSO-containing solution. Antiproliferative activity of new compounds was investigated against SW480, A549, MCF7, WI-38 and HCT-116 cell lines by means of standard MTT colourimetric assay.

This work was supported by the RSF (project № 19-13-00084).
It has been recently shown that cinnamonitrile (3-phenylpropenenitrile) reacts with various arenes in the superacid CF₃SO₃H (TfOH) forming two types of compounds, 3-aryl-3-phenylpropanenitriles and 3-phenylindanones [1]. We continued this study and showed that substituted 3-arylprenenitriles 1a-d in the same reaction in TfOH gave products of hydroarylation of the double bond C=C, 3,3-diarylpropanenitriles 2, and products of their further cyclization, 3-aryllindanones 3. This reaction may proceed with an intermediate formation of cations A and B. The latter reacts with arenes Ar′H giving rise to species C, hydrolysis of which results nitriles 2. On the other hand, cations C bearing enough nucleophilic aryl rings Ar and Ar′ may undergo cyclization into species D, which form indanones 3 upon hydrolysis. This reaction is a novel method for the synthesis of nitriles 2 and indanones 3.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-001718).
Medium-sized rings have applications in a number of scientific fields, ranging from medicinal chemistry and supramolecular chemistry, to catalysis and nanotechnology. Such ring scaffolds (>8) generally have sufficiently well-defined conformations to bind to target receptors, but are more flexible than their smaller ring analogues. However, their use in these areas is limited by an important factor: large ring systems are very often difficult to make. Traditional end-to-end cyclisation reactions of long linear precursors are typically unpredictable and impractical processes. In contrast, the expansion of smaller ring systems is an attractive alternative way to synthesize such compounds [1].

One of the most promising ways to obtain such compounds is the hydrolytic imidazoline ring expansion (HIRE) methodology [2]. The reactions resulted in the facile formation of a rare medium-sized ring system that has an emerging utility in bioactive compound design. Thus, when primary aminoethanols are used, we get imidazoline-fused diazepines, and using of secondary aminoethanols leads to the formation of 10-membered lactams [3].

![Chemical structure](image)

**Figure 1**

References
The Diels-Alder reaction is widely used in organic synthesis due to its simplicity, reproducibility and high atom economy. The Diels-Alder reaction between furans and alkynes results in the formation of 7-oxabicyclo[2.2.1]heptene scaffolds, which are used as a framework for a wide range of bioactive compounds and intermediates for the synthesis of other types of useful organic substances [1]. The phenomenon of thermodynamic and kinetic control is unique in organic chemistry since it allows altering the direction of the reaction pathway by varying temperature. But on the other hand, the practical application of the kinetic/thermodynamic control is seriously hindered or rendered impossible by the formation of isomers [2].

Herein we report an interesting case of kinetic and thermodynamic control in the Diels-Alder reaction between hexafluorobutine and sulfamides on the basis of bis-(N,N)-furfurylamine. Depending on conditions, products of kinetic (3 a-e) or thermodynamic (4 a-e) control could be obtained in excellent yields.

![Figure 1. Synthesis of “pincer” and “domino” adducts.](image)

Synthesized products represent a promising class of novel potentially bioactive substances and were submitted on biotesting.

References

Funding for this research was provided by the Russian Science Foundation (RSF) (project No. 18-13-00456).
FLUORESCEIN-LOADED SOLID LIPID NANOPARTICLES BASED ON MONOAMINE PILLAR[5]ARENE: SYNTHESIS AND INTERACTION WITH DNA

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Great attention in modern pharmaceutical industry is paid to the problem of their targeted delivery directly to the affected organs, tissues and cells. Among many methods, the development of drug preparations containing lipids. Non-toxic amphiphilic derivatives of macrocyclic compounds have recently been used as lipid analogues. Pillar[n]arenes are new class of paracyclophanes, which have a number of attractive properties, i.e., ease of synthesis and functionalization possibilities. It was shown earlier, that substituted pillar[5]arene can form either host-guest complexes, or supramolecular associates, capable to targeted delivery of drugs.

We have synthesized the amphiphilic pillar[5]arene bearing DETA fragment. The presence of a single tail-group has opened wide opportunities for controlling the supramolecular associates formation in the form of various structures, i.e., pseudotaxanes, supramolecular polymers and SLNs all of which utilize only one type of the macrocycle. Water-insoluble macrocycle 3 forms the SLNs with controlled shape and size, stable in water. The simultaneous synthesis of the SLN with fluorescein made it possible to create the SLN-Flu particles containing luminescent marker, but not able to luminescence themselves. The light amplification is observed only when they interact with the DNA. This makes it possible to use the SLN-Flu as luminescent probes.

Figure 1. Synthetic scheme of the fluorescein-loaded SLN based on monoamine pillar[5]arene 3: i – ethylbromoacetate, K₂CO₃, KI; ii – DETA, EtOH/toluene (1:1); iii – THF/water.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-13-01208).
The present work is focused on the relevant issue of developing various biomedical composite materials. Composite materials were obtained in two stages: 1) using hydroxyapatite (HA) and 2) a pore-forming agent. NaCl forms ceramic frames that are calcined and subsequently soaked in distilled water to obtain porous ceramics. The resulting porous ceramic substrates are impregnated with a solution of poly(lactic-co-glycolic acid) (CLG) in chloroform under ultrasound exposure. The detailed obtainment and identification procedures of these materials have been described in the previous work [1].

<table>
<thead>
<tr>
<th>Sample</th>
<th>K1</th>
<th>K2</th>
<th>K3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content of NaCl at stage 1, wt.%</td>
<td>10</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Content of CLG in composites, wt.%</td>
<td>5</td>
<td>7</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 1. The ratio of components in composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>After impregnation</th>
<th>Before impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K1</td>
<td>K2</td>
</tr>
<tr>
<td>Diffusion coefficient, ( D \cdot 10^{-7} ), m²/s</td>
<td>0.66</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 2. Characteristic of the diffusion of composites and hydroxyapatite

The open porosity was confirmed by an experiment with the Franz diffusion cell. Diffusion coefficients for the composites were calculated both before and after CLG impregnation. After CLG impregnation, the diffusion coefficients decrease by 2-3 times, which correlates with a decrease in porosity during impregnation. Macroporosity of composites increases depending on the content of a pore-forming agent.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project number 17-03-00698\19).
The abuse of antibiotics was lead to appearance of resistant strains of bacteria and search of novel antibacterial agents is important. Mannich bases were found to possess broad spectrum of activities such as antibacterial, antifungal, antiviral and antimalarial [1]. Complexing to metals could increase the pharmacological effects and overcome the toxicity and side effects of these organic ligands [2]. Bismuth(III) compounds have been used for centuries in the treatment of a variety of microbial infections due to their high efficacy and low toxicity. Thus bismuth(III) complexes with Mannich bases present a promising field of search for compounds useful in producing such antibacterial agents.

Mannich bases of sterically hindered phenolic compounds were synthesized according to methods reported previously (Figure 1) [2]. Bi(III) complexes with Mannich bases were prepared and characterized by means of elemental analysis, TG/DTA, FT-IR, UV-Vis, XRD and conductivity measurements. They were isolated from acidic medium where phenolic ligands are protonated, and thus no bonding between the ligand and bismuth(III) was observed. The bismuth(III) ions are coordinated by chloride ions forming complex chloride anions. The charge of this ion is compensated with protonated phenolic ligands (ionic interactions). According to the results of pharmacological screening bismuth(III) complexes demonstrate high antibacterial and antifungal activities and may be considered as potential chemotherapeutic agents.

References
SYNTHESIS AND REACTIVITY OF 5-AMINO-2-METHYL-1,2,4-OXADIAZOLIUM BROMIDES.

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Cationic azaheterocyclic compounds are widely used in the chemistry of materials, as well as in synthetic organic chemistry as precursors of various nitrogen-containing heterocycles and acyclic substances. This work describes a new highly efficient synthetic method of preparation of 5-amino-2-methyl-1,2,4-oxadiazolium salts from aminonitrones and isocyanide dibromides [1]. The reaction proceeds under mild conditions, utilizing simple and easily accessible reagents. In the framework of this study, 16 new 5-amino-2-methyl-1,2,4-oxadiazolium salts were obtained in high yields (65–95%).

The charged character of these heterocyclic systems makes them suitable substrates for reactions with nucleophiles, and 5-cyclohexylamino-2-methyl-3-phenyl-1,2,4-oxadiazolium bromide, taken as a model compound for the reactivity study, reacts rapidly under mild conditions with hydroxylamine, hydrazine, or benzamidine, to give 5-cyclohexylamino-3-phenyl-1,2,4-
oxadiazole (88%), 5-cyclohexylamino-3-phenyl-1,2,4-triazole (95%), and 2-cyclohexylamino-4,6-diphenyl-1,3,5-triazine (64%), respectively. Treatment of the oxadiazonium salt with excess water provides \( N \)-benzoyl-\( N’ \)-cyclohexylurea (95%).

All of these compounds were unknown before, and in this work, they were characterized by HRESI+MS, IR, and \(^1\)H and \(^{13}\)C{\(^1\)H} NMR spectroscopies. In addition, six species were additionally characterized by single-crystal X-ray diffraction (XRD).


This work was financially supported by the Russian Science Foundation (grant 17-73-20004). Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).
SYNTHESIS OF BISULPHONAMIDE STRUCTURES BY DILS-ALDER REACTION ON THE BASIS OF DIAMIN-DERIVATIVES BIAROMATIC COMPOUNDS

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Various structures of sulfonamides had been holding the limelight of synthesis chemistry for a long time. Their structural diversity has led to the expansion of the action’s spectrum of drugs of this class. Recently many new containing two sulfonamide functions drugs have been synthesized. It allowed to increases their biological activity.

Based on the previously developed method for creating a sulfonamide function by Diels-Alder reaction using aniline derivatives, we synthesized compounds containing two sulfonamide fragments, as well as a fused and an isolated biaromatic fragment.

Figure 1. Synthesis of α-naphthylamine based sulfonamides

Figure 2. Synthesis of 1,5-diaminonaphthalene based sulfonamides

Figure 3. Synthesis of 4,4’-ethylenedianiline based sulfonamides

The structure of compounds 5-13 is confirmed by the data of FTIR, NMR. The structure of compound 11 is finally established by XRC.
FORMYLATION OF THIOPHENE FRAGMENTS IN THE SYNTHESIS OF POLYFLUORATED TRIARYLPYRAZOLINES-BASED CHROMOPHORES

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It was previously shown that aldehydes based on polyfluorosubstituted triarylpyrazolines can be used as donor blocks in synthesis of donor-acceptor NLO dyes [1, 2]. In this work, an attempt was made to elongate the polymethine chain of chromophore by including a thiophene fragment. For this purpose, Wittig condensation of aldehyde 1 and thiophene 2 was used for the synthesis of compound 3, which was then subjected to formylation. When the reaction was carried out in BuLi/DMF system the molecule 3 was destroyed. Vilsmeier formylation led to dialdehydes 4 and 5.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-13-10156).
Donor-acceptor organic molecules with conjugated polyene bridge are being investigated because of their nonlinear optical properties due to the charge separation [1].
Previously a range of thiophene-based dyes with dendroid substituents was made [2]. Here we expand that range by the synthesis of such dye with novel dendroid structure (TAFS) and analysis of possible byproducts.

Figure 1. Synthetic route to novel thiophene dye.

Novel nonlinear dye 3 was obtained from corresponding aldehyde 1 by the condensation with TCP and further acylation. The major product of condensation is 4, due to the equilibrium formation of TCP, so the target compounds 2 was isolated with a rather low yield.
Chromophore 3a showed second-order susceptibility of 60 pm/V (polycarbonate film, 20% wt.), $\lambda_{\text{max}}$ 936 nm (CHCl₃).

References
SYNTHESIS OF 2,2'-SPIROBI[INDENE] AND 5,5'-SPIROBI[CYCLOPENTA[B]THIOPHENE] AND THEIR MODIFICATION VIA STILLE REACTIONS

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High-efficient organic light-emitting diodes (OLEDs), organic light-emitting transistors (OLETs) and organic electrically driven lasers require materials combining efficient electroluminescence and high semiconducting properties. However, synthesis of such compounds is challenging since the dense packing that is crucial for improved semiconducting properties causes quenching of luminescence due to the aggregation effects.

Herein we develop synthesis and study properties of linear conjugated spirocyclic compounds — 2,2'-spirobi[indene]s and 5,5'-spirobi[cyclopenta[b]thiophene]s — which combines rod-like structure with the orthogonality of two independent π-systems.

The synthetic route to spirocyclic dihalogenide 5 includes the sequential alkylation of malonic ester with the corresponding halogenides 2, hydrolysis of the obtained ester 3, and the intramolecular acid-catalyzed cyclization of the resulting acid 4 in the presence of polyphosphoric acid (PPA). Spirocyclic dihalogenide 5 was further decorated with linear conjugated systems based on thiophene or phenylene-thiophene moieties via Stille reactions.

DFT and TD DFT quantum chemical calculations were used for theoretical study of ground and excited states of the molecules obtained. As a result, it was shown that spiroconjugation could be effectively used for design materials with specific optical and electronic properties.

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Two charge transfer bicomponent 1:1 crystals of polycyclic aromatic hydrocarbons (anthracene and tetracene) with a new acceptor molecule (perfluoroanthraquinone) were grown by slow evaporation from solutions in toluene. The perfluoroanthraquinone molecule exhibits structural reorganization from folded geometry to planar structure upon complex formation. The co-crystals exhibit charge transfer bands in the UV-Vis spectra. In both crystals π-π stacks of alternating donor and acceptor molecules are observed. In the tetracene-perfluoroanthraquinone complex face-to-face stacking is the prevailing intermolecular interaction, which results in the “ideal” ring-over-bond mutual orientation of the donor and acceptor molecules. Meanwhile in the complex of anthracene-perfluoroanthraquinone multiple interactions (stacking, F···H, O···H, F···F) of similar energy are observed as revealed by the R. Bader’s QTAIM method. This results in a significant shift of the molecules from the supramolecular arrangement favorable for the charge transfer and in polymorphic modifications of the anthracene-perfluoroanthraquinone complexes as determined by X-ray single crystal diffraction and DSC. The charge transfer degree was estimated to be equal to 0.04 and 0.08 e in anthracene and tetracene complexes, respectively, which complies with interplanar distances of 3.5 Å in anthracene complex and 3.3 Å in tetracene complex and perfect ring over bond arrangement in the latter.
MODIFICATIONS OF SIXTH POSITION OF DIMETHYL-DIAZAADAMANTANE DERIVATIVES

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3,7-Diazabicyclo[3.3.1]nonanes (aka “bispidines”) represent a very useful group of compounds that could possess multifunctional properties. For example, earlier we investigated copper complexes with bispidine-based chelates which could be used for diagnostic and medication of pathological diseases using PET [1]. In addition, molecules with bispidine backbone are promising as catalysts. The unsolved problem of such chelates is how to binding them to a vector for targeted delivery of a drug, or to solid support.

In this work, the role of sterical hindrance in the selective transformations of the sixth position in 5,7-dimethyl-1,3-diazaadamantanes was studied. We performed a series of reactions and showed that, indeed, the sterical hindrance of sixth position by two adjacent methyl groups highly restricted its reactivity. So, only a limited scope of modifications is proved to be synthetically useful for the creation of linking group at sixth position (Scheme 1).

Scheme 1. Synthetically useful reactions for modification of the sixth position of 5,7-dimethyl-1,3-diazaadamantane derivatives.

In future, this work could help in expanding the synthetic strategy for drug’s linking to a diazaadamantane, which itself is a precursor of variable bispidine derivatives.

References

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SYNTHESIS OF NOVEL TYPES OF TETRACYCLIC HYDROXAMIC ACIDS VIA THE CASTAGNOLI-CUSHMAN REACTION

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Hydroxamic acids are widely applied in medicinal chemistry as metalloenzyme inhibitors and drug-carriers. In addition, hydroxamic acids are often used as metal chelating agents for development of colorimetric or fluorimetric chemosensors. This work aimed to construct novel fluorescent tetracyclic hydroxamic acids by cyclization of the Castagnoli-Cushman reaction (CCR) products followed by post-modifications. The CCR products were obtained from homophthalic anhydride (HPA) and aryl-substituted oximes. Two types of cyclizations were studied: intramolecular esterification (Fig.1) of salicylic oxime derivative and Friedel-Crafts acylation (Fig.2). As a result, we accomplished the synthesis of three novel isoquinolinocoumarines using the first protocol. The structure of products was confirmed by 2D-NMR spectra and X-ray analysis. The reactions of aromatization for these compounds were also studied. The second synthetic approach was studied for two CCR products (Fig.2), which allowed to obtain one novel tetracyclic hydroxamic acid with five-membered cycle.

References

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Porphyrin photosensitizers (PPS) are macro heterocyclic pigments with peculiar physico-chemical properties which determine their extensive use in the medicine and catalysis. It should be pointed out that water-soluble porphyrins and their analogues – chlorins – may form complexes with surfactants, that boosts their photodynamic and photocatalytic activity. In particular, polyvinylpyrrolidone (PVP) increases the photosensitizing activity of PPS in 3-5 times [1]. The new tendencies in the improvement of the photodynamic therapy (PDT) efficacy in the treatment of hard-to-heal purulent wounds, trophic ulcers, infected burns, are exhibited in a combination of PDT with the effects of biologically active substances – enzymes, vitamins, natural bactericidal polymers, accelerating the healing process[2]. As one of such substances, chitosan (CT), a biologically active and bactericidal polysaccharide, is considered. However, the preliminary experience of its application as a polymer component in complex with PPS in model processes of photosensitized oxidation of organic substrates unambiguously indicated a diminished efficiency of PPS-CT systems. The objective of this study is to select the optimal ratio of the components in the three-component complex PPS-PVP-CT, which exhibits high photocatalytic activity in the temperature range of PDT sessions, on the example of a model (test) process of tryptophan oxidation in an aqueous medium. Also, the use of photoditazin-CT-PVP complexes in the treatment of model wounds of laboratory animals have shown effectiveness, in particular their use reduces the activity of inflammatory processes and increases the proliferation of fibroblasts, neoangiogenesis, growth and maturation of granulation tissue.

References

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NEW “ONE-POT” TECHNOLOGY FOR PRODUCING OLEANOLIC ACID FROM PLANT RAW MATERIALS BY SUBCRITICAL WATER (SBW)

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Oleanolic acid (OA) is one of the most common pentacyclic triterpenoid compounds, mainly occurring in various plant sources (more than 1,600 species of plants). The object of investigation used in the roots aralia (Aralia mandshurica Rupr.). Using the roots of a plant for therapeutic purposes related to their content of up to 5% of triterpene saponins - aralosides (I) [1-2]. Developed and studied «one - pot» technique for obtaining OA (II) from the roots of the Aralia in subcritical water environment. Procedure «one-pot» processing aralia roots in SBW were performed using a reactor (autoclave) [3]. The efficiency of the proposed method of obtaining OA in subcritical water environment studied in the temperature range from 140 to 230°C. It is established that «one - pot» equipment for subcritical water environment allows for output OA, comparable to the yields of traditional methods, without the use of - or catalytic additives. Time cost of the proposed approach reception OA is 16 times less than the traditional two-step process of getting OA (Fig. 1).

References

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THIOMETHYLATION OF 2-HYDROXY-1,4-NAPHTHOQUINONES: SYNTHESIS OF QUINONE-CARBOHYDRATE CONJUGATES

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1,4-Naphthoquinones comprise an important class of organic compounds that are widely distributed in plants, marine invertebrates, fungi, and bacteria. These compounds attract the attention of researchers due to a wide range of pharmacological properties including antibacterial, antiviral, trypanocidal, anticancer, antimalarial, and antifungal activity. In particular, dioncoquinone B (1) and related compounds 2-5 isolated from various terrestrial plants (Figure 1) are of interest due to their promising anti-tumoral and anti-infective activities [1].

We have previously developed a preparative method for the synthesis of compounds 1-5 and their homologues 6-8 [2]. Here we modified the structures of these compounds for further studying their biological properties. The thiomethylation of 2-hydroxynaphthoquinones 6-8 with 1,2,3,4-tetraacetyl-6-mercapto-6-deoxy-D-glucose 9 leads to acetylated conjugates 10-12, in which the carbohydrate moiety is separated from the quinoid core by a methylene spacer. The partial methylation of conjugates 10-11 with diazomethane leads to conjugates 13-14. The deacetylation of conjugates 10-14 of the related natural quinones 1-5 leads to conjugates 15-19 with a free fragment of glucose. The introduction of glucose fragment into a molecule increases water solubility and bioavailability of the substance. According to the Warburg effect based on increased glucose consumption by tumor cells it can also increase the cytotoxicity against tumor cells than normal ones [3].
Figure 1. The scheme of synthesis of quinone-carbohydrate conjugates.

References


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Currently, one of the promising areas of chemistry is the investigation of phosphorus compounds. This is an extensive group of substances containing P-C and P-O bonds, representatives of which are found in natural objects. Phosphonates are the subgroup of phosphorus compounds and correspond to organophosphorus compounds containing C–PO(OH)2 or C–PO(OR)2 groups (where R = alkyl, aryl). Phosphonates are of the greatest interest for science and technology as they can be used as plant growth regulators, drugs, antiviral treatments. That is why the creation of new phosphonate compounds with targeted properties is of great importance. In our research we deal with home-made member of the phosphonate family that is 6-methoxyphosphonate 3-amino-2-methyl-3H-thiazole [3,2-b] [1,2,4] triazole-7th (E151). Structural formula is presented in Fig 1.

![Figure 1](image-url)

Figure 1. The structural formula of 6-methoxyphosphonate 3-amino-2-methyl-3H-thiazolo [3,2-b] [1,2,4] triazole-7-I.

Based on non-experimental screening of biological activity using the PASS computer program, it can be assumed that this compound may have a wide spectrum of biological activity as a treatment for amyotrophic lateral sclerosis. The E151 investigations with absorption, Raman, FTIR spectroscopies and enzymatic method demonstrated possibility of laser-induced modification of physicochemical and functional properties of this substance. The difference between the irradiated and unirradiated sample was revealed, as well as the effect of laser radiation on the biological activity of the sample was also established.
ACCESS TO 5-ARYLPYRAZOLYL RECEPTORS ON A CALIXARENE SCAFFOLD THROUGH YNONE ROUTE

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At present, much attention is devoted to ketoacetylene molecules, which give access to diverse heterocycles. Such heterocycles often possess biological activity, such as antitumor, anti-inflammatory, antidiabetic, and many others. Assembly of such heterocyclic units on a calixarene scaffold is particularly attractive because of low toxicity of this macrocycle and a possible synergetic effect of the heterocycles on this macrocycle. This work is aimed at the synthesis of alkynyl, alkynone, and 5-arylpyrazolyl derivatives of calix[4]arene (Scheme 1).

\textbf{Scheme 1.}

In this work, a number of phenylpyrazolyl receptors on a calixarene scaffold in \textit{partial cone} and \textit{1,3-alternate} stereoisomeric forms (1 and 2) have been synthesized through alkyne–alkynone–arylpyrazole route and characterized using NMR and MALDI mass spectrometry. This approach proved effective in the synthesis of calixarenes containing \textit{tert}-butyl (1) and hydrogen atoms on the upper rim (2).

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NEW REARRANGEMENT OF 1,2-DIHYDROPYRIMIDINES

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Compounds containing dihydropyrimidine-5-carboxylate moiety exhibit various biological activities, and could serve as scaffolds in the development of effective vasodilative and hypotensive drugs. Trifluoromethyl-substituted analogues in this regard are of especial interest. However the introduction of CF₃ group into the 1,2-dihydropyrimidine ring is quite complicated task, and these derivatives remain hardly accessible compounds.

In this work a three-step synthesis of 2-CF₃-substituted 1,2-dihydropyrimidine-5-carboxylates 5 from azirine-2-carbaldehydes 1, amines and ethyl 2-diazo-3,3,3-trifluoropropionate 3 is developed. The latter serves as a source both of the CF₃ group at the C2 and the ester group at the C5 of the final dihydropyrimidine. Azirincarbaldimine 2, quantitatively formed in the first step, is subjected to three-atom ring expansion to dihydropyrimidine 4 in the second step under the action of diazo compound 3 under rhodium(II) catalysis.

The key stage of the synthesis is unusual thermal “1,2-dihydropyrimidine – 1,2-dihydropyrimidine” isomerization, which affords the targeted 1,2-dihydropyrimidines in good yields. The mechanism of this new rearrangement was investigated by DFT method.

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NEW FUNCTIONALLY SUBSTITUTED QUINAZOLINES: SINGLE CRYSTAL AND PXRD ANALYSIS

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Quinazoline derivatives are broadly used as anti-tumor agents (afatinib, gefitinib and erlotinib drugs), as radioligand, when labeled with $^{18}$F, in positron emission tomography and neuroimaging (altaserin), and in another areas of medicine, for example, prazosin is used to treat high blood pressure$^{1,2}$. Thus, their practical importance in pharmacology and biology is great.

Wide range of new quinazoline derivatives has synthesized during our investigations, part of them has obtained in the form of a single crystals and their structures has been determined by the single X-ray analysis. Compound 1 (Ar=O-F-Ph) forms monoclinic crystals with one independent molecule in the unit cells, while the compound 2 (Ar= p-Br-Ph) crystallizes with a dimethyl sulfoxide molecule in the ratio 1:1. The geometry of molecules, intermolecular interactions and packing in the crystals will be discussed in the report. It is interesting to note that when the solvent leaves, compound 2 loses its crystallinity and becomes amorphous. The peculiarities of behavior and reversibility of this process are studied by powder diffraction and are discussed in the report. Other derivatives are characterized by powder diffraction method.

References

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C-peptide is a short peptide produced during processing of insulin from proinsulin. C-peptide is stored in pancreatic β-cells secretory granules and released into bloodstream in equimolar ratio with insulin in response to blood glucose stimuli. In 1990s it was reported that compensation of C-peptide levels in laboratory animals and type I diabetes patients improved diabetes-induced abnormalities in some peripheral tissues. These observations on C-peptide functions encouraged the searching of novel methods for diabetes treatment. Although our understanding of C-peptide role in biochemical processes increased, there remains uncertainty regarding exact cellular targets of C-peptide. In order to identify those targets we proposed an approach based on fluorescent visualization of C-peptide binding sites in cells. The visualization is facilitated by click-reaction termed as azide-alkyne cycloaddition. For this purpose, C-peptide was covalently modified via N-acylation at N-terminus via introduction of an alkyne moiety to allow peptide interaction with N3-functionality of fluorescent dye. The latter was introduced after peptide binding to its targets. Therefore, we attempted minimal modifications of C-peptide molecule to preserve its biological activity and remove artifacts related to impact of fluorescent dye on the specificity of C-peptide binding. As has been previously reported, HEK-293 cell line responded to C-peptide treatment, therefore this cell line was utilized in our study. TAMRA-azide was chosen for fluorescent labeling. Cells were incubated with modified peptide and then the fluorescent dye was introduced. Then the catalyst promoting click-reaction between bound peptide and dye was added. In order to produce contrast, cell’s nuclei and membranes were stained with bisbenzimide (Hoechst 33342, blue) and CellMask™ (green), respectively. After removal of excessive dyes, the cells were studied by fluorescent microscopy. The same manipulations were carried out with human insulin, which served as a control to verify of proposed experimental approach. Thus, we developed a method for C-peptide covalent modification for fluorescent labeling. The labeling on HEK-293 cell line was carried out to gain images illustrating targets and distribution of the C-peptide in cells without impact of fluorescent probe on C-peptide specificity of binding.
The need for nonsteroidal anti-inflammatory drugs (NSAID) remains high. Despite the positive effect of NSAIDs, it has some serious side effects, such as gastrotoxicity [1]. The side effect can be eliminated by masking carboxyl group, such as was done in the case of ibuprofen glycoside [1]. The objects of the study were selected amino acid derivatives of 4-(1-adamantyl) benzoic acid, which reliably exhibit anti-inflammatory and analgesic activity [2,3]. These compounds were administered in O-glycosylation reaction using respectively acetobromoglucose 2, acetochloroglucose 3 and tetraacetylglucose 4. The effect of reaction conditions on the yield and purity of desired products.

For each compound obtained anomer composition analysis conducted using \(^1\)H NMR spectroscopy.

OXOTRANSFER PROCESSES ENTHALPY ON THE ACTIVE CENTERS OF DITHIOLATE MOLYBDENUM-CONTAINING COMPLEXES

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[Bu₄N]₂[MoO(mnt)₂] (1) can act as a synthetic analog of molybdenum oxotransferases [1]. The thermodynamic characterization of the oxotransfer processes involving complex 1 is important to understand the basic function principles of molybdenum oxotransferases.

Our work included two stages: synthesis of the complex 1 and the thermodynamic study of the oxidation process. The complex was synthesized by the following reaction [2]:

\[ \text{H}_2\text{MoO}_4 + 2\text{Na}_2\text{mnt} + 2\text{Bu}_4\text{NBr} + \text{NaHSO}_3 = [\text{Bu}_4\text{N}]_2[\text{MoO(mnt)}_2] + 2\text{NaBr} + \text{H}_2\text{O} + \text{NaOH} + \text{Na}_2\text{SO}_4 \]

The structure of the complex was determined by the X-ray diffraction structure analysis. The enthalpy of the oxotransfer was determined in an acetonitrile solution using a calorimeter of the Calvé type using following reaction:

\[ \text{Me}_3\text{NO} + [\text{Bu}_4\text{N}]_2[\text{Mo}^{IV}\text{O(mnt)}_2] = \text{Me}_3\text{N} + [\text{Bu}_4\text{N}]_2[\text{Mo}^{VI}\text{O}_2\text{(mnt)}_2] \]

The calorimetric curve shows: the first endothermic peak corresponds to the dissolution of 1, the value of dissolution enthalpy is -206.8 kJ/mol. The second step corresponds to the molybdenum oxidation. The enthalpy of oxotransfer was calculated as a difference between the total reaction enthalpy and the enthalpy of dissolution: -206.8 kJ/mol.

Two steps of the oxidation process can be seen on the calorimetric curve, which is in good accordance to the proposed reaction mechanism [1].

References

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Metal complexes with acyclic diaminocarbenes (ADCs) over the last few decades have been widely used in a broad range of catalytic reactions [1]. Diaminocarbene complexes of Pt(II) can be used as efficient catalysts for hydrosilylation reaction of unsaturated compounds [2].

Owing to the reactions of coordinated isocyanides with N-nucleophiles, the acyclic diaminocarbene complexes can be easily generated. We studied the interaction between \(3,4\)-diaryl-1H-pyrrol-2,5-diimine and \(\text{cis}\)-[PtCl\(_2\)(CNR)\(_2\)]. The reactions are depicted in the scheme below.

![Scheme of C,N-chelated diaminocarbene platinum(II) complexes.](image)

Unsaturated compounds undergo the platinum complexes catalyzed hydrosilylation, affording the corresponding silanes in high yields. The regio- and stereoselectivity of hydrosilylation will be discussed.

References

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SYNTHESIS OF STABLE, INDUSTRIALLY SCALABLE, EFFICIENT METATHESIS HOVEYDA-GRUBBS CATALYSTS WITH AN N→RU OR N→S COORDINATE BOND IN A SIX-MEMBERED RING

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The widespread application of various catalysts is required to achieve the best results in each of the many directions of metathesis reactions. This fact motivates the investigations into the development of new, efficient, stable, and highly selective catalytic system.

In this work the multigram synthesis of ruthenium catalysts was carried out using methods based on the interaction of the well known complex 1 with styrenes 2-4 that gave target Hoveyda-Grubbs type catalysts 5-7 in good yields [1, 2].

The synthesized catalysts demonstrated prominent stability in air at room temperature for at least 5 years. The catalysts have good solubility in CH₂Cl₂, CHCl₃ and hence, their can be used in any types of metathesis reactions.

Catalytic properties of metallo-complexes 5-7 were demonstrated in “standard” cross metathesis (CM), ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) reactions [1].
References


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SYNTHESIS OF A NOVEL NICKEL(II) COMPLEX AND ITS ANTIBACTERIAL ACTIVITY

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Infectious diseases are the major causes of death especially in developing countries. These diseases kill about 15 million people every year, which corresponds to about one-third of the number of deaths. The development of antimicrobial drugs, particularly antibiotics, has long been touted as one of the great medical success stories of the twentieth century. Although several classes of antimicrobial compounds are presently available, microorganism’s resistance to these drugs constantly emerges. In the search for new drugs against resistant infectious diseases, the modification of existing drugs or organic molecules by coordination to a metal center has attracted considerable attention [1]. Substituted thioureas are interesting as reagents for the separation of metal ions, as antibacterial, antiviral, or antifungal agents [1]. Herein, we report about synthesis of a novel nickel(II) complex (Scheme 1).

![Scheme 1. Synthesis of a novel nickel(II) phenylthiourea complex.](image)

The obtained complex was characterized and its in vitro antibacterial activity against S. aureus and E. coli was also studied.

References

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In recent years, targeted delivery of photosensitizers (PS) to tumor cell receptors has been used. It is minimize the side effect and increase the effectiveness of photodynamic therapy (PDT) of malignant tumors [1]. In this work, we studied the photosensitizing activity of hydrophobic PS - steroid conjugates of pyropheophorbide a (PPa) in the generation of singlet oxygen $^{1}$O$_2$ (playing the role of an active agent in PDT). Our PS were containing testosterone (PPT) and dihydrotestosterone (PdPT), isomers of PPT with a hexadecylamine (PPTH –I,II). These compounds have been solubilized by non-toxic amphiphilic polymer - pluronic F-127. The photoactivity of PS was studied in the model photooxidation reactions of tryptophan in water and anthracene in chloroform [2]. It has been shown that PSs modified with steroid molecules have affinity for androgen-dependent cancer cells — prostate carcinoma cells [3]. It was shown that the pluronic F-127 practically didn’t affect the value of the effective rate constant $k_{eff}$ for all bioconjugates pyropheophorbides a (PPa), in the reaction of photooxidation anthracene in chloroform. This is due to the fact that in chloroform the pluronic didn’t form micellar structures and didn’t interact with the substrate. In this case, the value of $k_{eff}$ photooxidation tryptophan in water in the presence of solubilized substituted PPa increased with the concentration of F-127. The observed effects are associated with the disaggregation of PS molecules due to the formation of complex a pluronic-conjugates PS. The obtained dependencies of $k_{eff}$ changes were confirmed by the data of electron and fluorescence spectroscopy. Thus, the fluorescence intensity of solubilizing pyropheophorbide PS was increased with increasing concentration of F-127, and indicating of process disaggregation. Thus, F-127 solubilization allows to obtain of water-soluble forms of PS, which are active in the processes of photocatalytic oxidation.

References

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Halogen bonding has found applications in organic and metal-organic synthesis, and the obtaining crystalline or liquid-crystalline materials in which halogen bonding involving molecular building blocks with interesting optical or emissive properties has been employed to generate materials exhibiting novel or improved optical properties. Halogen bond-based cocrystallization of platinum(II) complexes is an effective strategy for tuning the solid-state luminescence of crystals. In particular, heteroleptic square planar platinum(II) complexes with different kinds of ancillary ligands show significant scope for tuning their emissive properties over the entire visible spectra by modification of the cyclometalated and/or the ancillary ligands. [1].

In the course of our study of luminescent materials based on cyclometalated complexes platinum(II) with multifunctional isocyanide ligand was synthesized complex [Pt(ppy){C≡NC₆H₅}Cl] (ppy – phenylpyridine) and halogen-bonding cocrystallized with I-, o-Br,Br and p-Br,Br- PFB (PFB – perfluorobenzene).

Figure 1. Cocrystallizates of [Pt(ppy){C≡NC₆H₅}Cl]

References
Fluorescence imaging has emerged as a very powerful technique to carry out a research into chemical and biochemical processes. Due to considerable significance of metal ions’ detection in biological systems and environment, increased attention has been focused on design of rapid and highly selective fluorescent chemosensors on metal ions.

Recently in our research group was developed a general approach towards cyclic \(N\)-hydroxytetrahydroquinolonic acids, which are representative of cyclic hydroxamic acids (CHA), via Castagnoli-Cushman reaction of homophthalic anhydride and oximes [1]. Synthesized CHA showed high ability to chelate ions Fe\(^{3+}\) with strong complexes formation. Attaching fluorophores such as porphyrins derivatives to CHA may afford to obtain new fluorescent chemosensors for effective monitoring the concentration of metal ions.

In the present work we designed and synthesized a series of fluorescent dyes applying 5-(4-aminophenyl)-10,15,20-triphenylporphyrin as fluorophore and CHA with various substitutes as metal binding receptor. Synthesized compounds were investigated via UV/Vis absorption and fluorescence emission spectra and showed promising photo-physical properties.

References

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INTERACTIONS OF DIAZIRIDINES WITH ISOCYANATES AND ISOTHIOCYANATES

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Reactivity of diazaridines, three-membered ring, containing two nitrogen atoms, cause increased interesting, because on the one hand they can undergo opening of three-membered cycle on C-N bond, with generation of 1,3-dipole – azomethine imine [1], on the other hand, due to presence of lonely electron pairs in two nitrogen atoms, in some cases diazaridines act as nucleophiles [2]. The aim of our research is to investigate interaction 1,5-diazabicyclo[3.1.0]hexane with arylisocyanates and arylisothiocyanates under different conditions.

Figure 1. Interaction 1,5-diazabicyclo[3.1.0]hexane with arylisocyanates and arylisothiocyanates.

It would be determine, that interaction non-substituted in 6 position 1,5-diazabicyclo[3.1.0]hexane 1 with isocyanates results in products 2, which is result of interaction of three equivalents isocyanates with one equivalents diazaridines. At the same time reaction 1 with isothiocyanates, giving products 3 attachment two equivalents isothiocyanates.

References

Acknowledgments. NMR, HRMS and XRD studies were performed at the Saint Petersburg State University Center for Magnetic Resonance, Center for Chemical analysis and materials research and X-Ray Diffraction Center, respectively.
3-methyl-1,2-butadienyl phosphine oxides [X2(O=)P–CR=C=CMe2, X = Cl, OMe, NR2, or SAr] have undergone intramolecular cyclization into the stable 1,2-oxaphospholium ions in Brønsted superacid TfOH. These cations have been thoroughly studied by means of NMR. Solvolysis of superacidic solutions of these species has afforded cyclic phosphonic acid derivatives.

Contrary to that, P,P-dichloro-3-methylbuta-1,2-dienyl phosphine oxide [Cl2(O=)P–HC=C=CMe2] has reacted with Lewis acid AlCl3 in an intermolecular way forming non-cyclic intermediates, which have been investigated by NMR and DFT calculations. These intermediates react with arenes giving to products of hydroarylation of the allene system, phosphoryl substituted alkenes and/or indanes. Strong coordination of the oxygen of the P=O group with AlCl3 has prevented the formation of cyclic 1,2-oxaphospholium ions and played a crucial role in different reactivity of such allenes under the action of Brønsted or Lewis acids.

This is the first example of Lewis acid-promoted intermolecular hydroarylation of allenes bearing electron-withdrawing substituent.

Figure 1. Reaction of P,P-dicloro-3-methylbuta-1,2-dienyl phosphine oxide with TfOH or AlCl3.
Adamantane derivatives have a wide range of pharmacological properties and are of increased interest for the search of new medicine [1-2]. It is known that the 1,3-dipolar cycloaddition of nitrones to olefins is the most simple and effective method for the synthesis of isoxazolidines. Nevertheless, the reactions of adamantane derived nitrones are insufficiently explored.

The aim of this work is to investigate 1,3-dipolar cycloaddition of adamantane derived 1 and 4 with N-substituted maleimides 2.

Figure 1. 1,3-Dipolar cycloaddition of 1 and 4 with maleimides.

It has been established that 1,3-dipolar cycloaddition of considered nitrones proceeds giving from moderate to good yields of corresponding isoxazolidines.

References

Acknowledgments. NMR and HRMS studies were performed at the Saint Petersburg State University Center for Magnetic Resonance and Center for Chemical analysis and materials research, respectively.
NEW DIRECTION OF THE KNOEVENAGEL CONDENSATION OF OXINDOLES IN THE PRESENCE OF METAL ALKOXIDES

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The problem of low reactivity of benzophenones in the Knoevenagel reaction often causes difficulties during synthesis of biologically active compounds. When synthesizing AMPK activators of the benzylidene oxindole series using the convergent scheme, we proposed aluminum isopropoxide to carry out the first stage of the synthesis, consisting in the Knoevenagel condensation of N-unsubstituted oxindoles with various benzophenones [1]. Detailed study showed the possibility of alternative condensation pathway under these conditions (Figure 1).

![Figure 1. Possible pathways of condensation reaction](image.png)

In the present study, we consider the factors that influence the direction and yield of the condensation in the presence of aluminum isopropoxide and evaluate the aluminum isopropoxide activity in the target and alternative reaction directions.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-13-10358).

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Reactions of cyclic allenes with nitrones are one of the most effective and modern methods of creation five-membered heterocycles demanded in pharmacology. The selectivity of cycloaddition in the case of cumulated diene varies considerably depending on the nature of the 1,3-dipole and substituents in the allen. Reactions of cyclic allenes with nitrones insufficiently explored. Condensed polycyclic compounds containing the isoxazolidine cycle in the structure are used as pesticides [1] and cancer cell inhibitors [2].

The purpose of this work is to study the reactions of cyclic alleles 1 with medium-size cycles with keto- 2 and aldonitrons 3. The study of the regio- and stereoselectivity of cycloaddition.

The 1,3-dipolar cycloaddition of ketonitrons with cyclic alleles proceeds with the formation of adduct 4 containing a double bond at the C⁴ atom of the isoxazolidine cycle, and benzazepinone 5. The interaction of aldonitrons with cyclic alleles proceeds regio-and stereoselectively to form a mixture of diastereomeric isoxazolidines 6 и 7, with predominance of the isomer with the cis-position of substituents on the atoms C³ and C⁵ of the isoxazolidine cycle.

References
FOLIC ACID BASED RADIOPHARMACEUTICALS FOR PET-DIAGNOSTICS


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Folate receptors are considered to be a new promising target for radiopharmaceuticals. Currently, a number of radiopharmaceuticals for SPECT, PET and RNT (with $^{99m}$Tc, $^{111}$In, $^{18}$F, $^{177}$Lu) have been developed. The purpose of this work is to study new folic acid based molecules labeled with the PET radionuclide $^{68}$Ga.

In the course of this work two new compounds were synthesized. A procedure for labeling I and II with $^{68}$Ga was developed. It allows obtaining target complexes with a yield of at least 95%.

Both compounds contain NODAGA chelating group for $^{68}$Ga binding. First compound studied (I) is the closest analogue of folic acid based radiopharmaceuticals reported in the literature [1].

The biodistribution was studied using animal model (nude mice with KB tumor cell line xenograft). The biodistribution of $^{68}$Ga-I is very similar to that of other folic acid based labeled compounds [1]. However an interesting finding occurred in the course of this experiment. One of male animals developed a spontaneous neoplasma located in the scrotum. Histological study determined it as a cyst. $^{68}$Ga-I showed high accumulation in the neoplasma. Finding like this were never described before.

According to previously reported data this type of labeled compounds tends to be accumulated in the kidneys. That is why a His-Glu-His-Glu fragment was introduced into the second molecule (II) and the effect of this modification on the biodistribution was studied.

Data on the labeling process as well as the comparison of biodistribution of $^{68}$Ga-I and $^{68}$Ga-II in animal models with aseptic and septic inflammation foci will be presented.

References

Acknowledgements. The reported study was funded by RFBR (project No 19-33-70048).
SYNTHESIS OF NOVEL BIS(INDAZOLYL)ALKANES

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Bis(azolyl)alkanes and their derivatives act as both mono- and bidentate ligands forming coordination compounds with transition and main group metals [1]. We have developed novel approaches to synthesis of this type of ligands based on indazole. The first method is the double alkylation of indazole by dichloro- or dibromoalkanes in superbasic medium KOH-DMSO.

Figure 1. Double alkylation of indazole in superbasic medium.

The second approach is the addition of indazole to glyoxal leading to 1,2-bis(indazol-1-yl)-1,2-ethanediol, which can be converted to 1,2-bis(indazol-1-yl)-1,2-dichloroethane by the reaction with thionyl chloride. Such dichloroethanes are of interest as precursors to obtain bis(azolyl)alkenes and symmetrical and asymmetric tetra- and tris(azolyl)alkanes.

Figure 2. Synthesis of bis(indazol-1-yl)-1,2-ethanediol and 1,2-bis(indazol-1-yl)-1,2-dichloroethane

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-33-50034). Physicochemical studies were performed at the Research park of Saint Petersburg State University.
New practical approach to the preparation of methyl naphthoxazole-2-carboxylates for lanthanides chelation was developed [1]. This coumarin ring contraction-based method utilized cheap reagents, simple purification and can be used in multigram scale (Fig. 1). Isomeric oxazole-based chelators show very good IR photoluminescence with ytterbium cations (Fig. 2).

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-00250 and 18-33-20210).
Modern research is concerned to the design of N-heterocyclic carbene palladium complexes (Pd-NHCs), since studies [1-2] showed their high anti-proliferative activity. However, obtaining these compounds is often multistage. Acyclic diaminocarbene palladium complexes (Pd-ADCs) are an alternative to NHCs complexes. They can be generated by a simpler method and these complexes have a number of special advantages.

The metal-mediated nucleophilic addition of propargyl functionalized secondary amines to isocyanide palladium(II) complexes was performed to give alkyne bearing ADCs-Pd (Figure 1).

Complex 5 was not obtained under these conditions, mainly due to the steric effects of the benzhydrylamine substituent. \(^1\)H NMR spectroscopy monitoring of the reaction of PdCl\(_2\)(CN-\(t\)-Bu)\(_2\) with propargylamine confirmed the formation of product 3, but this complex was not isolated because of rapid decomposition. Complexes 1, 2, 4 can be easily isolated with yields from moderate to high (44-95%). The products were stable in the solid state under air. The resulting complexes can be used for subsequent functionalization by the CuAAC reaction. The synthesized complexes are unstable in solution, and a possible mechanism of their destruction involves the carbopalladation stage. The mechanistic details of the decomposition of the complexes will be covered in a poster presentation.

References:


Acknowledgements: Scientific measurements were performed in the Research Park of the Saint Petersburg State University Magnetic Resonance Research Centre.
DOMINO-REACTION IN ONE-POT SYNTHESIS OF THE
3,4-DIHYDRO-2H-THIOPYRANS

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There are two types of domino-reactions leading to the formation of the 3,4-dihydro-2H-thiopyran derivatives. The first is a three-component domino-Knevenagel – hetero-Diels-Alder reaction of dithioester containing active methylene group via formation of thiabutadiene as intermediate. Another type, the intramolecular domino thionation – hetero-Diels-Alder reaction, is presented as the only example interaction of α, β-unsaturated ketones with 1,2,3-triazole fragments methyl acrylate and phosphorus pentasulfide as a thionation agent.

Previously, we have developed a one-pot method of synthesis of 3,4-dihydro-2H-thiopyran derivatives by Diels-Alder reaction between in situ generated sulfur-containing α, β-unsaturated dienes and various dienophiles. Following the example of the dibenzalacetone and other compounds with 1,4-pentadien-3-one moiety interaction with derivatives of vicinal dicarboxylic acids, we have demonstrated the first example of a three-step domino reaction, including the steps of thionation, hetero-Diels-Alder, and repeated [4+2] cycloadditions with high yields. As an example, the domino-reaction product of the dibenzalacetone with maleic anhydride shown below:

References
New materials with improved properties and sustainable manufacturing are in demand in industry and materials science. Terpenols have a great potential as initial substrates due to wide abundance in essential oils and resins. Some of them can be directly isolated or synthesized from renewable raw materials by simple methods. Modification of natural compounds requires enough amounts of a co-reagent (modifier). Calcium carbide, a known inexpensive vinylating agent, is also mined in large quantities in sustainable manner. Transformation of a hydroxyl group in terpenols into a vinyl group, using CaC$_2$, and subsequent polymerization of ethers provides the pathway to new materials [1].

We carried out the vinylation of several terpenols using calcium carbide according to the literature procedure [2]. Isolated monomers were purified and polymerized under cationic conditions (standard procedure without optimization, Scheme 1). Corresponding polymers were isolated, purified and studied.

![Scheme 1. Obtaining of terpenol-based polymers](image)

The synthesized monomers were characterized by NMR-and ESI-spectroscopy. Size exclusion chromatography, the average molar mass and molar mass distribution values were determined for all the synthesized polymers. The presented method is convenient, safe and allows to obtain new materials from
inexpensive natural sources. Further investigations for biodegradability of terpenol-based polymers are in progress in our group.

References
SYNTHESIS AND STRUCTURE OF TRIS(5-ARYL-1H-TERAZOL-1-YL)METHANES

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A series of tris(5-aryl-1H-terazol-1-yl)methanes were synthesized by reaction of 5-aryl-NH-tetrazoles with trichloromethane in strong aqueous basic condition. The compounds obtained were fully characterized by means of HRESI MS, $^1$H, $^{13}$C{$^1$H}, and $^{19}$F NMR spectroscopies, DSC/TG analysis, as well as by X-ray diffraction analysis. Specific features of the crystal structure of tris(5-aryl-1H-terazol-1-yl)methanes were determined. In the crystals ($\pi \cdots \pi$) and (C-N $\cdots \pi$) interactions between a lonely pair of nitrogen with a positively charged carbon region of the heterocycle, where a $\pi^*$-orbital orbital is located, were found.

Figure 1. Noncovalent interactions involving tetrazole moieties $\pi-\pi$ interactions (blue); $\pi(C)\cdots\text{lp}(N)$ interactions (red).

References

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HYDROGEN BOND ILLUSION IN AN “AMIDE PROTON SPONGE”

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The search for factors determining the spatial structure of proteins is traditionally one of the main tasks of biochemistry and organic chemistry [1]. Recently it was found that NH…pi type hydrogen bonds make a significant contribution to the protein molecules conformation, in which, for example, the amide nitrogen atom can participate as an unexpected proton acceptor, that was showed by Lectka [2]. Thus the X-ray diffraction analysis of “amide proton sponge” 1 for the first time allowed to fix the NH…pi interaction with the sp²-hybrid amide nitrogen atom (Fig. 1). However, a detailed review of the evidence presented in the original work, as well as our study of the X-ray structures of other similar amides 2, raised some doubts about the correctness of the assumption put forward. In addition to X-rays, chemical shifts of acidic NH protons in ¹H NMR spectra, the values of the acidity constants pKₐ, as well as quantum chemical calculations of the hydrogen bond energy and proton transfer, indicate the illusory nature of this interaction. Understanding the energy of such weak non-valent interactions is of particular importance for insight into the acid and enzymatic hydrolysis of the amide bond.

![Figure 1. Structures of amides 1 and 2.](image)

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project № 18-33-00259).
A NEW APPROACH TO THE SYNTHESIS OF DONOR-ACCEPTOR CHROMOPHORES CONTAINING 2-(2-OXOPYRROL-3-YLIDENE)MALONONITRILE FRAGMENT


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Investigations in the field of creation of novel groups of donor-acceptor chromophores with a cyano-substituted acceptor in the structure are urgent nowadays due to a wide possibility for the practical use of these compounds in various areas. Herein, an approach to novel group of donor-acceptor chromophores containing an electron-withdrawing 2-(2-oxopyrrol-3-ylidene)malononitrile fragment 1 is reported. Previously, it had been shown that compounds 1 could be synthesized from 4-oxoalkane-1,1,2,2-tetracarbonitriles by the action of bases [1]. Firstly, tetracarbonitrile 2 was directly synthesized from tetracyanoethylene and 4-fluoropropiophenone to introduce an electron-donating moiety into structure 1.

Then compound 2 was heterocyclized into pyrrole 3 by the action of morpholine. The presence of a fluorine atom in the compound 3 allowed us to carry out a nucleophilic substitution reaction by the action of secondary amines leading to the formation of chromophores 4a–c.

It was found that an introduction of the electron-donating group in structure 1 significantly shifts the absorption band in the visible region in comparison with a fluorine-substituted pyrrole 3. Thus, compound 3a in ethanol has an absorption maximum at 530 nm whereas chromophore 4a has the band with maximum at 603 nm.

References

Acknowledgements
The reported study was funded by RFBR according to the research project № 18-33-20268 mol_a_ved.
The HIV/AIDS pandemic is a major health concern worldwide and Sub-Saharan Africa is the most affected region than any other part of the world and this marks a severe development crisis in these countries. As the number of people on treatment continues to increase so will the demand for antiretroviral therapy (ARV) continue to increase. With virtual no local production of Active Pharmaceutical Ingredients (APIs) used in the formulation of ARV drugs, most countries rely on imports and this increases the cost of medication. To develop production capacity of APIs in Africa, we envisage the use of continuous flow technology to meet local demand. treat HIV. The technology offers many advantages compare to batch technology such as, lower costs, reduced waste, higher yields, while solvent and energy waste is reduced. In this study we synthesized Zidovudine (AZT) using batch process (Figure 1) as a benchmark followed by the transfer into continuous flow process to develop a better and reproducible process. All the synthetic steps are optimized in continuous flow systems with the aim of developing a continuous synthesis process.

![Figure 1. Synthetic process of zidovudine.](image)

References


Acknowledgements. This work was supported by the National Research Foundation (NRF) and Postgraduate Research Scholarship (PGRS).
Different BODIPY-type dyes found extensive use in modern science and technology, especially in biotechnology. However, the main challenge of their application is a luminescent in the red region, which is needed for imaging of biological objects. This problem can be solved by conjugation of BODIPY core with aromatic fragments. Generally, it is possible to make BODIPY-dyes with 3 types of conjugated benzyl ring (A–C, presented on Fig. 1). Structures A [1] and B [2] are well known, however, structure C was not studied before. This is likely related to the low stability of corresponding anion D.

Figure 1. Types of aromatic-conjugated BODIPY-dyes.
To obtain the target structure C we decided to use 3-hetarylpyrroles F, which give stable betaines [3]. Retrosynthetic scheme of the target BODIPY-dye E is presented on Fig. 2. Luminescent properties of the target compounds were studied in details.

Figure 2. Retrosynthetic scheme of the target structure.

References

Acknowledgements. This work was supported by the Russian Science Foundation (grant №16-13-10036).
TARGETING ANTITUMOUR METAL-BASED COMPOUNDS.

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The discovery of anticancer properties of platinum based complexes became a significant breakthrough in cancer treatment. Currently cisplatin, carboplatin and oxaliplatin remain major drugs for the first line treatment (alone and in combinations) for a variety of malignancies including head and neck, testicular, breast and ovarian tumors. However, despite the success of platinum containing drugs the intrinsic or acquired resistance, general toxicity and other severe side effects are clinically unfavorable. To overcome these problems novel strategies for the search of active antitumor compounds are being developed.

One of the strategies in the modern medicinal chemistry of anticancer drugs is the design of multifunctional targeting compounds able to bind to more than one molecular target. The activity and specificity of metal-based anticancer compounds can be modulated by ligand environment. Attachment of Pt or Ru moiety can create dual action compounds that upon reduction in the cell environment generate two or more active components with the defined molecular targets, increase anticancer properties and provide a multitargeting mode of action.

This presentation will focus on the hybrid complexes of Pt(IV), Ru(II) and Ru(III) bearing targeting moiety. Several compounds found to be highly cytotoxic against several human cancer cell lines with excellent selectivity towards cancer cells.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-13-00084) and the Russian Foundation for Basic Research (project No 19-03-00394).
The rapid development of various industries in the modern world leads to an increase of waste materials. Particular attention in the past few decades, given to purification of wastewater from heavy metal, which in large quantities is released into the environment. Heavy metals are not biodegradable unlike organic waste, besides one of the most dangerous properties of heavy metals is their accumulation in living organisms for which they are toxic. In this regard, the identification of residues of heavy metals is of paramount importance. The application of metacyclophanes (calix[n]arenes and thiacalix[n]arenes, cucurbit[n]urils, cyclodextrins) is currently shown in separation and extraction of heavy metals. Unlike metacyclophanes classical paracyclophanes are scaffold structures that are rather difficult to further functionalize. However, in the last decade, a macrocyclic platform, namely pillar[n]arenes, synthesized by the Ogoshi group, has become widespread. With the advent of the pillararenes it was appear the opportunity to fully reveal and show the interesting properties of paracyclophane, which can be functionalized due to the presence of free phenolic groups.

Under this research work, a number of new monofunctionalized pillar[5]arenes containing 1-aminophosphonate and phosphonate fragment were obtained, as well as their binding ability to metal cations were studied. The structure of the new synthesized derivatives was fully proved by NMR $^1$H, $^{31}$P, $^{13}$C, IR spectroscopy, mass spectrometry (MALDI-TOF) and elemental analysis.

Acknowledgements. This work was supported by the RFBR according to the research project № 18-33-00276 mol_a, the research project № 18-03-00315.
ANTIOXIDANT ACTIVITY OF PYRIDINES WITH 2,6-DI-TERT-BUTYLPHENOL MOIETIES

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Oxidative stress participates in a pathogenesis of many diseases. 2,6-Di-alkylphenols are widely used as antioxidants and stabilizers of cellular membranes. On the other hand, pyridines are engaged in structures of many biologically active compounds.

New substituted picolylamines with 2,6-di-tert-butyl-4-hydroxyphenyl groups were synthesized and characterized by IR, NMR, X-ray and elemental analysis.

\[
\text{Bu}^t \quad \text{HO} \quad \text{Py} \quad \text{NH} \\
\text{Bu}^t \quad \text{But} \quad \text{But} \quad \text{(CH}_2\text{)}^n \quad \text{Py} \quad \text{n = 0: 1-3} \\
\text{n = 2: 4-6}
\]

Antioxidant potential of compounds was studied as an inhibition of lipid peroxidation (LP) in rat liver homogenates. To elucidate the possible mechanisms of antioxidant activity the radical scavenging activity (in DPPH-test), superoxide radical anion $\text{O}_2^{-}$ scavenging activity (xanthine-xanthine oxidase assay), reducing ability (CUPRAC-test) and inhibition of lipoxygenase (LOX 1-B) were evaluated.

All the compounds showed high antioxidant activity depending on the length of the linker and the position of nitrogen atom in the pyridine ring (Table 1). Moreover, compounds possess moderate superoxide radical anion scavenging activity and act as mild inhibitors of lipoxygenase. Thus, studied compounds can be considered as potential antioxidants and cytoprotectors.

Table 1. Antioxidant activity of compounds 1-6.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>TEAC (CUPRAC)</th>
<th>% of reduced DPPH, 20 h</th>
<th>IC$\text{}_{50}$, µM ($^\text{t}$BHP-induced LP)</th>
<th>IC$\text{}_{50}$, µM (Fe$^{3+}$-induced LP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.89 ± 0.03</td>
<td>24.2 ± 1.2</td>
<td>11.0 ± 3.9</td>
<td>22.8 ± 6.4</td>
</tr>
<tr>
<td>2</td>
<td>0.29 ± 0.01</td>
<td>3.0 ± 0.1</td>
<td>5.3 ± 1.0</td>
<td>14 ± 2.8</td>
</tr>
<tr>
<td>3</td>
<td>0.35 ± 0.01</td>
<td>n/a</td>
<td>24.1 ± 6.4</td>
<td>4.47 ± 0.47</td>
</tr>
<tr>
<td>4</td>
<td>1.71 ± 0.05</td>
<td>85.2 ± 3.3</td>
<td>0.9 ± 0.2</td>
<td>3.4 ± 0.8</td>
</tr>
<tr>
<td>5</td>
<td>1.00 ± 0.03</td>
<td>87.3 ± 3.4</td>
<td>0.45 ± 0.11</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>6</td>
<td>1.10 ± 0.03</td>
<td>89.1 ± 3.4</td>
<td>0.82 ± 0.17</td>
<td>3.9 ± 1</td>
</tr>
</tbody>
</table>

Acknowledgement: The financial support of RFBR (17-03-01070, 18-03-00203) is gratefully acknowledged.
SYNTHESIS AND BIOLOGICAL ACTIVITY EVALUATION FOR ISOMER SERIES OF PYRROLIDIN-2-ONE DERIVATIVES


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A series of Castagnoli-Cushman acid derivatives of the pyrrolidin-2-one chemotype with high proapoptotic activity was identified by virtual screening of a combinatorial library of compounds consisting of more than a million structures and the subsequent biological evaluation of hit compounds [1]. The presence of cis-/trans- and optical isomerism is a feature of the newly identified MDM2 inhibitors. During the synthesis of the target structures, four possible isomers are formed (Figure 1). In the study, we developed the methods of synthesis and isolation of a series of individual isomers and evaluated their activity within the used pharmacophore hypothesis. The target activity of the obtained compounds was studied in different cell models.

Figure 1. Synthesis of individual isomers of active compounds

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 16-13-10358).
SYNTESIS AND STUDY OF 4-OXO-1,4-DIHYDROCINOLINE DERIVATIVES - PROMISING INHIBITORS OF PROTEIN PHOSPHOTYROSINE PHOSPHATASE 1B

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The enzyme protein phosphotyrosine phosphatase 1B (PTP1B) is the most important negative regulator of the insulin and leptin systems functioning through the activation of a cascade of tyrosine phosphorylation. The increased activity of PTP1B leads to the insulin (IR) and leptin resistances (LR) and is the cause of obesity, diabetes mellitus and other socially significant metabolic disorders [1]. In this regard, an actual problem of modern medicine are deciphering the mechanisms of action of PTP1B and developing its selective inhibitors, which will allow to treat the metabolic disorders associated with IR and LR. [2]. In present work we proposed a structure of PTP1B inhibitors based on the 4-oxo-1,4-dihydrocinnoline scaffold. The Sonogashira reaction to obtain ortho-ethynyl substituted anilines and the Richter reaction to generate the cinnoline core were used to synthesize several PTP1B inhibitors (Scheme 1).

**Scheme 1.**

We have shown that synthesized 4-oxo-1,4-dihydrocinnoline derivatives stimulate the insulin and leptin signaling pathways and normalize the metabolic parameters in obese rats. Details of the synthesis and biological tests will be presented in the report.

References:

Acknowledgements. This work was supported by the Russian Science Foundation (project No 119-73-00228).
Today palladium catalysts and cross-coupling reactions are used for the synthesis of a variety of substances (drugs, new materials, natural compounds). Plastics, pharmaceuticals, materials for the electronics industry and many other substances can be synthesized using cross-coupling reactions [1].

The new versatile synthetic approaches for the synthesis of modern drugs as heterocyclic compounds have been developed [2]. Within the framework of this research project, the task was to work out a strategy for the synthesis of potential inhibitors of protein tyrosine phosphatase 1B (PTP1B). The target biological activity of the studied compounds is aimed at the treatment of type 2 diabetes mellitus (DM2) [3]. We have been developed the synthetic approach specially selected sequence of Sonogashira reactions and subsequent Richter cyclization (Scheme 1).

Scheme 1. Synthesis of 6-bromo-3-(hydroxyalkyl)cinnolin-4(1H)-one

We have carried out a study of influence of the hydrocarbon chain length in the starting hydroxyalkynes for Sonogashira coupling and Richter cyclization. The possibilities and limitations of the applicability of this method are shown.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 119-73-00228).
Attempted use of glutamine in the Ugi reaction with aldehydes or ketones and isocyanides for the synthesis of substituted glutarimide\textsuperscript{1} via Ugi-5C-4CR\textsuperscript{2} resulted in an unexpected formation of iminopyrrolidine-2-carboxylic acids. We optimized the transformation to a useful synthetic procedure by synthesizing more than 15 derivatives, exploring scope and limitations. The reaction is accelerated in water and involves an Ugi reaction followed by an intramolecular condensation (Figure 1). The reactions proceed under mild and green conditions and lead to a biologically relevant iminopyrrolidine scaffold otherwise inaccessible via conventional synthetic methodologies.

\textbf{Figure 1.} A reported strategy to the iminopyrrolidine-2-carboxylic acid core and our new methodology

The structure of compounds was unambiguously confirmed by NMR, HRMS, IR, and single-crystal X-ray diffraction study. The resulting compounds can be applied for further functionalization or subsequent post condensational modification and are of interest as scaffolds for drug design

\textbf{References}

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Since its discovery in 1999 [1], the tandem Ugi/Diels-Alder reaction has proven to be a convenient tool for the construction of densely substituted tricyclic compounds 1 in a high-yielding and stereocontrolled fashion. Moreover, these compounds can undergo numerous transformations providing access to a wide range of nitrogen heterocycles [2]. However, in most cases the isocyanide scope remains somewhat limited due to instability and revolting odor of isocyanides. *In situ* dehydration of formamides to generate isocyanides first reported by Dömling in 2015 [3] provides a solution for both of the aforementioned limitations; thus, we investigated the Ugi/IMDA reaction under “isocyanide-less” conditions attempting to broaden the scope of accessible products.

We successfully applied the “isocyanide-less” protocol to the Ugi/IMDA sequence and obtained compounds 1 in moderate yields as single isomers [4].

References

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF ISOALANTOLACTONE-FUROPYRIMIDINE HYBRIDS

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Synthesis of hybrid structures containing a fragment of sesquiterpene lactone and N-containing heterocyclic fragment has great interest for the creation of biologically active agents [1]. We proposed an effective method for the synthesis of isoalantolactone-furopyrimidine hybrids 5 based on the Sonogashira-coupling of iodide 2 with acetylene 3 and subsequent Ag-catalyzed cyclization of 4. Antimicrobial and antiviral activity of 5a-f compounds is discussed.

Figure 1. Synthesis of furopyrimidine derivatives of isoalantolactone and the molecular structure of compound 3c

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research and the Government of the Novosibirsk Region (project No 19-43-543042).
POST MODIFICATION OF ACETYLENE FUNCTIONAL 4-OXO-1,4-DIHYDROCINNOLINE DERIVATIVES BY CuAAC

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The compounds bearing 4-oxo-1,4-dihydrocinnoline fragment have been reported as the protein tyrosine phosphatase 1B inhibitors (PTP1B) [1]. PTP1B is a negative regulator of leptin system which plays an important role in many physiological processes. Direct modification of these compounds using click-reagents would be useful for pharmacodynamic studies and bioimaging.

CuAAC reaction is an effective way to obtain 1,2,3-triazoles regioselectively, which can be carried out with the use of copper complexes (N-heterocyclic carbene) halide [(NHC)CuX] in mild conditions giving the target triazoles in high yields. These copper complexes have unique properties in homogeneous catalysis and showed excellent activity in the azide-alkyne cycloaddition[2,3]. Present work is devoted to the development of the conditions for the propargylation of 4-oxo-1,4-dihydrocinoline substrates and for the click reaction. Some NHC-CuX complexes showed excellent activity in the CuAAC modification. The developed method provides an extremely simple path to modification of propargyl-functionalized 4-oxo-1,4-dihydrocinoline derivatives, and makes it possible to vary azide radical (R²), which can be a phosphor, labeled or possess new biological properties. Details of the synthesis and the study of the catalytic activity will be reported in the poster session.

References

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SYNTHESIS OF ADAMANTYL DERIVATIVES OF VARIOUS NAPHTHALENE DIOLS

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The naphthalene core exists extensively in natural products and bioactive molecules. [1] A wide application of adamantane derivatives allows to suggest that containing in its structure various naphthalenediols are of definite practical interest. [2]

The interaction of adamantane with ten derivatives of naphthalenediols (1,2-; 1,3-; 1,4-; 1,5-; 1,6-; 1,7-; 1,8-; 2,3-; 2,6- and 2,7-) has not been studied systematically before. We have shown that the interaction of 1-adamantanol (1-AdOH) with naphthalenediols in such acid media as CF₃COOH or CH₃COOH:H₃PO₄ are convenient method of C-alkylation of these compounds with formation mono- and di-adamantyl substituted derivatives. Moreover, we developed environmentally friendly solvent free and metal catalyst free method (1-AdOH with 1-bromoadamantane (1-AdBr) as an alkylation agent in a sealed tube at 200 °C) for the preparation of diadamantyl-substituted naphthalenediols.

Figure 1. Schemes for synthesis of adamantyl derivatives of naphthalenediols.

Thereby, series of fifteen mono- and di-adamantyl-substituted naphthalenediols were synthesized and characterized by 1D and 2D NMR spectroscopy (Bruker Avance III 600, Krasnoyarsk regional research equipment centre of Siberian branch Russian academy of science). [3]

References
HPLC-MS/MS METHODS FOR METHIONINE, INOSINE, NICOTINAMIDE, AND SUCCINIC ACID DETERMINATION IN RABBIT AND HUMAN PLASMA: APPLICATION TO PRECLINICAL STUDY

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Developing and registration process of a new drugs requires to conduct a pharmacokinetic and pharmacodynamic studies in the framework of preclinical and clinical trials. To determine the active pharmaceutical ingredients and biomarkers in physiological fluids and tissues a bioanalytical method is developed and validated in accordance with the European Medicines Agency (EMA) requirements. A special approach is needed for the analysis of endogenous compounds.

The aim of our study was a quantification of four active substances (Figure 1): methionine (MTN), inosine (INO), nicotinamide (NAM), and succinic acid (SuA) in blood plasma. These analytes are endogenous compounds and present in biological matrix in a normal diet.

Figure 1. Chemical structures of MTN, INO, NAM and SuA

Two HPLC-MS/MS methods have been developed and validated for analytes determination in biological samples: the first one for simultaneous analysis of MTN, INO, and NAM, and individual method for SuA analysis.

There are several challenges for these tasks: low sample volume; absence of analyte-free matrix; stability of analytes in whole blood plasma and during sample preparation and analysis; selection of low limit of quantification (LLOQ) according to endogenous level and circadian rhythm.
For the analysis of MTN, INO, and NAM the chromatographic separation was achieved on YMC Triart PFP column (100 ×2.1 mm, 5 μm) in gradient elution mode, the retention times were 0.91; 1.44 and 2.94 min for INO, NAM and MTN respectively. For SuA the YMC Pack-SIL column (100 ×2.1 mm, 5 μm) was used in isocratic mode, retention time was 1.16 min. Mass-spectrometric detection was implemented on API 4000 Sciex triple quadrupole tandem mass spectrometer with atmospheric pressure ionization source. Ions were monitored in a positive (MTN, INO, and NAM) and negative (SuA) modes with transitions: m/z 150.0→104.1 for MTN, m/z 269.1→137.1 for INO, m/z 123.0→80.0 for NAM, and m/z 116.9→72.9 for SuA.

Protein precipitation technique using acetonitrile was employed for both methods. Calibration curves showed linearity in following concentration ranges: 3-100 mkg/mL for MTN, 0.1-50 mkg/mL for INO, 0.2-6 mkg/mL for NAM and 0.3-30 mkg/mL for SuA. The methods allow analyzing small aliquot of biosample: 50 mkl for MTN, INO, and NAM determination; 100 mkl for SuA. Due to absence of analyte-free matrix working solutions and calibration standards were prepared in plasma diluted with water. Quality control samples must be prepared in non-diluted plasma, as a result plasma pool with known endogenous level was spiked with working solution.

MTN, INO and NAM in plasma were found to be stabled up to only 4 hours at 4 ± 2°C. Therefore, the sample preparation, thawing (for three freeze–thaw cycles) for these analytes was carried out at temperature about 4°C. Autosampler stability of MTN, INO, NAM was found for 20 hours at 4 ± 2°C. Stabilities of SuA in plasma at room temperature, in autosampler at 15°C, three freeze–thaw cycles (thawing at room temperature) were examined.

The overall recoveries were 48±9 %, 68±13 %, 63±11 % for MTN, INO, and NAM, respectively, and 100±4 % for SuA. Average endogenous level for each analytes were measured in rabbit plasma, concentration of MTN, INO, NAM, SuA were 5.1-11.8 mkg/mL, 0-3.4 mkg/mL, 0.3-0.6 mkg/mL, and 1.4-3.5 mkg/mL, respectively.

The methods were successfully validated on rabbit and human plasma according EMA and local requirements, applied to preclinical study and could be applied to clinical trials within a Phase I study.
NEW N-SUBSTITUTED DERIVATIVES OF INDOLE-3-CARBOXYL ACID: DESIGN AND SYNTHESIS

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The indole moiety represents certainly an important structural subunit for a large number of natural products and pharmaceuticals [1]. This research presents new N-acyl- and N-sulfonylsubstituted indole-3-carboxylic acid derivatives obtained (received) from commercially available 2-iodoaniline. Palladium (II) phthalocyanine complex was used as a Sonogashira reaction catalyst for the first time at second stage [2].

![Scheme 1. Synthesis of N-substituted derivatives of indole-3-carboxyl acid.](image)

The compounds obtained were characterized by physicochemical methods: FTIR, 1H, 13C NMR spectroscopy, HRMS, and thermogravimetry.

References

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SYNTHESIS OF ETHYNYLPYRIDINE DERIVATIVES

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We have developed a new method for the synthesis of 2-amino-5-aryl-6-(trimethylsilylethynyl) nicotinic acid esters by the reaction of 2-aryl-5-trimethylsilyl-1-ethoxypent-1-en-4-in-3-ones with endiamine hydrochlorides.

![Reaction of Enynones and Endiamines](image)

\[ \text{Ar} = \text{Ph, 4-ClC}_6\text{H}_4, 4-\text{O}_2\text{NC}_6\text{H}_4; \text{R} = \text{H, Me} \]

72–96%

Figure 1. Reaction of Enynones and Endiamines

The reaction proceeds regioselectively with high yields of the corresponding products, and some compounds have noticeable fluorescent properties. It turned out that the best results are achieved at a lower temperature (cf. [1-4]), but, despite the high activity of endiamines, the trimethylsilyl group is retained in the reaction products.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-73-00089).
THE SYNTHESIS OF BENZO[4,5]THIENO[2,3-f]ISOINDOLE-CARBOXYLIC ACIDS BY IMDAV REACTION

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The broad implementation of the [4+2] cycloaddition reactions in advanced organic chemistry paved the way for easily approachable syntheses of heterocyclic scaffolds. The reaction of vinylthiophenes with unsaturated carboxylic acids anhydrides yields thienoisooindole derivatives, a class of compounds that are expected to exhibit biological activity [1].

The recent researches indicate the formation of thieno[2,3-f]isoindole-4-carboxylic acids by interaction of 3-(thien-2-yl)allylamines with maleic anhydride. The initial N-acylation of allylamines is supervened by cyclization of intermediate maleinamides through the step of intramolecular Diels-Alder vinylthiophene (IMDAV) reaction [2].

We successfully managed to expand the described approach to benzothiophene derivatives. 3-(Benzothiophen-2-yl)allylanilines were made to react with maleic anhydrides, a number of benzo[4,5]thieno[2,3-f]isoindole-10-carboxylic acids were obtained in different yields.

Figure 1. The synthesis of benzo[4,5]thieno[2,3-f]isoindole-10-carboxylic acids.

References


Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant No. 17-53-45016).
Electrophile-promoted cyclization of unsaturated compounds is one of the most effective transformation for the synthesis of heterocyclic compounds [1]. Nevertheless, iodoalkynes have hardly been studied as starting materials for the electrophile-promoted cyclization. Pursuing the goal of using diiodoheterocycles in the synthesis of enediynes fused to a heterocyclic core [2], iodine-promoted cyclization of ortho-functionalized iodoethynylarenes could be thought as a convenient synthetic tool towards diiodoheterocycles.

Starting iodoalkynes were prepared by a three-step protocol: the Sonogashira reaction, desilylation and iodination of terminal alkynes. The cyclization study revealed the significant influence of a nucleophilic group nature on the regioselectivity of cyclization. Thus, iodine-promoted cyclization of thioanisole and aniline derivatives was found to be a facile approach for the synthesis of diiodobenzo[b]thiophene and diiodoindole through the 5-endo-dig ring closure, meanwhile 5-exo-dig is a predominant process for “biatomic” nucleophilic functions. Subsequent Sonogashira reaction of 2,3-diiodoheteroindenes proceeded regioselectively affording 2-ethynyl-3-iiodoheteroindenes. Extension of this approach is in progress.

References

Acknowledgements. The research was carried out by using the equipment of the SPbSU Resource Centres: Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for X-ray Diffraction Studies.
EFFECT OF ISOCYANIDES NATURE ON THE REACTION OF BIS-ISOCYANIDE COMPLEXES OF PLATINUM METALS WITH MERCAPTOAZOLES.

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In recent decades, transition metal complexes with aminocarbene ligands (NHC - N-heterocyclic carbenes, ADC - acyclic diaminocarbenes) have taken a special place in coordination chemistry due to their wide application in catalysis, material design and medical chemistry. One of the promising and easy in processing methods for generating complexes with various types of aminocarbene ligands is metal-mediated addition of nucleophiles to coordinated isocyanides.

Recently in our research group it was found that the reaction of Pd\textsuperscript{II} isocyanide complexes with ambident nucleophiles such as aminozoles leads to C,N-chelate carbene complexes, which themselves can act as nucleophiles and react with another moiety of the isocyanide complex, yielding binuclear products [1,2]. In the present work, we have studied the coupling of \textit{bis}(xylisocyanide) Pd\textsuperscript{II} and Pt\textsuperscript{II} complexes (1) with the another type of ambident nucleophiles – mercaptoazoles \textsuperscript{2–6} (Figure 1), which leading to C,S-chelate carbene complexes.

![Figure 1. Reaction. Coupling of bis-(xyllysocyanide) Pd\textsuperscript{II} and Pt\textsuperscript{II} complex with mercaptoazoles.](image)

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-13-00008).
The development of approaches to the design and synthesis of compounds with the ability to molecular recognition is one of the promising directions in modern supramolecular chemistry. Interest in the directed synthesis of multivalent macrocyclic structures is due both to the prospects of practical use and importance for the development of basic science. The tendency to self-assembly and self-association of various cyclophane due to specific and non-specific interactions allows to create synthetic receptor systems that are comparable with natural analogues or have superior properties. The basis for the creation of such multifunctional "hosts" are calix[4]arenes. The main obstacle for the practical application of calixarenes, as well as other numerous cyclophane structures, is their low solubility in water. The introduction of betaine fragments into the structure of macrocycles opens new possibilities for their use due to an increase in water solubility.


The aggregation in water of the obtained betaine derivatives of \textit{p-}tert-butyldihydroxy-calix[4]arene in cone and 1,3-alternate conformation was studied by dynamic light scattering. Ability of the resulting systems to inhibit acetylcholinesterase and butyrylcholinesterase was studied. Acute toxicity in mice of the synthesized compounds was also evaluated.

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SYNTHESIS OF POLYCONDENSED HETEROCYCLES THROUGH REACTIONS OF PARTIALLY HYDROGENATED 2-AMINO[1,2,4]TRIAZOLO[1,5-a]PYRIMIDINES WITH BIELECTROPHILES

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1,2,4-Triazolo[1,5-a]pyrimidines (TP) are purine analogues that are important in agricultural chemistry and medicine [1]. In this report, we describe a new methodology for the synthesis of polycondensed heterocycles based on reactions of partially hydrogenated 2-aminoTP with carbonyl-containing bielectrophiles and discusses its features [2-4].

![Diagram showing the synthesis of various polycondensed heterocycles from 2-aminoTP and carbonyl-containing bielectrophiles.]

Figure 1. Synthesis of various polycondensed heterocycles from 2-aminoTP and carbonyl-containing bielectrophiles.

References

This work was supported by the Russian Science Foundation (project No 14-23-00078) and Russian Foundation for Basic Research (project No 13-03-00253).
The classic Castagnoli-Cushman reaction (CCR) represents a lactam synthesis, based on interaction of succinic or glutaric anhydride and imines. In this study six novel spiro-annelated analogs of glutaric anhydride (1-6) were synthesized and tested in reaction with imines (7) to give a series of novel lactams (8-13). Comparing the obtained results with corresponding carboanalogs (n=1, X=Y=CH₂), it was demonstrated that heteroatoms (X,Y=O,S) and ring size of spirocyclic system dramatically affect the yield and scope of applicable imines for CCR. In this case novel compounds with sulfur and oxygen atoms showed significantly higher reactivity in the Castagnoli-Cushman reaction. All products were fully characterized and their trans-configuration was supported by X-ray analysis data.

References

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FLUORINATED α-BROMOENONES
IN REACTIONS WITH C-NUCLEOPHILES


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Fluorine-bearing compounds have a wide range of applications in the pharmaceutical industry, agrochemistry, and materials science due to unique properties provided by fluorine presence. Among such type of compounds the trifluoromethylated derivatives (including halogenated CF₃-ketones) have received a great attention [1]. The conjugate nucleophilic addition to functionalized enones is a straightforward method for the carbon–carbon or carbon–heteroatom bond formation.

In this context, we studied the reaction of fluorinated α-bromoenones 1 with carbon-centered nucleophiles. Malonate derivatives 2 react with enones 1 to give corresponding cyclopropane derivatives 3 in good yields (Figure 1, direction A). In all cases cis-stereoisomer was isolated as a sole product.

Organomagnesium bromides in the reaction with the same enones 1 undergo either 1,4- or 1,2-addition (Figure 1, direction B). The regioselectivity of reaction depends strongly on the nature of the Grignard reagent [2]. Thus, arylmagnesium bromides 4d-f give 1,4-adduct as a dominant product while in the case of alkyl-, alkenyl-, and alkynylmagnesium bromides 4a-c the ratio is shifted towards 1,2-adduct. The stereo- and regioselectivity as well as mechanisms of reactions are discussed.

![Figure 1. Reaction of CF₃-α-bromoenones 1 with C-nucleophiles.](image)

References


Acknowledgements. This work was supported by the Russian Foundation for Basic Research (projects No 18-33-00119 and 19-03-00206).
Bis(imino)acenaphthenes (BIANs) are highly conjugated, redox active, and sterically bulky α-diimines that have been used widely as bidentate ligands in coordination chemistry and catalysis. The key characteristic of BIANs as strong π-acceptor molecules is their ability to reversibly accept up to four electrons and reversibly exchange them with the coordinated metal, that can facilitate redox based chemical processes [1]. Indeed, BIANs have been shown to be active in many catalytic transformations. In addition, a reversible intermolecular metal-to-ligand electron transfer (redox isomerism) has been established in such metal complexes [2].

In this work, the octahedral complex [Rh$^{III}$(dpp-bian)(H$_2$O)Cl$_3$] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and the square pyramidal complex [Rh$I$(cod)(dpp-bian)Cl] (cod = 1,5-cyclooctadiene) have been synthesized from rhodium trichloride and bis(1,5-cyclooctadiene)dirhodium(I) dichloride, respectively. Heteroleptic complexes [Pd(dpp-bian)(dmit)] and [Pd(dpp-bian)(dsit)] have been obtained by the reaction of [Pd(dpp-bian)Cl$_2$] with (TBA)$_2$[Zn(dmit)$_2$] or (TBA)$_2$[Zn(dsit)$_2$]. The complexes have been characterized by IR, UV/vis and NMR spectroscopies, ESI-MS, elemental analysis and cyclic voltammetry (CV). Their molecular structure has been determined by single-crystal X-ray analysis. The CV of all complexes show reversible redox events assigned to reduction of the dpp-bian ligand. DFT calculations have been performed to interpret redox behavior of the complexes in solution. The complex [Rh$^{III}$(dpp-bian)(H$_2$O)Cl$_3$] shows catalytic activity in electrochemical reduction of CO$_2$. 

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Figure 1. Molecular structures of [Rh$^{III}$](dpp-bian)(H$_2$O)Cl$_3$] and [Pd(dpp-bian)(dmit)].

References

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NOVEL SYNTHESIS OF 2-HALO-2H-AZIRINES AND THEIR APPLICATION IN SYNTHESIS OF AZIRINE DERIVATIVES


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2H-Azirines are valuable synthetic intermediates widely used in the preparation of various nitrogen-containing compounds [1]. In this work, a convenient and efficient synthesis of 2-halo-2H-azirine-2-carboxylic acid derivatives via catalytic isomerization of readily available 5-heteroatom-substituted isoxazoles has been developed. The reaction makes use of cheap Fe(II) salts as catalysts and can be conducted on a gram scale.

We also studied the reactivity of obtained 2-halo-2H-azirines in nucleophilic substitution reactions. Using appropriate nucleophiles, 2-acyloxy, 2-azolyl, 2-sulfonyl, 2-fluoro-2H-azirines were synthesized in good yields. According to the DFT calculations, the formal substitution of the halogen in these reactions proceeds via an unusual S_N2'-'S_N2' cascade mechanism.

References

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RADICAL-MEDIATED DEAROMATIZATION OF INDOLES WITH SULFINATE REAGENTS AND PHOSPHITES FOR THE SYNTHESIS OF FLUORINATED AND PHOSPHONATED SPIROCYCLIC INDOLINES.

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The spirooxindole scaffold is frequently found in natural products and biologically active compounds¹. Some pharmaceuticals containing spirooxindole motif were also reported, stimulating a great interest in construction and modification of this skeleton². However only few works were done to replace the carbonyl in position 2 by another valuable functional group³.

Considering the importance of CF₃, CF₂H and PO(OR)₂ groups in therapeutic and radical chemistry, we believe that the diastereoselective introduction of these functional groups into the structure of spiroindolines can lead to compounds of biological interest. Based on the recognized expertise of our group in the creation of spiroindoline compounds using the umpolung of indole, we developed a simple and efficient diastereoselective method for the synthesis of fluorinated and phosphonated spirocyclic indoline using respectively sulfinate reagents and CAN* as oxidant [⁴] or phospithes and Mn(OAc)₃ [⁵].


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SUPRAMOLECULAR STRUCTURE OF NEW PHOSPHORYLATED 1,2,4-TRIAZOLES

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1,2,4-triazole-3-thions possess a rich spectrum of biological activity [1,2], which makes the synthesis of new structures, in particular, containing the pharmacophoric phosphoryl group, the advanced direction. According to previously published synthesis [3], a number of new 1,2,4-triazoles derivatives was obtained by the heterocyclisation of phosphorylated thiosemicarbazides.

Here we present the results of X-ray analysis of new phosphorylated 1,2,4-triazole with the functionalization on N- and S-atoms. The interesting feature of the crystals of these compounds is the formation of hydrophobic and hydrophilic areas due to the presence of a bulky diphenylphosphoryl fragment in the molecules. The geometry of molecules, intermolecular interactions and packing in the crystals of various forms will be discussed in the report.

References

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2\(H\)-AZIRINES IN A NOVEL SYNTHESIS OF 5-AMINOBUTENOLIDES

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A butenolide (2-furanone) ring is often found in a variety of pharmaceuticals and naturals products, including vitamin C, lanthellidone G, lanthellidone H, rofecoxib, PD 156707, butyrolactone I. Besides, butenolides due to high reactivity of the lactone ring serve as important synthetic building blocks in organic synthesis.

5-Aminobutenolides being hardly accessible compounds are of particular interest as scaffolds in diversity-oriented synthesis and compounds with useful biological properties.

In this work an effective synthetic scheme for the preparation of fully substituted 5-aminobutenolides based on the new reaction of 2\(H\)-azirines is described. The method uses commercially available starting materials and provides high yields of the products at each step of the synthesis. The key step of the scheme is the base-promoted cyclocondensation of the 2-bromo-2\(H\)-azirine-2-carboxylates with functionally substituted carboxylic acids. The scope and limitations of this domino reaction as well as its mechanism are discussed.

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UNUSUAL PSEUDOPOLYMORPHIC BEHAVIOR OF THE PHENYL-SUBSTITUTED THIOSEMICARBAZIDE DERIVATIVE

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By the modification of diphenylphosphoryl acetic acid hydrazide (fosenazid, active pharmaceutical ingredient) with thiosemicarbazide fragment a series of new phosphorylated thiosemicarbazide derivatives was synthesized [1]. Establishing of the molecules geometry and the crystal structure of compounds with potential pharmacological properties, the study of solid state phase behavior is important and is one of the directions in the development of new polyfunctional biologically active compounds.

It was established that, by varying the nature of the solvent, it is possible to purposefully obtain various crystalline modifications, both in individual form (polymorphs) and in crystal solvates (with acetone, methanol and two different types with DMSO). The structures of individual forms and its various solvates were determined by the method of a single X-ray analysis. The geometry of molecules, intermolecular interactions and packing in the crystals of various forms will be discussed in the report. To study the possible solid-phase phase transitions, all modifications were investigated by DSC and powder X-ray diffraction, the results of which will be presented in a report.

References

Acknowledgements. Crystallographic study was funded by Russian Foundation for Basic Research according to the research project № 18-33-00228
SYNTHESIS OF N-(SILYLMETHYL)BENZENESULFONAMIDES

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N-(Silylmethyl)-4-chlorobenzenesulfonamides 1-5 were obtained by interaction of 4-chlorobenzenesulfonic acid chloride with N-(silylmethyl)amines (Scheme 1). The reaction proceeds in benzene solution at room temperature with using an excess of triethylamine as an acceptor of hydrogen chloride. N-(Silatranylmethyl)-4-chlorobenzenesulfonamide 6 was prepared as result of the treatment of N-[(trimethoxysilyl)methyl]-4-chlorobenzenesulfonamide by tris(2-hydroxyethyl)amines. The interaction of N-methyl-N-(trimethylsilylmethyl)amide of 4-chlorobenzenesulfonic acid with amines lead to form the corresponding N-methyl-N-(trimethylsilylmethyl)amides of 4-aminobenzenesulfonic acids 7-10. The structure of the synthesized compounds was confirmed by NMR and IR spectroscopy.

Scheme 1. Synthesis of N-(silylmethyl)benzenesulfonamides

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SYNTHESIS OF 2-(ARYLAMINO)ACETOHYDRAZIDE DERIVATIVES AND PRELIMINARY ASSESSMENT OF THEIR BIOPROPERTIES

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Acyl hydrazines have high phytotoxicity and have been proposed for use as herbicides [1], and among 1,3,4-oxadiazole derivatives a number of biologically active compounds have been found, which are used not only in medicinal practice, but also in agriculture [1-5].

For the purpose to synthesize new biologically active compounds, the functionalization of 2-(arylamino)acetohydrazides were carried out, and the corresponding acyclic N’-benzylidene-2-(phenylamino)acetohydrazides and N’-(4-oxopentan-2-ylidene)-2-(phenylamino)acetohydrazides were obtained. Heterocyclization of the same hydrazides afforded 5-((phenylamino)methyl)-1,3,4-oxadiazole-2(3H)-thiones, and the alkylation of latter led to S-alkyl substituted derivatives.

The synthesized compounds demonstrated a stimulating effect on plant growth. The substances with the activity higher than 80% (compared to heteroauxin) were selected for deeper study and further field trials.

Available at http://www.alanwood.net/pesticides/class_pesticides.html.
COLCHICINE-BASED LIPID PRODRUGS AS EFFECTIVE ANTICANCER AGENTS

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Two examples of heterocyclic colchicinoid-based lipid prodrug were synthesized. The corresponding prodrugs were incorporated into enzyme-responsive liposomal nanocarriers. The lipid forms were designed to address important issues: to be hydrolyzable with PLA2 – enzyme, accompanying inflammation and cancerogenesis process, and to release an active compound by action of unspecific esterases.

Fig 1. Structural design of a colchicinoid-containing phospholipid
Scheme. 1. Active colchicinoids and their lipid prodrugs.

References
During the two last decades, gold homogeneous catalysis of organic transformation has been developed into a highly useful tool for the construction of valuable synthetic building blocks [1]. Au-catalyzed oxidation procedures using N-O species as oxygen donors were established, which strongly enriched the field of oxidation chemistry [2]. Notable results were obtained by Hashmi and co-workers who developed an Au-catalyzed acid-supported approach to glyoxals via oxidation of terminal alkynes using pyridine N-oxide derivatives as convenient oxygen carriers [3]. Later, we expanded this strategy to obtain 1,2-diaryldiketones from internal alkynes [4]. A significant drawback of the last two approaches is the need to use stoichiometric quantities of strong acids (TfOH, Tf2NH), which limits the reaction scope.

We have developed an efficient acid-free gold(I)-catalyzed transformation of both terminal and internal alkynes to vicinal dicarbonyl compounds by 2,3-dichloropyridine N-oxide (Scheme). The advantages of this method include mild reaction conditions and high functional-group tolerance with good yields of target compounds at the same time.

![Scheme]

References

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SYNTHESIS OF NEW DERIVATIVES OF 1,3,4-OXADIAZOLES

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Heterocyclic compounds, in particular oxadiazoles and their derivatives, are an important area of research attracting the interest of a large number of scientists. As is known, compounds containing an oxadiazole moiety in their composition have a wide range of a wide variety of biological active properties, including anti-inflammatory, antimicrobial, analgesic, anti-parkinsonian, anticonvulsant, antimalarial, hypotensive, antioxidant, anti-tuberculosis, sedative, etc. Oxadiazole derivatives are also used as bleaching agents, inhibitors, pesticides, etc. \cite{1}.

This paper presents the synthesis of a new compound, the ethylene derivative of 1,3,4-oxadiazole from commercially available 2-iodobenzoic acid (1) in three stages.

At the first stage, 2-iodobenzohydrazide was synthesized under one pot from 2-iodobenzoic acid with the help of thionyl chloride (SOCl\textsubscript{2}) and hydrazine hydrate. At the next stage, we modified the literature method of synthesis 1,3,4-oxadiazoles, combining the stages of obtaining diarylhydrazines and their cyclization \cite{2}. Also, by optimizing this reaction, the addition of solvent and base was excluded. In summary, benzoyl chloride was added with stirring to a solution of 2-iodobenzohydrazide in POCl\textsubscript{3}, followed by keeping the mixture for 3 hours at 110 °C. As a result of oxidative cyclization, 2-(2-iodophenyl)-5-phenyl-1,3,4-oxadiazole (3) was obtained; the yield was 55%.

For the introduction of the vinyl fragment, we used the Heck reaction on a palladium catalyst in DMFA with 2- (2-iodophenyl) -5-phenyl-1,3,4-oxadiazole (4) and ethylene.
Figure 1. Obtaining ethylene derivative of 1,3,4-oxadiazole.

All synthesized compounds were characterized using modern methods of analysis.

References:

STABLE INTERMEDIATES IN THE REACTION OF DIRECT C–H PHOSPHORILATION OF AZINES

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The azines containing the C – P bond are increasingly used as effective ligands for metal complex catalysts, components of optoelectronics, and are widely used in organic synthesis. Phosphonate fragments are present in many biologically active compounds that exhibit antiviral, antibacterial and anti-cancer activity.

However, traditional methods for the synthesis of phosphorylated azines are based on the use of halides and organometallic reagents, which is accompanied by the formation of difficult to dispose of wastes.

One of the atom economy variations of cross-coupling, which does not require the use of halides and transition metal catalysis, is the aromatic nucleophilic substitution reaction of hydrogen (\(S^\text{N}_\text{H}\)) [1]. \(S^\text{N}_\text{H}\) - reactions proceed through a stage of formation of an intermediate \(\sigma^\text{H}\) - adduct, which can be selectively oxidized to the desired product at the anode under the conditions of electrosynthesis [2].

\[
\begin{align*}
\text{Het} + \overset{\text{R}}{\overset{\text{P}}{\text{O}}} & \rightarrow \overset{\text{Het}}{\overset{\text{H}}{\overset{\text{P}}{\text{O}}} \overset{\text{R}}{\text{H}}} \\
\text{Anode} & \rightarrow \overset{\text{Het}}{\overset{\text{P}}{\text{O}}} \overset{\text{R}}{\text{R}}
\end{align*}
\]

In order to obtain quantitative data on anodic dehydroaromatization of azines, and to estimate effects of both electronic and steric factors on oxidation of these compounds, a series substituted dihydroazines have been synthesized. The compounds were studied in detail using physicochemical and electrochemical methods of analysis. This allowed us to develop a simple, convenient, selective method for electrochemical C – H phosphorylation.

References

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SYNTHESIS OF NEW HETEROMETALLIC CUBANE-TYPE CLUSTERS

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A large variety of heterometallic cubane-type clusters \{M_3S_4M'\} (M = Mo, W; M' = transition metal) with relevance in bioinorganic chemistry and organic catalysis are known\(^1\). These species are easily accessible by direct incorporation of a metal atom in low oxidation state (zero to two) into homometallic \{M_3S_4\} clusters (M = Mo, W) as represented at Figure 1.

In this work we report reactions of trinuclear complexes, [M_3S_4(dbbpy)_3Cl_3]PF_6 and [M_3S_4(py)_3(acac)_3]PF_6 (M = Mo, W), previously prepared in our laboratory\(^3\), with Pt(PPh_3)_4, Au(PPh_3)Cl and Ag(CF_3SO_3) as heterometal M' sources. New heterometallic complexes of general formula [M_3S_4(M'PPh_3)(L^1)_3(L^2)_3]^n+ (M' = Pt, Au, Ag; L^1 = py, dbbpy; L^2 = acac, Cl; n = 1-2) have been isolated and thoroughly characterized by X-ray single crystal analysis, multinuclear NMR and IR spectroscopies, ESI-MS, cyclic voltammetry and elemental CHN analysis.

The obtained complexes were tested as catalysts in C-H bond activation processes.

![Figure 1. General scheme for preparation of \{M_3S_4M'\} clusters.](image)

References

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Ru(II)-ARENE COMPLEXES WITH LONIDAMINE AND BEXAROTENE LIGANDS: STABILITY AND BIOLOGICAL ACTIVITY

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After platinum drugs widely used in the cancer chemotherapy, the most promising compounds are Ru(II)-arene complexes such as RAPTA-C. Earlier we reported analogues of RAPTA-C with biologically active targeting ligands [1] based on lonidamine and bexarotene (compounds with well-known tumor specific molecular targets). It was reported earlier that Ru(II)-arene complexes with heterocycle ligands may enter in ligand exchange reactions with coordinating solvents, for example, water or DMSO. To increase the stability of our complexes with bioactive targeting ligands we replaced chloride ligands with a ligand that can resist hydrolysis or fast ligand exchange.

For all Ru(II)-arene complexes cytotoxicity were studied by MTT-test using a small library of the human cancer cell lines, the lipophilicity of complexes with oxalate moiety 4-6, 13-15 was determined by HPLC. Stability of new compounds was investigated in DMSO containing solutions, it was shown that our complexes resistant for ligand exchange reactions.

References

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SYNTHESIS AND TRANSFORMATIONS OF NEW ISOXAZOLIDINES

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Today 1,3-dipolar cycloaddition of nitrones to unsaturated compounds is one of the most universal and convenient methods of synthesis of N,O-containing heterocycle structures, including isoxazolidines [1]. The special interest is in research of new ways of synthetic application for this cycloadducts, which are supposed to be perspective substrates for obtaining of different classes of organic compounds, which were hard-accessible before [2]. The aim of this work is to investigate regio- and stereoselectivity of 1,3-dipolar cycloaddition of arylpropenones with nitrones and to study subsequent transformation of formed isoxazolidines.

Figure 1. Synthesis and reactions of isoxazolidines

It was found that the cycloaddition of nitrones with 1,3-diarylpropenones proceeds regio- and stereoselectively giving isoxazolidines as a single diastereomer. The reduction of the isoxazolidines was carried out with various reagents. It was shown that the reaction with NaBH₄ proceeds with the formation of bicyclic 6-oxoperhydrofuroisoxazoles. Upon reduction of isoxazolidines with zinc in acetic acid 1,3-amino alcohols are produced, further cyclization of which leads to formation of α-amino lactones.

References
SYNTHESIS AND BIOLOGICAL ACTIVITY OF ALKYL-2-DIARYLMETHYLENEHYDRAZONO-5,5-DIMETHYL-4-OXOHEXANOATES

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New alkyl-2-diarylmethylenehydrazono-5,5-dimethyl-4-oxohexanoates were obtained by the reaction of decyclization of various hydrazonofuranones under the action of alcohols (Figure 1). It was shown that compounds of similar structure possess various types of biological activity with low toxicity [1, 2]. The chemical properties and biological activity of hydrazonofuranone derivatives with an alkyl substituent in the fifth position of the cycle are not investigated.

Figure 4. Decyclization of various hydrazonofuranones under the action of alcohols.

The structure of the synthesized compounds was confirmed by the data of IR, $^1$H NMR spectroscopy, and mass spectrometry. According to the spectral data, the obtained esters exist in enhydrazine (A) and hydrazone (B) forms in
solution. A pharmacological screening of the synthesized compounds was carried out.

References

SYNTHESIS OF PHOSPHINE LIGANDS FROM CALCIUM CARBIDE AND PHOSPHORUS COMPOUNDS

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In the contemporary period of science development phosphine ligands are very demanded substrates. Their gold (I) coordination complexes demonstrate antitumor activity and this is why they can be used for the mechanistic investigations [1]. Especially valuable are bidentate organophosphorus compounds due to a plethora of application ways. The most significant among them are extraction, creation of ion-selective electrodes and medical treatment [2], [3].

There is still no effective method for producing such compounds. Michaelis-Arbuzov reaction is at the core of already existing methods, which allow obtaining bidentate phosphorus ligands, but the yields of the products are below 70%. Therefore, new methodology of the synthesis has been developed. It requires available and cheap calcium carbide and phosphorus compounds and implies the incorporation of the acetylene fragment (fig.1). The yields are around 96% and the purity of the products is sufficient.

![Synthesis of bidentate phosphine ligands with its further reduction.](image)

Figure 1. Synthesis of bidentate phosphine ligands with its further reduction.

References
SYNTHESIS OF N-CYANOMETHYL SALTS OF α-PICOLINES AND THEIR INTERACTION WITH ENAMINONES

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Quaternary salts of pyridines are excellent substrates for the creation of various heterocyclic systems. We recently showed that the interaction of 4-substituted N-(cyanomethyl)pyridinium salts with vinamidium perchlorates or enaminones leads to the formation of pyrido[2,3-b]indolizine-10-carbonitriles - compounds with highly potent optical properties. We continued our research on the N-cyanomethyl salts of α-picoline.

Salts 1 were synthesized through alkylation of corresponding 2-methylpyridine with bromoacetonitrile.

Scheme 1. Synthesis of N-(cyanomethyl)pyridinium salts 1.

The reaction of salts 1 with enaminones 2 in the presence of sodium acetate did not give the expected pyridoindolizine-10-carbonitriles 3 but proceeded with the formation of pyrido[2,3-b]indolizines 4.


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Heteroleptic C,N-cyclometallated platinum(II) complexes \([\text{Pt}(\text{C}^\text{N})(\text{L}, \text{L}')]^2\) have an ability to luminesce in the whole visible spectrum region. The wavelength of the emission are modulated by the variation of the cyclometallated \((\text{C}^\text{N})\) and auxiliary \((\text{L}, \text{L}')\) ligands [1]. Addition of the strong \(\sigma\)-donor ligands – particularly, isocyanides – leads to an increase of energy difference between HUMO and LOMO, shows blue-shifted emission maximum and makes it possible to get highly phosphorescent emitters with emission maximum in the blue to red region.

In this work we have synthesized isocyanide cyclometallated platinum(II) complexes [(ppy)Pt(CNCy)\(_2\)](OTf) and [(ppy)Pt(PPh\(_3\))(CNCy)](OTf) (Hppy = 2-phenylpyridine, yield 70–90\%). The obtained compounds were characterized with ESI\(^+\)-MS, IR, \(^1\)H, \(^{13}\)C\\(^{\{}\)\(^\text{H}\}\) and \(^{195}\)Pt\\(^{\{}\)\(^\text{H}\}\) NMR spectroscopies. The structures were confirmed with the X-ray diffraction method.

Figure 5. Scheme of synthesis cyclometallated platinum(II) complexes with isocyanide ligands

References

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Compounds containing activated triple bond are widely used in the creation of new materials and in the total synthesis of natural compounds. A special place in the series of electrophilic-activated acetylenes is occupied by the derivatives of propargyl aldehyde – compounds containing in their structure a sterically available aldehyde group coupled with a triple bond. We have studied the interaction of aldehydes 1 with Meldrum acid 2, malononitrile 3, malonic 4 and barbituric 5 acids. These reactions occur in different conditions (catalysis with MeONa, the exposure with AcOH within a few days or without catalyst at all) and lead to the formation of enins with electron acceptor groups 7–10.

As a result of the interaction of aldehydes 1 with malonic acid 4 in the presence of substituted pyridines 6, previously indescribable betaines are formed 11. The resulting compounds can be subjected to further interaction on unsaturated bonds to obtain biologically active derivatives.

References
SYNTHESIS OF NOVEL PORPHYRIN-FULLERENE DYADS FROM AB₂C-TYPE PORPHYRIN PRECURSORS

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Investigation of porphyrin-fullerene dyads is an important direction in the field of solar energy conversion: materials based on such compounds can be used in photovoltaic devices and in photocatalysis [1]. The rates of photoinduced processes occurring in such molecules are described by Marcus electron transfer theory [2], they depend on the structural parameters of compounds such as distance between the chromophores and their electron interactions [3]. We propose new synthetic protocol for porphyrin-fullerene dyads with different chromophores separation distance which is provided by the variation of the spacer between donor and acceptor moieties.

Figure 1. Structure of the porphyrin-fullerene dyads.

The proposed approach allows modification of the electronic structure and nature of the intermolecular interactions of the target compounds by introducing various substituents either into the porphyrin or to the aziridine fragment, which makes it possible to expand the library of porphyrin-fullerene dyads for the further study of the electron transfer photodynamics dependence on the structure of molecules.

References

Acknowledgements. The studies were carried out using the equipment of resource centers of the Research Park of St. Petersburg State University "Magnetic Resonance Research Methods", "Substance Composition Analysis Methods", "Chemistry Education Resource Center"
The work is devoted to the investigation of the interaction of pyrazoles with rhodium(II) α-iminocarbenoids generated from 1-sulfonyle-1,2,3-triazoles. It was shown that the result of the reaction significantly depends on the nature of the substituent at the N1-position of pyrazole. In the case of N-arylpyrazoles, the reaction leads to the formation of 2,6,8-triazabicyclo[3.2.1]octa-3,6-diene derivatives in almost quantitative yield. For N-alkylpyrazoles, the reaction does not stop with the formation of the bicyclic product and proceeds further to yield imidazole derivatives in high yields.

Taking into account the availability of the starting compounds, the discovered reaction is a simple and reliable method for the synthesis of previously unknown 2,6,8-triazabicyclo[3.2.1]octa-3,6-diienes and 2-(2-aminovinyl)imidazole derivatives. The study also considers limitations of the methods with regard to the structure of pyrazole, as well as a detailed study of the product formation mechanism, including quantum-chemical calculations. In addition, it has been shown that some bicyclic products can be quantitatively converted to the corresponding imidazoles by heating in the presence of silica gel.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 17-13-01078). This research used resources of “Magnetic Resonance Research Centre”, “Chemical Analysis and Materials Research Centre”, “Centre for X-ray Diffraction Studies”, and “Computing Centre” of St. Petersburg State University.
A condensation of amidoximes with dicarboxylic acid anhydrides represents a general route to 1,2,4-oxadiazole-based acids [1]. Typically this reaction is carried out in “two-step, one-pot” fashion via O-acylamidoxime intermediate generation and subsequent thermal cyclodehydration to the 1,2,4-oxadiazole. A number of reagents have been developed for the room-temperature synthesis of 1,2,4-oxadiazoles: TBAF, TBAH [2] and MOH/DMSO [3]. A mild and efficient protocol for the synthesis of 1,2,4-oxadiazoles containing a carboxyl functionality from readily available starting materials such as amidoximes and dicarboxylic acid anhydrides is highly desirable [4].

Figure 1. Reaction.

In conclusion, an effective, convenient one-pot protocol for the synthesis of 1,2,4-oxadiazoles bearing carboxyl group from bifenyl dicarboxylic acid anhydrides and amidoximes has been developed. We hope that the simple work-up procedure, mild condition (particularly, the ambient temperature), inexpensive and readily available starting materials, and a low-toxicity solvent, will make this method a useful tool in medicinal and process chemistry.

References
SYNTHESIS AND TRANSFORMATIONS OF ADDUCTS OF ITACONIMIDES WITH NITRONES

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Isoxazolidines cause an increased interest due to a wide range of pharmacological properties [1], including antiviral, antibacterial and antitumor activities. 5-Spiroisoaxazolidines have attracted enlarged interest in recent years [2]. High efficiency and selectivity of 1,3-dipolar cycloaddition of nitrones to exocyclic double bonds allows to create complex heterocyclic scaffolds possessing valuable biological properties. Another distinct advantage of isoxazolidines is the possibility of cleavage of N-O bond when acted upon by various reagents to form 1,3-amino alcohols, the subsequent intramolecular cyclization of which can lead to different classes of organic compounds.

The aim of this work is to investigate regio- and stereoselectivity of nitrone cycloaddition to N-arylitaconimides and transformations of obtained spiroisoxazolidines under zinc in acetic acid conditions.

Figure 1. Synthesis and transformations of cycloadducts.

It was found that the cycloaddition reaction proceeds regioselectively and with high diastereoselectivity to form isoxazolidines as a single 5-spiro regioisomer. Also it was found that the reduction of N-O bond gave α-amino lactones or 1,3-amino alcohols depending on the structure of the substrate.

References
SYNTHESIS OF PYRIMIDINES VIA Rh(II)-CATALYZED REACTION OF 1-SULFONYL-1,2,3-TRIAZOLES WITH ISOXAZOLES AND 2H-AZIRINES

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In recent years, the development of new methods for the synthesis of heterocyclic compounds using 1-sulfonyl-1,2,3-triazoles is an actively developing area of organic synthesis [1]. Earlier in our research group, it was shown that Rh(II)-catalyzed reaction of 2-acetyl substituted 2H-azirine 1 with triazole 3 leads to the formation of substituted pyrimidine 4. In this study, it was found that the use of 5-methylisoxazole 2, which is an isomer of azirine 1, as a substrate also leads to the formation of product 4 and gives higher yield of pyrimidine 4 (Fig. 1).

The aim of this work is to develop a method for the synthesis of substituted pyrimidines 5 using above-mentioned reactions. During the study, the most effective catalyst was found and the reaction conditions were carefully optimized. From substituted 3,5-dimethylisoxazoles and 1-sulfonyl-1,2,3-triazoles, a wide range of pyrimidines was synthesized with yields of 40–90%. Much attention was paid to the study of reaction mechanism. The experimental results and the results of DFT calculations evidence in favor of the formation of 1,3-oxazine intermediate in course of the reaction.

Figure 1. Reaction scheme.

References

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SYNTHESIS AND STRUCTURAL STUDY OF POLYNUCLEAR COPPER(II) COMPLEXES WITH HALIDES AND DIALKYL CYANAMIDE NCNR₂ LIGANDS

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Catalysis by copper complexes containing halides and N-donors as ligands is an actual field in chemical redox catalytic processes. Besides that, design of supramolecular structures for catalysis is a rapidly developing area today, and copper complexes can serve as building units for these compounds. Therefore in this work, tetranuclear clusters Cu₄Cl₆OL₄ (L is NCNR₂) were chosen for further design of supramolecular structures and the study of their catalytic activity that is relevant in developing selective catalysts for biochemical processes [1, 2]. The synthetic procedure for tetranuclear complexes is presented on the Scheme 1.

Scheme 1. Scheme of tetranuclear cluster synthesis

The chemical compositions of the synthesized complexes, geometric parameters of crystal structures, the thermal stability of the products, the solvent effect on the composition and structure of products and reactivity of coordinated NCNR₂ will be under discussion.

References

Acknowledgements. This work was supported by the Russian Science Foundation (project No 19-13-00013).
[n]Helicenes constitute a class of polycyclic aromatic molecules in which $n$ ortho-condensed aromatic rings give rise to a helical structure with extended π-system. Initial research was concentrated on carbohelicenes, but recently more interesting physical properties have been observed for the heterohelicenes.$^{[1]}$ However, examples of helicenes based on heterocyclic rings (except of pyridine, pyrrole and thiophene rings) are rare because of the lack of common methods for their preparation.

We developed a general synthetic approach to [4]-, [5]- and [6]helicenes annelated by azine rings (pyridine, pyrazine, quinoxaline) starting from commercially available ortho-dihaloazines (Scheme 1).$^{[2]}$ The effectiveness of the above strategy was demonstrated by the example of the synthesis of pyrazine-fused helicenes.

Scheme 1. Synthesis of pyrazine-fused helicenes.

Physical properties of the azine-fused helicenes 1-4 (UV-vis spectra, cathodic and anodic electrochemistry, X-ray structures) were compared to the parent [n]helicenes to discern the effect of merging an azine moiety within a helical skeleton.

References


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LUMINESCENT DINUCLEAR COPPER(I) HALIDE COMPLEXES BEARING PYRIDYLPHOSPHOLANES

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Complexes Cu(I) based on P,N-ligands attract great interest of researchers due to their remarkable luminescent properties [1]. Recently, we obtained new pyridyl-containing cyclic phosphines - pyridylphospholanes and a number of their luminescent complexes with copper (I) iodide. [2]. This work presents the synthesis of new complexes of phospholanylpyridines with copper (I) halides (Cu(MeCN)$_4$BF$_4$, CuCl and CuBr) (Scheme 1).

Scheme 1. Synthesis of complexes 4-8.

Obtained complexes are charged dinuclear species formed by three molecules of ligands coordinated to two metal ions via both donor atoms. Depending on the crystallization these compounds could be crystallized in two isomeric forms: head-to-head or head-to-tail. In both cases the coordination geometry around each metal atom is different: one being three- and the other one is four-coordinated. All complexes exhibit distinct luminescence in the solid state at room temperature with emission maxima at the range 520-540 nm.

References


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SYNTHETIC AND NATURAL 2-PYRIDONES AS SCAFFOLDS FOR ELABORATION OF ANTI-INFLUENZA AGENTS: FROM IN SILICO PREDICTION TO REAL INHIBITION OF VIRUS REPRODUCTION

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On the basis of data about anti-influenza activity of derivatives of quinolizidine alkaloid (-)-cytisine [1] a virtual library of potential influenza A virus (H1N1) neuraminidase (NA) inhibitors was obtained as a result of the procedure of ‘peripheral design’ (LeadIT software package, ReCore and SeeSAR) of 2-pyridone matrixes I-IV (Figure 1). Docking of all predicted NA ligands into the 4B7R active site of NA of A (H1N1) flu virus (reference ligand zanamivir) was carried out using the software package Schrödinger Suite 2018-4 (Schrödinger, LLC, New York, NY, 2018) in order to identify the molecules with best calculated properties.

Figure 1. Starting quinolizidine matrixes I-IV

Synthetical approaches to the hit-compounds identified on the basis of the docking data have been developed, and potential NA inhibitors have been synthesized (Figure 2).

Figure 2. Potential NA inhibitors – derivatives of 2-pyridone IV

Obtained compounds were studied for their ability to inhibit reproduction of A (H1N1)pdm09 flu virus reproduction (reference drugs were zanamivir and ribavirin); the compounds with selectivity indexes more than 80 were found.

References

This work was supported by RFBR (project No 18-33-00877_mol_a).
SYNTHESIS OF ANTIMITOTIC DRUG CONJUGATES BASED ON PSMA LIGANDS WITH DOCETAXEL

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Methods of selective delivery of drugs and other agents directly to the tumor, including prostate, have been actively developing. A promising protein marker for the diagnosis and treatment of prostate cancer is the prostate-specific membrane antigen, PSMA. The high expression of PSMA in prostate cancer cells compared with normal cells and vascular tumors has made it very promising for study. Urea-based low molecular weight ligands are described, providing selective binding to PSMA, and used to create therapeutic and diagnostic conjugates [1].

The results of docking show that ligands containing dipeptide linkers, based on amino acids (phenylalanine and tyrosine), has good affinity to PSMA and show high selectivity. Also, the modifications of the urea-based vector-molecule with various benzaldehyde fragments has a positive effect on affinity to PSMA. The modifications of urea-based vector and the dipeptide linkers for urea-based ligands PSMA were synthesized and optimized in present work. In vitro series of 24 ligands demonstrates the highest selectivity (IC₅₀ = 22.5 nM and 9.7 nM for LNCaP) were selected, while urea-based ligand without modification has low selectivity (IC₅₀ = 2149 nM for LNCaP). Antimitotic conjugates with Docetaxel were synthesized with high selective ligands.

Docetaxel drug conjugates were obtained and characterized in vitro and in vivo tests. The results show good cytotoxicity (comparable to Docetaxel without modification) and will be presented on the report.

References

This work was done mainly in MSU and kindly supported by Ministry of Education and Science of the Russian Federation (03.G25.31.0219).
The crystallization of ciprofloxacin - an antibacterial fluoroquinolone compound - with salicylic acid resulted in the isolation of five distinct solid forms of the drug, namely, an anhydrous salt, two polymorphic forms of the salt monohydrate, methanol and acetonitrile solvates, and the salt-cocrystal hydrate. The salicylate salts were investigated by different analytical techniques ranging from powder and single crystal X-ray diffractometry, differential scanning calorimetry, thermogravimetric analysis, variable temperature powder X-ray diffraction, dynamic vapor sorption analysis, dissolution, and solubility investigations. Real-time in situ Raman spectroscopy was used to investigate the mechanochemical formation pathways of the different solid polymorphs of ciprofloxacin salicylate. The mechanism of the phase transformation between the crystalline forms was evaluated under mechanochemical conditions. It was found that the formation pathway and kinetics of the grinding process depend on the form of the starting material and reaction conditions. The analysis of the solid-state thermal evolution of the hydrated salts revealed the two-step mechanism of dehydration process, which proceeds through a formation of the distinct intermediate crystalline products [1].

Figure 1. Packing arrangement of [CIP+SA+H2O] (1:1:1) (a) form I and (b) form II.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-00485 мол_а).
A NOVEL SYNTHESIS OF 1,2,4-TRIAZINES

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Earlier we have developed a new synthesis of 1,2,4-triazines by Zn-catalyzed hydroamination of propargylamides with BocNHNH₂ (Fig.1) [1].

![Figure 1. Hydroamination of propargylamides with Boc-NHNH₂ by Zn(CF₃SO₃)₂ catalysis [1]](image)

Based on these results we investigated the hydroamination reaction of a variety of propargylamides (1) with different phenylhydrazines by Zn(CF₃SO₃)₂ catalysis. To our surprise depending on the initial propargylamide the main products of the reaction was N-(phenyl)amino imidazoles (2) on the one hand, and 2-methyl-1H-indoles (3) on the other hand (Fig.2).

![Figure 2. Hydroamination of propargylamides with different phenylhydrazines by Zn(CF₃SO₃)₂ catalysis](image)

References
Cisplatin has expressive cytotoxic, bactericidal and mutagenic properties. The mechanism of action is similar to the action of other alkylating drugs and is a violation of the functions of DNA caused by chemical damage to the DNA bases. At the cellular level, cisplatin causes replication and transcription disruption, leading to cell cycle delay and apoptosis. In recent years, the world's leading medical institutions are trying to find bioactive drugs among other compounds of the platinum group, including palladium. Palladium compounds are significantly less toxic than platinum complexes. The literature also contains information about the high antitumor activity of palladium complexes with organic ligands. A large number of scientific articles are devoted to analogues of cisplatin, in which ammonia ligands are replaced by N-heterocyclic ligands and analogues of cisplatin, which contain heterocyclic ligands having unsaturated substituents, such as substituted vinyls, allyls, allenyls, etc. It is shown that such complexes have antitumor biological activity[1]. Therefore, we decided to synthesize palladium chloride complexes containing terpenyl benzimidazole ligand (Scheme). It is known that terpenyl substituents have the ability to pass through lipid cell membrane some organic molecules for targeted action at the cell biological target. Terpenyl benzimidazole ligand (I) was synthesized as described in the article [2].
Acknowledgements. This work was performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

References
Indoloquinolinones are very important in the fused indole family due to their wide occurrence in numerous bioactive natural products.[1] Isocyanide-based multicomponent reactions (IMCRs) have attracted a lot of attention, due to the fact that versatile functional groups can be introduced in the MCR adducts, which can undergo further condensations or cyclizations reactions leading to an array of structurally diverse scaffolds.[2]
MULTIFUNCTIONAL LIGANDS COMBINING 5-HT\textsubscript{6} RECEPTOR ANTAGONISM, INHIBITION OF CHOLINESTERASES AND BETA-AMYLOID AGGREGATION AS POTENTIAL DISEASE-MODIFYING AGENTS AGAINST ALZHEIMER’S DISEASE

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Alzheimer’s disease (AD) is a fatal neurodegenerative disorder caused by a set of pathological processes including impaired neurotransmission, aggregation of amyloid-β (Aβ) and inflammation [1]. Currently available anti-AD drugs, developed on the one-target one-drug paradigm, do not stop or reverse the progression of the disease. Complex diseases, like AD, require a multi-target approach for effective treatment. Selection of appropriate combination of biological targets to obtain multi-target (multifunctional) molecules able to interfere with several pathological processes at the same time is crucial for the effectiveness of the new therapies. Based on the results of preclinical and clinical trials, we have selected 5-HT\textsubscript{6} receptors, cholinesterases and Aβ as biological targets of key importance for AD [2]. Previously, we have developed the first series of multifunctional molecules combining activities against these three targets [3]. Although the compounds displayed unique pharmacological profile \textit{in vitro} and \textit{in vivo}, their physicochemical and pharmacokinetic properties needed improvement (compound I, Figure 1). Herein we present design, synthesis and biological evaluation of a new set of multifunctional compounds with improved drug-like properties promising for the development of new anti-AD therapeutics.

![Figure 1. Design of new multifunctional ligands addressing disease-modifying and symptomatic targets](image)

References


Acknowledgements. This work was supported by the National Science Centre Poland, grant No 2016/23/D/NZ7/01328.
NEW METHOD OF PRODUCING 5-DIALKYLAMINO-1,2,4-TRIAZOLE
FROM ACYL HYDRAZIDES AND DIALKYLICYANAMIDES

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1,2,4-Triazole and its derivatives represent an important class of five-membered heterocycles. These heterocycles and their derivatives are widely used in materials chemistry (gas adsorbents and separators, components of OLEDs, proton conductive nanotubes), in medical chemistry (display broad spectrum of biological activities) and in synthetic chemistry as synthons for generation of other heterocyclic systems.

This work describes new highly efficient synthetic methodology to preparation of 5-dialkylamino-1,2,4-triazoles from acyl hydrazides and dialkylcyanamides in the presence ZnII [1]. The protocol utilizes simple and readily available reagents and proceeds under mild conditions giving the triazoles in good to excellent yields (76–99%) (Scheme 1). The ZnII-catalyzed reaction proceeds via initial generation of the [Zn{RC(=O)NH2}3](ZnCl4) complexes.

In this work, 17 new 5-dialkylamino-1,2,4-triazoles have been obtained and characterized by a set of physicochemical methods of analyses (HRESI+-MS and IR, 1H, and 13C{1H} NMR spectroscopies; five species were additionally characterized by single-crystal X-ray diffraction (XRD)).

![Scheme 1. Zinc(II)-mediated benzoyl hydrazide–dimethylcyanamide coupling.](image-url)
In order to estimate electronic effects of the substituents at the acyl hydrazide moiety, we performed a kinetic study with a series of para-substituted benzoyl hydrazides. We found that neither the nature of the solvent, nor the substituent electronic effects significantly influence the observed pseudo-first order rate constant \( k \), which is ca. \( 10^{-3} \text{ s}^{-1} \) in all cases (Table 1.). Based upon the kinetic study it can be concluded that electronic effect of substituents in acyl hydrazide do not significantly affect the reaction rate and these data are useful for further control of the coupling.

Table 1. Observed pseudo-first order rate constant.

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<tr>
<th>Nos</th>
<th>R</th>
<th>( k \times 10^{-3} \text{ (s}^{-1}) )</th>
<th>( (\text{CD}_3)_2\text{CO} )</th>
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</table>

In order to estimate electronic effects of the substituents at the acyl hydrazide moiety, we performed a kinetic study with a series of para-substituted benzoyl hydrazides. We found that neither the nature of the solvent, nor the substituent electronic effects significantly influence the observed pseudo-first order rate constant \( k \), which is ca. \( 10^{-3} \text{ s}^{-1} \) in all cases (Table 1.). Based upon the kinetic study it can be concluded that electronic effect of substituents in acyl hydrazide do not significantly affect the reaction rate and these data are useful for further control of the coupling.

Table 1. Observed pseudo-first order rate constant.

[1] Yunusova, S. N.; Bolotin, D. S.; Suslonov, V. V.; Vovk, M. A.; Tolstoy, P. M.; Kukushkin, V. Yu., ACS Omega, 2018, 3 (7), 7224-7234

This work was financially supported by the Russian Science Foundation (grant 17-73-20004). Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).
THE 5-(ARYLMETHYLIDENE)-2,4,6(1H,3H,5H)-TRIONES IN REACTION HETEROCYCLIZATION WITH N-OXIDE MORPHOLINE

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The reaction of 5-(arylmethylidene)-2,4,6(1H,3H,5H)-trions (1-3) with morpholine (4) in the presence of hydrogen peroxide and catalytic amounts Na₂WO₄ ends with the formation of cycloaddition products of substituted 2-aryltetrahydro-1′H,2H-spiro[isoxazole[3,2-c][1,4] oxazin-3,5'-pyrimidine]-2′,4′,6(3′H)-trions (5-7).

Ar=Ph (1,5); 4-MeOC₆H₄ (2,6); 4-Me₂NC₆H₄ (3,7)

It is likely that in the process of interaction of morpholine (4) with hydrogen peroxide and Na₂WO₄, morpholine N-oxide (A) is generated, which is converted into cycloadducts (5-7) as a result of the process of 1,3-dipolar cycloaddition. The structure of the compounds was established by the methods of IR, ¹H, ¹³C NMR, mass-spectrometry, and the composition by elemental analysis.

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SYNTHESIS AND SOLID STATE FLUORESCENCE OF PYRROLE-2-CARBOXAMIDE BF₂-COMPLEXES

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We have synthesized a number of new dyes - BF₂-complexes of pyrrole-2-carboxamides (1), exhibiting fluorescent properties both in solution and in the solid phase. Synthesis of 1 (with a total yield up to 87.5%) was carried out according to the following scheme:

Scheme 1. Route to BF₂-complexes of pyrrole-2-carboxamide

Synthesized dyes exhibit solid-state fluorescence in a wide blue-violet region of the spectrum (with an absorption maximum in the region of 370-404 nm) with a quantum yield up to 40% (Figure 1). The magnitude of the Stokes shift is 38-80 nm.

It should be emphasized that the development of stable blue-light emitting organic diodes is still an urgent task, attracting considerable attention of researchers in this field.

Figure 1. Solid-state fluorescence parameters of synthesized complexes.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-01042).
Today clinically approved Pt(II) anticancer complexes, cisplatin, carboplatin and oxaliplatin, are used in about 50% of all chemotherapeutic regimens. However, they have a lack of selectivity and a number of severe side effects. For the last two decades, octahedral Pt(IV) complexes became an important platform for the development of new anticancer agents due to their kinetic inertness, low general toxicity and a possibility for oral administration.

Combinations of two drugs in one molecule are a widely used approach in modern drug discovery. We introduced lonidamine, a specific inhibitor of aerobic glycolysis in cancer cells, and bexarotene, a selective agonist of retinoid X receptors, as an axial ligand in Pt(IV) complexes [1].

New complexes were characterized by NMR, ESI-MS and elemental analysis. Antiproliferative activity of the complexes was investigated using SW480, A549, MCF7, MCF7D and HaCat cell lines by means of standard MTT colourimetric assay. Investigation of the mechanism of action and results of in vitro and in vivo studies will be presented.

Figure 1. New Pt(IV) complexes with lonidamine and bexarotene ligands.

References:

Acknowledgements. This work was supported by the RSF (project № 19-13-00084).
EFFECT OF PH ON RADICAL REACTIONS OF TRYPTOPHAN AND LYSOZYME PHOTOSENSITIZED BY KYNURENIC ACID

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Human eye lens contains low-molecular mass compounds, kynurenine (KN) and its derivatives, which absorb in UV-A region (315-400 nm) and protect eye tissues from harmful Sun irradiation. KNs are effective molecular UV filters but products of their thermal degradation could act as effective photosensitizers able to generate reactive triplet states under UV-A light. Reactions of these triplets with aromatic amino acid residues (mainly tryptophan, Trp, and tyrosine) yield free radicals within the eye lens, which subsequent reactions could inevitably change the eye lens proteins. As a result lens proteins accumulate various modifications during an individual lifetime that predisposes the eye lens tissue to the development of cataract, which molecular mechanisms are still weakly studied. Oxidative stress is the necessary condition for the cataract onset. Though the origin of oxidative stress formation in a healthy lens is unclear, it could be followed by acidosis, a shift of cell pH to lower values. In this work we studied the influence of pH on the photoinduced radical reactions between Trp-derivatives and kynurenic acid (KNA), one of the most effective photosensitizer of the human eye lens.

Time-resolved optical experiments have shown that pKa value for KNA radical (KNA⁺) is 5.5 and for Trp radicals (Trp⁺) lies in the range of 4-5 depending on a substituent in amino acid backbone. Aqueous solutions of KNA and various Trp derivatives were UV-A photolyzed at three pHs, corresponding to three different pairs of protonated/neutral radicals of KNA and Trp. HPLC-MS analysis of photolyzed samples have shown a decrease of decomposition yield of both reagents at pH<pKa (Trp⁺) without qualitative changes in the composition of formed products. This indicates an acceleration of the back electron transfer rate between KNA⁺ and Trp⁺ with the Trp⁺ protonation that was confirmed by time-resolved experiments.

Experiments with model protein lysozyme have shown that protein environment could significantly redirect the radical reactions even without protonation of Trp⁺ within protein structure. We found that Trp⁺ in lysozyme has pKa of 3.1 and the change of pH from 7 to 5 has no effect on the lysozyme degradation, but largely increases its oxygenation and lowers the formation of covalent cross-links. To clarify pH-influence of the eye lens proteins additional experiments have to be done.

This work was financially supported by Russian Science Foundation (project 18-73-10014).
1-(VINYLHETARYL)ISOQUINOLINES IN THE TANDEM REACTION OF THE ACYLATION / [4 + 2] CYCLOADDITION WITH MALEIC ANHYDRIDE

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The following example describes a rare case of the diastereospecific [4 + 2] cycloaddition of maleic anhydride to 1-(vinylhetaryl)tetrahydroisoquinoline \(2\) [1-3]. 1,2,3,4-Tetrahydroisoquinolines \(2\) were obtained from amides \(1\) by the Bischler-Napiralski reaction, followed by reduction of the C=N bond. The interaction of compounds \(2\) with maleic anhydride proceeds through the stage of nitrogen atom acylation and the subsequent intramolecular Diels-Alder reaction, which allows to obtain polycycles \(3\) or \(4\) as individual diastereomers in one step. Moreover, at temperatures below zero degrees, it is possible to isolate the “non-aromatic” adducts \(3\). At high temperatures, the adducts \(3\) undergo prototropic tautomerism, turning into compounds \(4\) with an aromatic furan (thiophene) cycle. The reaction of transformation \(2\) to \(4\) can be carried out without isolation of intermediate product \(3\).
Reference


*This work was supported by the Russian Foundation for Basic Research, grants. № 17-53-45016 and 16-03-00125.*
Homogeneous gold catalysis provides wide opportunities for heterocycles synthesis from simple organic “building” blocks. In particular, multicomponent reactions of gold-activated acetylenes, pyridine $N$-oxides and nitriles lead to formation of 1,3-oxazole scaffolds with different functional moieties (Figure 1). [1-2].

Figure 1. Gold-catalyzed multicomponent reactions leading to different 1,3-oxazoles scaffolds.

At this work we investigate reactivity patterns of ynamides (acetylenes with amide, sulfonamide or carbamate moiety) in gold-catalyzed multicomponent reaction with pyridine $N$-oxides and cyanamides to achieve 2,4-bisamino-1,3-oxazoles scaffold.

Figure 2. Gold-catalyzed multicomponent reactions leading to 2,4-bisamino-1,3-oxazoles scaffold.

References

This work was supported by Russian Foundation for Basic Research (project No 18_33_00277).
VICINAL SUBSTITUTED ALKENES IN AZA-MICHAEL REACTION:
THE REGIOSELECTIVITY PROBLEM IN NUCLEOPHILIC ADDITION

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Aza-Michael reaction is one of the most widely used in modern green organic synthesis of bioactive compounds. As a rule, it proceeds under mild conditions and does not require the use of toxic solvents and organometallic catalysts. Despite aza-Michael addition has already been studied rather thoroughly, there are some unsolved items. In particular, regioselectivity of the nucleophilic addition to alkenes bearing two vicinal electron-withdrawing moieties is still a challenge task for chemists.

In our work the reactions of primary and secondary amines (benzylamine and morpholine) with acrylic esters bearing acetyl-, cyano-, or trifluoromethyl groups were studied. The influence of the introduction of bulky groups (methyl or phenyl) is also discussed.

To explain the observed ratios of regioisomers, we applied a modified model, which had been originally proposed by Mayr at al. in [1]. We have found that the model is in good agreement with the results obtained.

Figure 1. General scheme of the reaction

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 19-03-00206).
The interaction of 5-acetyl-4-hydroxy-2H-1,3-thiazin-2,6(3H)-dione (1) [1] with cyclohexyl- and benzyl-N-(4-aminophenyl)carbamates (2,3) when boiling in ethanol in the presence of a catalytic amount of glacial acetic acid the corresponding cyclohexyl (benzyl) N-(4-[(E)-1-(4-hydroxy-2,6-dioxo-3,6-dihydro-2H-1,3-thiazin-5-yl) ethylidene]amino)phenyl)carbamates (4,5) were prepared. Boiling the obtained Schiff bases (4,5) in DMF for two hours is accompanied by release of COS and the formation of cyclohexyl (benzyl) N-{4-[6-methyl-2,4-dioxo-3,4-dihydro-1(2H)-pyrimidinyl]phenyl}carbamates (6,7) (Figure 1).

![Reaction scheme](image_url)

Figure 1. Synthesis of uracils with phenylcarbamate fragment.

Structure of the compounds (4-7) was confirmed by $^1$H, $^{13}$C NNR spectroscopy.

References

Acknowledgements. The work was financially supported by the Ministry of Education and Science of the Russian Federation (project no. 4.9288.2017BCH).
4 section

COMPUTER MODELING AND CHEMINFORMATICS
EXTENDED INTERACTIVE GREENE’S REACTIVITY CHARTS

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Multi-stage organic synthesis very often leads to using protective groups for selective blockade of undesirable interactions with certain functional groups. Chemists usually obtain information on the reactivity of protective groups either on the basis of their own experience or on the basis of such literary sources as "Greene's Protective Groups in Organic Synthesis" [1]. Unfortunately, in the latter case, it is not clear how the authors assessed the reactivity of the protective groups in one-step and selective reactions with molecules containing several protective groups. In addition, it is not indicated what exactly the number of reactions was the basis for the conclusion about the degree of reactivity of a particular protective group.

The use of chemoinformatics methods allowed us to overcome these shortcomings [2] and create spreadsheets, equivalent to tables from Greene's book [1]. As a source of data, we used the dataset of one-step catalytic hydrogenation reactions, which was extracted from Reaxys database [3]. Retrieving information about the reactivity of the protective groups included the following steps. The protective group and its class were determined (namely, the protective group leaves or remains) by using the Condensed Graph of Reaction (CGR) approach [4] and the substructural search. Reaction conditions were pre-standardized using a synonyms dictionary that includes “raw” and “standard” compound names.

Moreover, we expanded our equivalent of Greene’s Reactivity Charts by adding some interesting, frequently occurring combinations of conditions, for example, Pd with amines. The results of this system are presented in the form of a web interface containing a list of accessible protected groups for catalytic hydrogenation reactions and an interactive table including the reactivity estimates of the protective groups (corresponding to those presented in Greene).

This system is fully automatic, in addition, it allows us to look in Reaxys, on the basis of what kind of reactions was made predictions about the reactivity of protective groups.

References

Acknowledgements. This work was supported by Foundation the the Ministry of education, youth and sport of Czech Republic, agreement number MSMT-5727/2018-2 and by the Ministry of Education and Science of the Russian Federation, agreement No 14.587.21.0049 (unique identifier RFMEFI58718X0049).
MODELING THE BASIS OF HOMODESMIC REACTIONS
OF CHEMICAL COMPOUNDS

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Thermodynamic calculations are a common and important element of many chemical studies. They underlie the development of highly efficient technologies for the industrial synthesis of compounds. Thus, it becomes necessary to accumulate reliable information about the thermodynamic properties of individual substances [1]. Experimental data on thermodynamic properties are available for a limited number of compounds, and therefore the development and improvement of methods for calculating thermodynamic quantities is an important and urgent task. The development of computer technology and the development of new quantum-chemical methods allows one to carry out theoretical calculations of the thermodynamic properties of chemical compounds with an accuracy comparable to experimental errors.

The principle of maximum similarity, implemented in the form of the concept of isodesmicity, was proposed as early as the 70s of the last century. This approach proved to be very fruitful for analyzing the relationship between the structure of organic compounds and their energy content, but the accuracy of thermochemical calculations was limited to a low level of development of computational quantum chemistry. It was quickly found out that the quality of calculations can be improved by adding to the set of balances of the isodesmic reaction with the requirement of group balance. This approach was called homodemic [2-3]. Any chemical compound can be represented as a molecular graph. The vertices of the graph are the atoms that make up the molecule, the edges are the bonds between the atoms. The experience of using the homodemic method has shown a high reliability of the theoretical prediction of the enthalpies of formation of various compounds.

References

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-07-00584 A).

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MOLECULAR DYNAMICS SIMULATIONS OF GAS PERMEABILITY IN THERMOPLASTIC R-BAPB POLYIMIDE

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Gas separation is among the key processes in chemical and petrochemical industry. During recent years polymer gas separation membranes have emerged as a promising class of materials in various applications including air enrichment with oxygen, extraction of such valuable resources as helium and hydrogen and reduction of carbon dioxide emissions into the atmosphere. Along with improving transport properties of the existing polymers, another important problem is developing new polymers with high selective properties. Aromatic polyimides (PI) are widely used to create such polymeric gas separation membranes due to their unique physico-chemical properties. Various methods are actively used to access this issue. Recent years have seen active development of computer simulations methods employing fully-atomistic models to evaluate transport properties of various polymers. In the present work, molecular dynamics simulations are for the first time used to determine transport properties of promising crystallizable thermoplastic R-BAPB PI synthesized from 1,3-bis(3', 4-dicarboxyphenoxy) benzene (dianhydride R) and 4,4'-bis-(4 '-aminophenoxy) diphenyl) (diamine BAPB) in the Institute of Macromolecular Compounds. For this purpose diffusion coefficients and solubilities of various gases including helium (He), oxygen (O2), nitrogen (N2) and methane (CH4) were determined. It was found that R-BAPB PI has a high selectivity with respect to He/CH4, which makes it a promising candidate to be used for the separation of helium from natural gas. The results of computer simulations are in good agreement with the recently obtained experimental data, which provide a strong basis for further investigations of transport properties of nanocomposites based on R-BAPB PI by means of molecular dynamics simulations.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (RFBR), (grant No. 18-29-17040). The simulations have been performed using the computational resources of the Institute of Macromolecular Compounds of the Russian Academy of Sciences, Lomonosov-2 supercomputer at Moscow State University, Joint Supercomputer Center of the Russian Academy of Sciences and resources of the federal collective usage center “Complex for Simulation and Data Processing for Mega-science Facilities” at NRC “Kurchatov Institute” (http://ckp.nrcki.ru/).
MOLECULAR DYNAMICS SIMULATIONS OF WATER/HYDROCARBON MIXTURE IN PRESENCE OF DIFFERENT SURFACTANTS

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Studying of the confined water/hydrocarbon mixtures is important for understanding and improving of the ways of oil recovery. The extraction of hydrocarbons from narrow pores is an essential problem for oil production industry. Methods of computer modeling allow one to describe different interactions between water solution and adsorbed hydrocarbon nearly solid surface of the different nature and define proper conditions for oil recovery.

In this work computer simulation is used to study the mobility of decane and water in amorphous silica and graphite slit pores. Different systems were investigated at pore width $H = 6$ nm in a range of decane concentration from 0 to 100 vol.%. Furthermore, we investigated an efficiency of addition of different surfactants (Span 80 and AOTNa) on the diffusion coefficients of decane and water in a different range of concentrations in pores.

Figure 1. Water/decane mixture in graphite pore at 30 vol.% decane.

References

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THE D$^1\Pi$ AND d$^3\Pi$ STATES OF LIRB: AN ANALYSIS OF A SPIN-COUPLED COMPLEX

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Ultracold molecules have, in recent times, become a highly useful tool in many fields of experimental physics, such as fundamental physics, metrology, ultracold chemistry, and experimental modelling of quantum computers. However, in order to employ ultracold molecules, one must first create them. This typically requires comprehensive and exact foreknowledge of rovibronic levels, the calculation of which requires highly accurate potential energy curves (PECs) and coupling matrix elements between the states involved.

In this work, the spin orbit coupled D$^1\Pi$-d$^3\Pi$ complex of LiRb is studied. Using high level ab initio data of the PECs and spin-orbit couplings (SOCs), the available experimental terms [1-2] assigned to the D$^1\Pi$ and d$^3\Pi$ states are described through a nonadiabatic perturbation treatment to within experimental accuracy (0.01 cm$^{-1}$).

Figure 1. The a) PECs, b) SOCs, and c) term energies for the D$^1\Pi$- d$^3\Pi$ complex of LiRb, as well as d) the error in describing the experimental terms.

References

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EFFECT OF BRANCHING OF SIDE GROUPS ON SELF-ASSEMBLY OF OLIGO(PHENYLENE-THIOPHENE)S ON GRAPHENE

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Nowadays, conjugated compounds are of considerable interest for application in a field of organic electronics. Rigid and planar oligo(phenylene-thiophene)s are excellent candidates for the design of electronic devices with relatively high conductivity values. However, one of the priority tasks in the field still remains the increase in efficiency of the devices by precise control over morphology in organic layers. This is usually a complicated task due to the fact that even a small change in chemical structure of either the backbone or the side groups of the molecules significantly affects the conductivity values. Thus, present study aims at investigating the effect of branching of side groups on self-organization of oligo(phenylene-thiophene) on monolayer graphene via the molecular dynamics simulations. The results obtained demonstrate that highly ordered molecular aggregates are observed only for unbranched alkoxy side chains, while branching, on the contrary, hinders the ordering.

![Figure 1](image)

Figure 1. Typical top views of the monolayers of oligo(phenylene-thiophene)s on graphene: a) the formation of molecular aggregates in the systems with alkoxy side groups; b) disordered structure of the systems with ethyl-hexyl side groups.

Acknowledgements. The simulations were performed using the computational resources of the Institute of Macromolecular Compounds of Russian Academy of Sciences and the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University. This study was supported by the Russian Foundation for Basic Research (project No 18-29-19123).
Reverse micelles are called associates of non-polar organic solvents in which hydrophilic groups form a core, in which, as a rule, is water, a hydrophobic outer shell. Micelles have the ability to solubilize (that is, include in their composition) molecules and even ultrafine particles of surface-inactive substances. Surfactants are essential to the phenomenon of life.

In this work, we investigated the systems using the molecular dynamics method of the structure of the surfactant AOT and the location of organic substances (benzene and pyridine oxy derivatives) in reverse micelles in the dean – water system of ionic surfactants AOT. To achieve the goal, the tasks were set: to establish the dependence of the position of the molecule in the reverse micelle.

Figure 1. Organic molecules.

Figure 2. Reverse micelle AOT.
DFT CALCULATIONS OF NAPHTHOQUINONE FLUOROSULFATE DERIVATIVES WITH POTENTIAL CYTOTOXIC ACTIVITY

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Naphthoquinone derivatives, including plant-derived naphthoquinones, exhibit a variety of pharmacological properties, including antimicrobial, antiviral, anti-inflammatory, and antitumor effects [1]. Electronic properties associated with the ability to accept electrons, such as energy of the lowest unoccupied molecular orbital (E_LUMO), vertical electron affinity (VEA), and general chemical reactivity (ω), are the most important characteristics related to cytotoxic activity of the naphthoquinone derivatives studied here. These properties are important in accordance with the general concept of donor-acceptor and nucleophile-electrophile interactions with target molecules, which are to a great extent defined by the energies of frontier molecular orbitals [2]. Hydroxyl derivatives of naphthoquinones can be converted into fluorosulfates by using the SuFEx reaction, which was successfully applied in the synthesis of small molecules, protein labeling, polymer synthesis, and surface derivatization [3]. Such derivatives potentially have greater potential to accept electrons, which is why they may have higher cytotoxic activity. Thus, the aim of this research was to investigate electronic properties of naphthoquinone fluorosulfate derivatives by the DFT method.

We performed a DFT study for a group of naphthoquinone derivatives to identify characteristics of their electronic structure related to cytotoxicity. Geometry optimizations were performed with BP86 functional, triple-zeta basis set def2-TZVPP, and D3BJ dispersion correction. This level of theory provides high-quality results for geometries of organic molecules [4]. Subsequent single-point calculations were then performed for each compound with ωB97X-D3 functional and the largest Pople basis set 6-311++G(3df,3pd) in order to obtain improved results for orbital energies [5].
In comparison with naphthoquinone hydroxyl derivatives, the fluorosulfates possessed higher chemical reactivity and lower LUMO energy. For example, plumbagin (1), a natural compound that has anticancer activity [6], has higher LUMO energy than its fluorosulfate derivative 2 (-1.719 eV and -1.812 eV, respectively), lower chemical reactivity (3.27 eV and 4.31 eV, respectively) and lower VEA (33.99 kcal/mol and 47.214 kcal/mol, respectively). We also observed such a tendency for other naphthoquinone fluorosulfate derivatives, e.g. 3 and 4. The results suggest that these derivatives can be used for future investigation as biologically active compounds. Synthetic routes for introducing fluorosulfate groups into the naphthoquinone scaffold are exemplified below.

Figure. General method for the synthesis of fluorosulfates

References

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Recently, more attention has been focused to use the molten salts for the interests of developing safe and efficient power engineering, and for nuclear technologies as well as. Herewith, data about the stability of compounds and phase boundaries are first priority in the problems related to materials science. Therefore, the thermodynamic data and state diagrams of salt systems are important in electrochemistry, metallurgy, energetics, nuclear engineering, etc.

Simulations of phase equilibria in molten salts are carried out by means of thermodynamic modeling, ab initio and molecular dynamic methods. The difficulty of statistical-thermodynamic calculations is the absence of exact solutions for realistic models of the interactions (e.g., with polarizabilities); therefore, in the framework of the statistical theory, this problem for molten salts has not been considered so far. In report, simulation results for fusion characteristics and thermodynamic properties of rubidium halides by means of variational thermodynamic perturbation theory will be given. Within this approach, the free energy for a molten phase has form

$$ F_{liq} \leq F_{chs} + 2\pi \rho \sum_{i,j} \int_0^\infty x_i x_j \left[ \phi_{ij}^{pol}(R) \cdot g_{ij}^{chs}(R) \cdot R^2 \, dR \right]. $$

Here $F_{chs}$ is the free energy for the reference system of charged hard spheres within mean spherical approximation, $g_{ij}^{chs}(R)$ is the radial distribution function of the reference system, $\phi_{ij}^{pol}(R)$ is the additive to the pair potential. The free energy for an ionic crystal can be written as sum of the potential energy in Born-Mayer formula and vibrational contribution in Debye’s model:

$$ F_{sol} = \frac{N A z_i z_j e^2}{R_0} \left( 1 - \frac{\rho e}{R_0} \right) + N k_B T \left[ 3 \ln \left( 1 - e^{-\frac{\theta_i}{T}} \right) + \frac{8}{3} \cdot \frac{\theta_d}{T} - D \left( \frac{\theta_d}{T} \right) \right]. $$

Then the position of phase equilibria can be found using the rule of equality of the chemical potentials for each phase at the equilibrium point.
Transition metal complexes with redox non-innocent ligands are among the most interesting objects of the modern coordination chemistry. The most popular redox non-innocent ligands are the dioxolene type ligands derived from o-quinones (Q), which can be in the dianionic catecholate (Cat), o-semiquinone (SQ) or neutral (Q) forms. Recently, two manganese complexes with dioxolene ligands, Mn(3,6-DBCat-pipe)(3,6-DBSQ-pipe)$_2$ (1) and (4-NIT-Py)$_2$Mn(3,6-DBCat-pipe)$_2$ (2), were synthesized and characterized using X-ray diffraction, EPR and magnetic susceptibility measurements [1]. The authors proposed the localized oxidation state for 1 – Mn$^{IV}$(Cat)(DBSQ-pipe)$_2$ – and the presence of valence tautomeric equilibrium for 2. This work presents the $ab$ initio multi-configurational study of the electronic structures and properties of both complexes and the analysis of their valence states.

References

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ALL-ATOM MOLECULAR DYNAMICS SIMULATIONS OF OLIGOIMIDES ORDERED BY GRAPHENE

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Investigation of the ordering of heterocyclic polymers on the graphene is a promising research area to develop heat-resistant substrates with controlled mechanical properties for different industrial applications. The orientation of polymer chains on the graphene plane could lead to different mechanical properties in various directions upon applying mechanical field. However, it remains unclear how the heterocyclic polymer chains are ordered on the graphene plane with respect to the symmetry axes at different temperatures and how this orientation might influence on the mechanical properties of polymer nanocomposites. In the present study, all-atom molecular dynamics (MD) simulations have been carried out to preliminary investigate the thermal, dynamic and structural properties of oligomers of crystallizable polyimide (PI) BPDA-P3 ordered by the graphene surface. The chemical structure of BPDA-P3 repeating unit consists of 3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA) and diamine 1,4-bis[4-(4-aminoxyphenoxy)phenoxy]benzene (P3). BPDA-P3 oligomers with polymerization degree \( N_p = 1 \) or 2 have been simulated in wide range of temperatures from 300 to 600 K. It was found that with increase of BPDA-P3 chain length, the value of glass transition temperature \( T_g \) also increases, that might be due to high mobility of oligoimides with \( N_p = 1 \) near the graphene surface than mobility of oligoimides with \( N_p = 2 \). The formation of oligoimide regions with a preferable orientation relative to the graphene symmetry axes was observed close to the graphene surface at the temperature higher and below \( T_g \).

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The adequate account of solvation effects is crucial in the calculation of the thermodynamic states of chemical substances in solution. This is particularly important if one considers a complex homogeneous catalytic process under non-standard conditions. Such systems are quite common in hydrogenation reactions catalyzed with transition metal complexes, where parallel processes and side reactions are ubiquitous. We present here the computational research of the thermodynamic parameters of competitive reaction pathways in the homogeneous hydrogenation of carbon dioxide [1-4].

This reaction takes place in a non-aqueous solution at high hydrogen pressures. To model such reactions adequately, the accurate calculation of the free energies of the substances in solution is necessary. The energies of the intermediates and transition states are highly non-standard in this case. We thus evaluated the available quantum chemical methods for solvation modeling to find the most effective method on the chosen model example.

This in turn led to new insights into the mechanism and kinetics of the catalytic homogeneous CO$_2$ hydrogenation. Moreover, the performed computational modeling allowed us to rationalize the optimal operating conditions for the catalytic process.

We performed DFT calculations at the RI-TPSS-D3/def2-TZVP level of theory to model the molecules in the gas phase and used COSMO-RS to account for the solvation effects. The dependences of the free energy of the reactions were calculated under varied temperature, pressure, and reaction components concentrations.

References:
The key challenge in the computer planning of chemical synthesis is generation of new compounds from the set of available molecules. As part of this work, we have developed an algorithm that generates new chemical structures from a given molecule, using transformation rules extracted from database of chemical reactions. This approach has one major advantage: information about mechanism of the transformation is saved.

List of possible reactants was extracted from databases of commercially available chemical building blocks, which were stored in reactant database based on our in-house Python-based CGR-DB cartridge. Chemical structures were indexed based on functional groups present in them. Transformation rules were classified into one-, two- and multi-component based on number of molecules required to perform reaction transformation. Based on extracted transformation rules, functional groups that are subjected to transformations were identified.

At the stage of generation of products, system identifies functional groups present in the initial molecule, and extracts from database only those transformation rules that can be applied to a given molecule. If selected transformation rule requires two or more reactants, the second reactant is also selected based on the list of functional groups. The groups absent in starting molecule but required for transformation rule is identified and corresponding molecules are extracted from the database. Having all required molecules reaction product is generated based on the transformation rule. In such a way, algorithm does not try to do unnecessary transformations with unsuitable molecules and it quickly generates new compounds and reactions.

Possibility to generate the whole reaction was also implemented. Algorithm was tested, speed and quality tests were performed.

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THE ISODESMIC REACTION SCHEME AS A TOOL FOR CONSTRUCTION OF SELF-CONSISTENT SET OF ENTHALPIES OF FORMATION OF ORGANIC COMPOUNDS

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The systematic study of the consistency of available experimental thermochemical data for the set of structurally close molecules allows to analyze the accuracy of measured values and predict the properties of unexplored compounds. The standard approach of calculating of the gas-phase enthalpy of formation uses the atomization reactions and requires exceptionally high levels of theory, that is widely available only for small organic compounds. Isodesmic reactions scheme as a concept of balanced reactions (isogyric, isodesmic, homodesmotic) results to better error cancellations and thermochemical predictions of chemical accuracy (<4 kJ/mol) when composite ab initio methods are used. A large number of calculations for different CHON organic compounds by Gaussian-4 method applied isodesmic reactions shows clear advantage in accuracy of theoretical values.

For consistent treatment of data of the group of compounds from one class the high-accurate data on enthalpies of formation of simplest reference species are needed. However, even for the smallest organic CHON compounds (for example methylamine and nitromethane) results of measurement are not always known or there are significant disagreements in published results. So careful prior analysis is required for these molecules.

This limitation can be avoided by considering of thermochemical network of reactions where the known experimental data is optimized in conjunction with data for other structurally close molecules. The simultaneous least-squares solution of a network of isodesmic reactions connecting enthalpies of formation of studied compounds provides the set of self-consistent data. The accuracy of these calculations was shown to be comparable to the accuracy of the experimental data and higher-level calculations.

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Despite the success of Ru-based polyhydride catalysts [1], their replacing by less expensive and less toxic Fe-based analogues can open new ways in applications where these parameters are particularly important [2]. Accordingly, we studied the reactivity of the tetrahydrides for common structural motifs of Fe and Ru precursors (Figure 1) [3] in hydricity and acidity terms, which can be predicted experimentally as well as by computationally [4]. We estimated them as Gibbs free energy of hydrogen species shuttling from metal complex to solvent molecule at D3-TPSS/ma-def2-SVP//ma-def2-TZVP level of theory in conjunction with COSMO-RS corrections for accurate accounting of the solvation effects. Moreover, observed classical and non-classical binding H$_2$ modes [5] studied by QTAIM analysis.

![Figure 1. Common structural motifs of Fe and Ru precursors](image)

References
Nowadays, chemoinformatics have high variety of solutions for molecular characteristics modeling. The opposite situation is for prediction of reaction characteristics that tend to stay challenging. Such characteristics as reaction rate and equilibrium constants are crucial for calculation of reaction yield, conversion, time etc. Taking into account rising interest to reactions and lack of straightforward modeling schemes for them it was decided to develop workflow for automatic reaction preprocessing and modeling. The designed workflow includes several stages: (i) Condensed Graph of Reaction (CGR) based data curation and analysis, (ii) modeling and validation, (iii) model applicability domain outline.

The first stage are the vital, so it was resulted into standalone CGR based data cleaning procedure. It includes chemical structure standardization, atom-to-atom mapping check, reaction condition verification (based on expert rules, e.g. temperature should be lower than the boiling point and higher than the melting point of solvent, etc.), duplicates filtering with following rate constant or equilibria constant verification. Additional Matched Molecular Pairs approach was proposed for reactions to assess substituent effect on reaction rate. It was shown that this approach can be used to identify reactions that were wrongly attributed to unimolecular substitution mechanism. Different types of fragment descriptor were used in the modeling of the reactivity parameters: Marked Atoms-based, CGR-based and mixture-based descriptors. The models predicting reaction rate of bimolecular substitution ($S_N2$), elimination (E2), cycloaddition as well as tautomeric equilibrium constants were built and validated. The pitfalls in model validation and applicability domain application will be discussed.

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Chemical and phase equilibrium data for reactive systems are of obvious interest to those who are engaged in designing processes involving reactive mixtures, such as processes combining product synthesis and isolation. One of the most important examples of combined processes in chemical engineering is reactive distillation. However development of new effective methods of organization of reactive distillation process requires the development of an experimental database. Presently, the most studied are chemical and phase equilibrium in systems with the reaction esterification carboxylic acids alcohols. This is due to the practical significance of the production of products this reaction - esters. Nevertheless, some experimental data on combined processes are lacking even for the above systems: the available database should be also augmented for advancing the fundamental theory of complex equilibria [1].

This report presents data on the chemical equilibrium in the systems with the ethyl acetate [2] and ethyl propionate [3] synthesis reaction. Present model calculation of the equilibrium between chemically equilibrium solutions and their vapor at different temperatures for these systems (Fig.1).

Figure 1. Isotherm–isobar lines on the chemical - equilibrium surface.

References

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ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF NITROXIDE RADICALS, DIRADICALS AND THEIR COMPLEXES WITH 3d-METALS: AB INITIO AND DFT STUDY

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One of the most effective approaches to the design and synthesis of molecule-based magnetic materials is the metal-radical (diradical or polyradical) approach.[1] Thus there is a growing interest in the diradicals and their complexes with transition metals.[2]

This report will present and discuss our recent results on the computational study of the magnetic properties of the nitronyl-nitroxide (NN) and iminonitroxide (IN) radicals, diradicals and their mono- and dinuclear complexes with transition metals (Cu(II), Ni(II), Mn(II)). These paramagnetic molecules and their complexes have been recently synthesized and characterized using XRD analysis, EPR spectroscopy and magnetic susceptibility measurements in a wide temperature range.2-4 To understand these properties on a molecular level we performed a large series of calculations using both the DFT and high-level CASSCF/NEVPT2 calculations.

Diradicals under study belong to the non-Kekule structures with both the disjoint or non-disjoint SOMOs. The DFT calculations predict well parameters of the EPR spectra (ZFS and HFC constants) of these diradicals, however, fail to predict singlet-triplet energy splitting for diradicals with disjoint SOMOs. Thus, high-level calculations (e.g. CASSCF/NEVPT2) are required in this case. Report will present analysis of a large series of calculations for diradicals, their transition metal complexes and clusters.

This work was supported by the RSF (project 16-13-10155) and RFBR (project 18-33-00143).

References
Methane is one of the widely used fuels, thus searching for the new sources of natural gas is an important task. It was shown that significant amount of methane can be obtained from its hydrates. A promising way of methane extraction from hydrates is the replacement of CH$_4$ by other gases, such as N$_2$ and CO$_2$.

In this work Grand Canonical Monte Carlo simulation was used to study the occupancy of SI and SII hydrate frameworks by ternary CH$_4$/CO$_2$/N$_2$ (1:1:1) gas mixture (Fig. 1). Simulation was carried out at 270 K and in the pressure range from 1 to 70 atm.

Figure 1. Snapshots of SI (left) and SII (right) mixed hydrates at 70 atm.

Hydrate framework – cyan, CO$_2$ – orange and red, N$_2$ – blue.

Total and partial occupancies of hydrate frameworks by gases were obtained. Occupancies of various types of hydrate cavities (large and small) were also calculated. For SI structure the composition of gas in completely filled hydrate is approximately 2:7:1 (CH$_4$/CO$_2$/N$_2$), and for SII structure this ratio is ca. 1:7:1. It was shown that CO$_2$ completely displaces CH$_4$ in large cavities, and N$_2$ competes with CH$_4$ for the small cavities.

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ARE WE OPENING THE DOOR TO A NEW ERA OF MEDICINAL CHEMISTRY OR BEING COLLAPSED TO A CHEMICAL SINGULARITY?

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The paradigm of “drug likeness” dramatically influenced medicinal chemistry community for a long time[1]. In recent years, scientists have empirically found a significant increase in key properties of drugs that have moved structures beyond the rule-of-five[2]. Herein, we show that for the past decade, the number of molecules claimed in patents by Big Pharma companies has dramatically decreased, which may lead to a “chemical singularity”. New compounds with increased 3D complexity are generally larger, slightly more lipophilic and polar. A core difference between this study and recently published papers is that we consider the nature and quality of sp3-rich frameworks rather than sp3 count[3]. We introduce the original descriptor MCE-18, which stands for Medicinal Chemistry Evolution, 2018, and this measure can effectively score molecules by novelty in terms of their cumulative sp3 complexity[4].

Figure 1. Medicinal Chemistry Evolution described with MCE-18 Score.

References

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Molybdenum disulfide, MoS$_2$, is one of the most intensively investigated sources of inorganic nanotubes. The properties found make MoS$_2$ nanotubes very useful in catalysis, tribology, hydrogen storage, and in electronics for the fabrication of field-effect transistors [1].

*Ab initio* quantum-chemical modelling of structural, phonon, and thermodynamic properties of MoS$_2$ multi-walled nanotubes of real size are practically impossible even using powerful computers. However, such simulation can be performed using the classical force field approach. Several versions of potential fields for MoS$_2$ systems have been proposed before. Further study of these potentials has shown that some of them do not well reproduce such substantial quantities as the unit cell parameters of two most stable bulk crystalline phases 2$H$-MoS$_2$ and 3$R$-MoS$_2$, and the formation energy of a monolayer from a bulk crystal.

In this work we present a new force field (SWMB-C) fitted to measured and calculated properties of 2$H$-MoS$_2$ and 3$R$-MoS$_2$ bulk phases, 2$H$-MoS$_2$ monolayer, and some single-wall nanotubes. Preliminary calculations show that the proposed field successfully reproduces structural and vibrational properties of single- and double-walled nanotubes obtained by DFT quantum-chemical simulations using CRYSTAL 17 [2] code and hybrid exchange-correlation functional HSE06. The optimization of the geometry of triple-wall nanotubes has also shown that the use of the proposed potential gave physically reliable results. In all considered cases the nanotube binding energy (difference between multi-wall tube and single-wall tubes) estimated by proposed force field agrees well with the quantum-chemical result.

References


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DEVELOPMENT OF A NEW SCREENING TOOL FOR LIGAND STRUCTURE BASED DRUG DESIGN BASED ON PHARMACOPHORE SIGNATURES

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Computer drug design can be divided into two approaches. The first approach is based on the structure of the target protein. But it is not always possible to determine the structure of the protein. The second method is screening for ligand structure – pharmacophore modeling.

Development of an approach to search for an active pharmacophore molecule based on the use of 3D pharmacophore signatures. An approach has been proposed to identify active pharmacophore based on a set of active and inactive molecules. The approach is based on the use of the pharmacophore signature algorithm proposed by us, a unique identifier that takes into account the distances between pharmacophore centers and their spatial location. The use of the signature made it possible to calculate the occurrence of pharmacophores in a set of molecules. The active pharmacophore was considered to be one that was found in highly active molecules and was not found in the set of inactive molecules.

The approach was validated on three different datasets: AChE, CYP450 3A4, A2a. Performance of the developed 3D pharmacophore models was comparable to or higher than the performance of a 2D pharmacophore similarity search. The developed 3D ligand-based pharmacophores were able to match important ligand-protein contacts of known ligands in their observed poses taken from PDB protein-ligand complexes.

The developed tool is open-source software, whereas the available free tool for ligand-based.

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A superhalogen $\text{F@C}_{20}(\text{CN})_{20}$, named $\text{X}$, was designed on DFT and DLPNO-CCSD(T) levels of theory. Some of its derivatives were considered: fluorine superhalogenide $\text{FX}$, superhalogen dimer $\text{X}_2$, hyperhalogen $\text{BX}_4$ and superacid $\text{HX}$. The latter is expected to be much stronger acid than fluorocarborane superacid $\text{H[CHB}_{11}\text{F}_{11}]$. Antimony pentafluoride was suggested as a possible solvent for $\text{HX}$ to attest its strength. Both $\text{HX}$ acid and $\text{X}^-$ anion were predicted to be thermodynamically stable, while neutral $\text{X}$ radical is expected to have only kinetic stability at low temperatures. Various ways of possible improvements to superhalogenic structures were investigated. The instability of some earlier-claimed superacids of record strength was established. [1]

Figure 1. A fluorine atom is encapsulated into a dodecahedrane cage decorated with twenty cyano groups. The resulting superhalogen has outstanding calculated electron affinity of 10.8 eV, forming a very non-nucleophilic anion of $I_h$ symmetry with calculated gas-phase basicity of just 208 kcal/mol.

References

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CHOLINE CHLORIDE BASED DEEP EUTECTIC SOLVENTS AS EXTRACTION MEDIA FOR SEPARATION OF AZEOTROPIC MIXTURES

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Nowadays chemists all around the globe try to solve actual environmental problems. Particularly, there are issues of reducing emissions of different volatile compounds, improving the technology of production energy from renewable sources and water purification. Deep eutectic solvents (DESs) are able to be the new generation of “green solvents”, due to its biocompatibility, biodegradability and sustainability. DES is a eutectic mixture composed of two (or three) high-melting point pure components at given stoichiometry and having a much lower melting point in comparison with parent compounds. These solvents are characterized by pronounced hydrogen bond interactions. According to recent researches [1], DESs can replace commonly used organic solvents as extractants for separation of azeotropic mixtures formed by alcohol and ester in esterification reaction, which has a broad application in chemistry. In this contribution we continue the investigation of liquid-liquid equilibrium (LLE) data in DESs choline chloride – dibasic carboxylic acids in alcohol-ester systems [2,3]. Herein we consider the ability to separate mixtures of alcohols with its propanoate esters (ethyl propanoate, n-propyl propanoate, n-butyl propanoate) using choline chloride – urea and choline chloride — glycerol deep eutectic solvents. Tie-lines were obtained at temperatures 293.15 K and 313.15 K and atmospheric pressure. The compositions of coexisting organic and DES phases are determined by $^1$H NMR-spectroscopy. The extraction performance was characterized with distribution coefficients and values of selectivity for used alcohols. NRTL equation was used for LLE data correlation.

References

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A series of platinum(0) dialkylbiarylphosphine complexes with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) were synthesized with 72-96% yield and structurally characterized using NMR, IR and XRD. Prepared complexes found to be efficient catalysts in hydrosilylation reaction between phenylacetylene and diphenylsilane in mild conditions and in cross-linking process of PDMS. The ligand set was based on commercially available XPhos, JohnPhos and SPhos and their tailored derivatives and in total contained 7 ligands. These catalysts sufficiently increased the selectivity of β-(E) isomer formation up to 98% with increasing of total yield up to 95%. The structural parameters were extracted from both XRD structures and optimized phosphine oxide derived template structures. Parameters were set as percent buried volume, sterimol values, and percent buried volume values of phosphines in 4 quadrants. Constructed library of complexes allow to include other types of ligands with the same structural scaffold for further optimization of hydrosilylation processes and study QSPR for selectivity and activity of homogeneous catalysts in Si-H activation processes.

For complex 1a platinum(0)-ortho carbon atom from aryl group distance averages 3.204 Å platinum(0)-ipso carbon distance was 3.293 Å, these values are less than the sum of platinum and carbon Van der Waals radii (3.57 Å) [1]. The same effect, when d(metal-C_{ortho}) is quite shorter than d(metal-C_{ipso}) observed in palladium (0) diphosphine complexes [18], in contrast to gold(I) complexes of JohnPhos [2] which prefers interactions with ipso atom rather than ortho, preferred ipso-coordination also occurs in allylpalladium complexes of dialkylbiarylphosphines with formation of strong Pd-C_{ipso} bond, as it seems from bond length varying from 2.3 to 2.5 Å which refers to monohapto coordination of palladium to benzene ring [3]. Estimation of hapticity for Pt-arene interaction in 1a using Kochi and co-workers proposed equation [4] equation gave hapticity value of x=1.68, this is comparable with gold(I) complexes with x in range 1.55-1.95.


Figure 1. (i) Chemical structure of part of the crystallographically determined complex 1, used in the calculation of buried volume, 34.9% $V_{\text{bur}}$. (ii) Chemical structure of the crystallographically determined complex 2, 45.0% $V_{\text{bur}}$. 

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ARTIFICIAL INTELLIGENCE APPLICATION IN SYNTHETIC CHEMISTRY: FROM DATASETS TO RETROSYNTHESIS


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Enhancement of discovery speed in synthetic chemistry has led recently to accumulation of big amount of data. It opened the door for applications of big data analytics and data mining technologies (including artificial intelligence approaches) in synthetic chemistry [1]. We will review four applications: synthesis design, selectivity prediction, reaction kinetics and condition prediction. Condensed Graph of Reaction [2] is a cornerstone of the developed methodologies.

Two main approaches to synthesis design will be considered: older, based on manual rule coding, and newer, based on machine learning application. Machine learning classification algorithms can be applied to predict reaction selectivity, which will be shown on Markovnikov/antiMarkovnikov addition reactions. The importance of substrate structure, electrophile/nucleophile and reactions condition will be demonstrated.

Regression algorithms of machine learning can be naturally applied to predict reaction rate and equilibrium constants. It will be shown how structure of reactants and products, solvent and physical conditions can be encoded in descriptor vector used for modeling.

Assessment of optimal reaction conditions can be effectively solved using ranking algorithms, whose task is to rank applicable conditions as high as possible.

In such a way, despite synthetic chemistry introduce rather new challenges to chemoinformatics and artificial intelligence, there are quite universal approaches to address them.

References

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Formation of micelles and stability of the spatial structure of proteins, as well as a number of other phenomena in aqueous solutions are governed by the hydrophobic effect. Experimental data show that such phenomena are typical not only for water. The hydrophobic effect is a particular case of a more general phenomenon, the solvophobic effects.

In the studies of solvation properties, the concept of cavity formation is often used. Unlike water, for which the thermodynamics functions of cavity formation have been extensively analyzed, there were almost no studies of the cavity formation process in other solvents exhibiting solvophobic effects.

In this work, we calculated the thermodynamic functions of cavity formation in a number of models of individual solvents using molecular dynamics trajectories (NPT-ensemble). The Gibbs free energy of cavity formation $\Delta_{\text{cav}}G$ was calculated from the probability of existence of a cavity of certain radius at the random point of simulation cell. For probability calculation, 10,000 configurations were chosen from 10 ns-long trajectory. For each configuration, $10^5$ random points of space were selected. The enthalpy of cavity formation $\Delta_{\text{cav}}H$ was determined from the temperature dependence of $\Delta_{\text{cav}}G$.

The calculation showed that $\Delta_{\text{cav}}G$ increases in the solvent series hexane $<\text{THF} \approx \text{acetone} < \text{benzene} < \text{propylene glycol} < \text{ethylene glycol} < \text{formamide} < \text{glycerol} < \text{water} < \text{hydrazine}$, which generally corresponds to the order of increase in the Gibbs energy of solvation of inert gases. The enthalpies and entropies of solvation processes of inert gases and cavity formation also change in the same order. The link between the solvophobic effects and thermodynamics of the process of cavity formation is clearly seen on the plots in coordinates $\Delta_{\text{cav}}G$ – $\Delta_{\text{cav}}H$. For solvents that do not exhibit solvophobic effects (hexane, benzene, acetone, THF, acetonitrile), the lines representing relationships between $\Delta_{\text{cav}}G$ and $\Delta_{\text{cav}}H$ for the cavities with different sizes lie parallel to each other at a relatively short distance. For the solvents exhibiting solvophobic effects, similar lines on the plot lie much higher, and their slope is larger. Comparison of positions of various solvents on these graphs for a cavity of the same size shows that solvophobic effects are weakening in the series water $> \text{glycerol} > \text{formamide} > \text{ethylene glycol} > \text{hydrazine} > \text{propylene glycol}$, which qualitatively corresponds to the results of experimental studies of these effects.

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Colchicine (Figure 1) is the main representative of the family of colchicine alkaloids, which has a unique biological property to bind to the special fragment of the tubulin macromolecule (colchicine site), preventing the formation of microtubules and, as a consequence, the mitosis of tumor cells. Because of the high nonspecific toxicity, colchicine cannot be used in the treatment of cancer. Therefore, one of the main tasks of medicinal chemistry is the search for and synthesis of molecules similar to colchicine and possessing higher antitumor activity.

To assess the biological activity of colchicine analogues, we studied the coordination ability of more than 30 $[2H, 3H]$oxepinoallocolchicinoids to the colchicine site of tubulin using the method of molecular docking. All calculations were performed with the Autodock 4.2 program [1] using the AutoGrid software to create a docking area and the MGLTools 1.5.6 shell for initial data preparation and visualization. Each docking run was carried out using the genetic algorithm LGA (200 conformations, 25000000 calculations per each conformation). The $\alpha$- and $\beta$-subunits of the stathmin-like domain 1SA0.pdb [2] were taken as the source protein structure. The geometry of allocolchicinoid molecules was optimized using Gaussian 03 [3] by DFT at the B3LYP/6-31G(d,p) theory level. The highest binding energies were found for colchicinoids 1, 2, 3, 4 and 5 (Figure 2) and ranged from 9.42 kcal/mol (5) to 9.98 kcal/mol (1). These compounds are synthesized, their structure is confirmed by the method of $^1H$ and $^{13}$C NMR spectroscopy. At the moment, their activity is being investigated by biological methods.

References
QSPR MODELING OF POTENTIOMETRIC SELECTIVITY CONSTANTS FOR MAGNESIUM IONOPHORES

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Quantitative structure-property relationship (QSPR) modeling mathematically connects the structure of a molecule formalized in a set of descriptors with its physicochemical properties [1]. QSPR approach was successfully employed for the prediction of metal-ligand interactions in liquid extraction processes [2] and studies of metal toxicity [3]. The response of polymeric membrane potentiometric sensors is also based on metal-ligand interactions. Therefore, the application of QSPR modeling to develop a relationship between the ligand structure and electrochemical behavior of the corresponding polymeric sensor membrane could significantly facilitate the development of sensors with desired properties and save the resources required for the electrochemical characterization of new ionophores.

In this work, the feasibility of QSPR modeling was studied in the prediction of the potentiometric Mg/Ca selectivity of Mg-selective electrodes based on the ionophore structure. The dataset was created using literature data on various lipophilic di- and triamide magnesium ionophores with selectivity constants determined by the separate solution method.

The ISIDA/QSPR program package [4] was used for modeling and prediction with multiple linear regression as a machine learning method and substructural molecular fragments descriptors as independent variables. The evaluation of the model predictive performance was performed with 20-fold external cross-validation. The coefficients of determination were 0.95 and 0.63 for calibration and test sets, respectively, showing good promise for reliable prediction of sensor properties based on the ionophore structure.

References

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Molecular logic gates (MLGs) are molecules that implement logic operations. Nowadays, they can detect ions in a living cell[1]. It is expected that in the next two decades autonomous therapeutic systems based on MLGs will come into practice[2]. Such systems should have suitable computing capabilities. However, “quantum problems” have stalled development the system[3]. Guliev was able to connect two gates using energy transfer like a signal[4]. The goal of this study is to discover suitability of electron transfer as a signal in a large logic system.

The model logic system was based on TTF moieties linked as a chain. The terminal moiety was modified to alter HOMO and LUMO energies.

It was proposed that an electron in such system moves together with a hole, as an exciton in a semiconductor. The process is ongoing while exciton recombination is forbidden - more specifically, the electron cannot transfer from an excited state to a ground state. A hypothesis is right only if a transfer rate is greater than a recombination rate. We used Marcus model to evaluate rates[5]. Parameters were calculated by MCSCF method in Gamess[6]. A basis is 6-31G(d) with SBKJC, an active space is (8,8). Radiative transition was calculated by CASSCF, 6-31G(d), (8,8).

The calculated transfer rate is $3.59 \cdot 10^9$ sec$^{-1}$, while the recombination rate is less than $2.45 \cdot 10^7$ sec$^{-1}$. The exciton transfers in several steps. In the first phase, the exciton is located on the first moiety. Then it spreads over the entire molecule. Then the exciton finally transfers to the second moiety. Exciton transfer is preferable to electron transfer because needs less energy.

References
Multicomponent mixtures and the examination of mutual solubility of their components attract steady interest of scientists nowadays, because of the fact that information about phase equilibria in such systems is demanded not only for fundamental studies but for modern industry. Moreover, predicting of liquid-liquid equilibria (LLE) in these systems is one of the main tasks of scientific basic research. That is why both the experimental obtaining of solubility data and development of different approaches to description of phase equilibria are relevant today. Experimental part of our investigation includes studying of mutual solubility in ternary mixtures acetic acid - amyl acetate - water, acetic acid - amyl alcohol - water, amyl alcohol - amyl acetate - water at 318.15K and atmospheric pressure. During the theoretical study an semiempirical equation was derived, that can describe LLE in ternary systems with one splitting subsystem based on solubility data for splitting binary subsystem. The equation was used to describe phase equilibria in systems that have already been studied at present, such as mixtures acetic acid - ester - water, acetic acid - alcohol – water [1-4]. The results, obtained by using this equation, were compared with widely used model describing LLE - UNIFAC and NRTL model for those mixtures.

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References
CALCULATION OF VAPOUR PRESSURE USING EXCESS MOLAR ENTHALPY OF BINARY MIXTURES OF NON-ELECTROLYTES

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Studies of liquid vapor equilibrium is largely used for optimization of various chemical and physical processes, in particular, for extracting and separating elements of mixtures. As part of systematic studies from NRNU MEPhI's chemistry department, cluster model equation, connecting vapor pressure of a solvent and some excessive properties with liquid phase composition has been justified before [1]. This model is applicable to binary solutions of completely miscible nonelectrolytes, showing positive deviations from Rault's law and nonideality of them is mainly from association of one of its components.

Using mixes of aliphatic alcohols with alkyl halides [2] as an example, the objective of modeling vapor pressure of a solvent above a solution with concentration dependence of molar excess enthalpy with fixed temperature. Initial data for the task is concentration dependence of molar excess enthalpy with fixed temperature. Because multitude of parameters, describing dependency of vapor pressure of a solvent above a solution, is a subset of parameters of the equation, describing molar excess enthalpy, it is possible to directly substitute solution of parameter identification task in a equation, describing vapor pressure of a solvent above a solution.

Modelling has been done via minimising of RMS error function. As a consequence of the fact that there are a lot of approximately the same local minima, the objective was completed via clusterization. Mass center of the most dense cluster was added to the equation, describing dependency of vapor pressure of a solvent above a solution. Alcohol association was assumed. For 1-bromobutane + 1-butanol, 2-methyl - 2-propanol systems, solutions were obtained, describing vapor pressure of a solvent with a relative error no more than 10%.

References


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We used an integrated approach to reveal fine changes in the surface–normal structure of DMPS monolayers at the air/lipid/water interface occurring during the monolayer compression. We performed MD simulations at several points (circles, Fig. 1) of monolayer compression, validating calculated electron density profiles to those reconstructed from X-ray reflectivity data [1]. From MD simulations, we found that the extrusion of water molecules from lipid headgroup region is responsible for Volta potential changes during monolayer transition (Fig. 1, red curve).

Figure 1. Compression diagrams of the DMPS: surface pressure (black) and Volta potential (red) are plotted against area-per-lipid. Circles marks the area-per-lipid values used in MD simulations.

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One of the most prospective areas of the application of reverse micelles (RMs) is biochemistry.[1] In particular, RMs are used as biological extractors and bioreactors that can solubilize proteins and enzymes into a water aggregate surrounded by an organic medium. Many researchers studied biological properties of RMs and pointed out that some physical and chemical factors like pH and ionic strength have the extensive influence on extraction processes. [2] The sodium chloride increases ionic strength inside the water pool of the RM. In this work, we used molecular dynamics simulations to find how the electrical potential and dipole moment of RMs depend on the presence of salt and its concentration.

Figure 1. The snapshot of the AOT reverse micelle in isooctane.

References
Halogen bond (XB) is one of the most abundant non-covalent interactions, which can be formed by electron donors and halogen-containing (Cl, Br, I, in some cases F and At) molecules and ions, in which halogen atom is bonded to an electron-withdrawing group. Therefore, halogen atom has an electron poor region, so-called σ-hole, due to which it acts as an electron density acceptor (i.e. halogen donor). Various molecules, ions and individual atoms (e.g. Hal, O, S, Se, N etc.) can act as electron-donating halogen bond acceptors.

Halogen bonds can be observed in solids, in solution and in gas phase. They play an important role in catalysis, drug design, crystal engineering and design of new materials with various useful properties (e.g. luminescent emitters). Halogen bonds are usually detected by their geometric (valence angles and bond lengths) or energetic characteristics. While geometric parameters can be rather straightforwardly determined for single crystals by X-Ray analysis, complexation energy is notoriously hard to determine, especially in other media (liquids and solutions, where the information on interatomic distances is absent) and especially for intramolecular halogen bonds (where the complexation energy needs an additional definition). Besides, it is desirable to design tools for prediction of the complex’s characteristics based on the electronic properties of halogen donor molecules.

In this quantum-chemical work we consider a series of more than 100 halogen bond donors (F-, Cl-, Br-, I- and At-containing) and their complexes with \((\text{CH}_3)_3\text{PO}\) as a probe halogen bond acceptor. All calculations were performed in vacuum at the DFT level of theory using Def2-TZVPPD basis set and hybrid functional M06-2X, which is one of the most effective functionals for the study of non-covalent interactions.

Our first goal is to evaluate the possibility to use \(^{31}\text{P}\) NMR chemical shift, \(\delta^{(31}\text{P})\), and P=O stretching vibrational frequency, \(\nu(\text{P}=\text{O})\), as descriptors of halogen bond energy and geometry. Our second goal is to analyze the QTAIM (Quantum Theory of Atoms In Molecules) parameters at the halogen bond critical point \((3; -1)\) in order to construct correlations that would allow one to use topological analysis of the electron density in order to predict the energy and geometry of \(\text{O} \cdots \text{XR}\) halogen bonds.

This work was supported by RSF grant 18-13-00050.
Figure 1. Equilibrium structure of halogen-bonded complex of trimethylphosphine oxide (CH$_3$)$_3$PO and trifluoriodomethane CF$_3$I
In this study, the molecular dynamics (MD) simulation of vitamin D receptor (VDR) was performed with the Desmond package of Schrödinger Small-Molecule Drug Discovery Suite. The structure of VDR was obtained by refining 1VD2 crystal structure, which is analogous to 1DB1 from PDB but with higher resolution and less residues missing. First, the validation procedure was done according to the protocol described in [1]. We used a VDR structure, with a peptide derived from TRAP220 coactivator complexed with calcitriol (VD$_3$). Validation procedure revealed the important role of histidine rotamer states. It is known that the ligand in the binding pocket of VDR should maintain at least six hydrogen bonds: HIS305 and HIS397 with 25-OH, ARG274 and SER237 with 3β-OH, TYR143 and SER278 with 1α-OH [2]. However, after the standard minimization performed by Protein Preparation Wizard (Schrödinger) both HIS305 and HIS397 were in HID conformation. This led to their constant competition for the hydrogen atom in ligand and, consequently, to the formation of extra water bridges inside the binding pocket. This obviously weakened ligand binding to the VDR, thus the solution was to manually change the HIS397 conformation to HIE rotamer with Interactive H-bond Optimizer tool (Schrödinger). After validation procedure had been finished, we ran 18 experimental simulations. For this, VDR has been set up with different motifs from two coactivator peptides (hSRC1 and hPGC1α) and with three ligands (VD$_3$, Gemini, TX527). The various peptides used from hSRC1 and hPGC1α contain one LXXLL-motif, which interacts with VDR. The final parameters of MD simulations were 300K at 1 bar for 10 ns using the water model TIP3P. The binding energies for all the complexes after MD simulations were calculated using MM-GBSA method. MD simulations showed stabilization of the VDR regions important for allosteric communications and interaction with coactivators such as helices H3, H4-5 and H12.

References
MODELING OF THE EFFECT OF GRAPHENE EDGES ON THE ELECTRON TRANSFER KINETICS

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Using the method of classical molecular dynamics, we have obtained the structure of the electrode/electrolyte interface for various types of surface — a single-layer graphene edge, a multilayer graphene edge, a graphene plane [1-3]. We have obtained the distributions of mass and charge densities in the near-electrode layer, the distribution of the electrostatic potential, and the orientational ordering of the solvent. Also, the kinetics of oxygen adsorption to the model surfaces and the corresponding distributions of the equilibrium concentrations were calculated. Within the framework of the density functional theory, we studied heterogeneous electron transfer from two clusters of graphene with different edge types. Using the Landau-Zener and Marcus theory, the values of electron transfer constants with spatial resolution both along the surface and varying the distance to the surface of the clusters were obtained [4, 5]. The effective electron transfer constants were calculated, taking into account the equilibrium distribution of the oxygen molecules in the near-electrode region. The edge of graphene showed a less ordered interface structure with less dense layers of electrolyte compared with the plane of graphite. As a result, the edge of both single and multilayer graphene is an effective surface for adsorption of the oxygen molecules. Also, the accelerated kinetics of the electron transport from the zigzag graphene edge was found in comparison with the graphene plane. At the same time, the armchair graphene edge does not show such electrocatalytic activity.

References

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PHASE EQUILIBRIUM IN THE QUATERNARY SYSTEM WITH THE ESTERIFICATION REACTION OF N-PROPYL PROPIONATE: EXPERIMENTAL AND SIMULATED BY NRTL MODEL DATA

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The relevance of phase equilibria studying of liquid-phase systems is associated with the extraction processes. Classic examples of extractants are the innocuous esters of carboxylic acids. The advantage of the non-toxic n-propyl propionate discussed in this study is its low cost and dissolving ability of a wide range of compounds. Thus, it can be a full-fledged replacement for deficient butyl acrylate [1]. However, data on the thermodynamic behavior of systems involving such ethers as biodegradable n-propyl propionate which are necessary for optimization the technology of synthesis of organic substances, are practically absent. The aim of the work is a detailed experimental study of phase equilibria in a multicomponent reaction system with n-propyl propionate (fig. 1) and using the NRTL [2] model to simulate the liquid-liquid equilibria data.

References

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New insights into non-classic phenomena in cross-coupling reactions are often obtained via DFT computations; understanding phenomena as formation of M(0) nanoparticles or M(II) oligomers \textit{in situ}, metal-metal cooperativity, redox processes, and processes involving radical species can direct design of new catalysts [1]. In Pd systems, dynamic interconversions of Pd nanoparticles and Pd complexes often determine the activity [2].

We have recently proposed a model of interconversions of Pd species in coupling reactions with ArX [3]. The model allowed to determine, which pools of species can form under reaction conditions (Figure 1). In this presentation, we will report results of our DFT modeling of mechanisms of activation and deactivation of Pd catalytic systems in couplings involving ArX.

References
DFT STUDY OF ABSORPTION AND EMISSION SPECTRA OF BODIPY DYES

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Boron-dipyrromethene dyes (BODIPY) are of great interest nowadays mostly due to their valuable optical properties. Nevertheless, no systematic research of optical properties dependence on the structure of a dye has been done yet. So, at first we carried out calculations of electronic spectra of BODIPY derivatives using the available methods and proposed the best method that allows to predict experimental data with high accuracy. Next, using the suggested method, we studied the influence of the nature of the substituent and its position in BODIPY core on the optical spectra of the dye.

All the calculations have been performed with Gaussian program. Accuracy of eight different DFT functionals was analyzed. Solvation effects upon excitation were considered using SMD model in terms of Linear Response (LR) and State Specific (SS) schemes. Eleven BODIPY and aza-BODIPY derivatives with absorption and emission maxima in the range of 490 – 850 nm were considered. Comparison of linear regression coefficients showed that M062X functional is the most accurate for LR-scheme of calculation of absorption and emission spectra, while wB97XD functional is the most accurate for SS-scheme. Model structures with various donor and acceptor groups in different positions of BODIPY core were proposed to evaluate the influence of substituents on optical properties of BODIPY dyes. The calculations of their absorption and emission maxima revealed complex pattern of red- and blue-shifts (Fig.1), nature of this pattern was explained in terms of HOMO and LUMO energies.

The results of this work provide the way for efficient design of BODIPY derivatives with desired properties.

Figure 1. Influence of the substituents on absorption and emission maxima.
One of the OECD principles for model validation requires clearly defining the Applicability Domain (AD) for the QSAR/QSPR models. This is important since the models provide the reliable predictions only for those objects, that are structurally similar to the training set objects used to build the models. Currently, more and more attention is drawn to chemical reactions as objects of QSAR/QSPR modeling. When building quantitative structure-reactivity relationship (QSRR) models and their applicability domains it is necessary to take into account the structures, conditions and types of chemical reactions.

In this study AD definitions extensively used in QSAR/QSPR studies, their modifications and proposed by us for reactions were benchmarked. In the study more than 10 simple AD definitions, 24 combinations of AD and 2 types of consensus AD approaches were compared. Four criteria (coverage, ability to exclude wrong reaction types, ability to improve model performance and to detect outliers) for assessing quality of model with applicability domain were used. Four data sets of reactions were used for benchmarking study. Some applicability domain definitions requires selection of optimal hyperparameters, for doing that we developed especial procedure that includes both internal and external cross-validation of model and applicability domain.

Generally, most applicability domain definition approaches are quite good in ability to exclude wrong reaction type and to improve model’s performance. Combination AD approaches with fragment control or reaction type control led to much better model performances than single AD definition approaches. Based on ranking we selected optimal AD definition approaches suitable for reactions.

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Perovskite-type oxides have been widely investigated for their potential applications as advanced materials for solid oxide fuel cells, sensors, electrochemical devices, etc. The experimental studies [1] indicate the existence of Fe-clusters with the ferromagnetic exchange in LaGaO$_3$-LaFeO$_3$ solid solutions, whereas they are not observed in LaAlO$_3$-LaFeO$_3$ system. In our work, we focus on ab initio modeling of the magnetic properties of these solid solutions.

Calculations were performed with CRYSTAL14 computer code [2]. The solid solutions were presented as an average over a set of configurations with distributions of different species over a given set of atomic positions. We treated all symmetry non-equivalent configurations, including not only all the possible distributions of Fe-atoms on the $p$-metal positions (Ga or Al) but also the different spin distribution of the Fe-atoms. Statistical weights and probabilities were estimated for each configuration within the canonical ensemble. Magnetic moments were calculated considering these probabilities.

We used a simple Ising model to describe the contribution of the magnetic exchange to the total configuration energy of considered structures. However, the accounting of the magnetic contribution was not sufficient to explain the differences between the two solid solutions. To account for non-magnetic contributions, a new «extended Ising model» has been proposed, using the lattice approach based on the concept of interchange energy. Two model parameters (the magnetic coupling constant and interchange energy) were fitted to the calculated energies of configurations for both LaGaO$_3$-LaFeO$_3$ and LaAlO$_3$-LaFeO$_3$ solutions.

The extended Ising model confirmed the benefit of Fe-clustering in doped lanthanum gallate against aluminate. The different sign of the estimated interchange energy enables to explain the reasons for such differences.

References

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Using the method of thermodynamic modeling of NRTL to calculate the liquid-liquid equilibrium in a system with ethyl propionate

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Experimental study of phase equilibrium in systems involving ethyl propionate is of enormous importance for both practical and theoretical purposes. Ethyl propionate is one of the most used in the production of esters. It is used in paint and varnish production, the perfumery and food industry and so on. Therefore, to optimize and modernize production processes, knowledge of the physicochemical properties of ethyl propionate is necessary. In addition to the experimental method of studying phase equilibrium, computational methods are also used to predict liquid-liquid equilibrium.

This work is devoted to the prediction of phase equilibrium in a liquid-phase splitting system propionic acid - ethyl alcohol - ethyl propionate - water at 20 and 30°C using the thermodynamic model NRTL. The non-random two liquid (NRTL) model is based on the concept of a local composition, namely the difference in concentrations near the molecule and in the depth of the solution. This difference is due to different energies of interactions of molecules of the same type (U_{ii}) and molecules of a different type (U_{ij}). Based on this concept, an equation was obtained that relates the activity coefficient of one component to the energy parameters of all system components (Fig. 1).

To verify that the model is suitable for predicting the phase equilibrium of this system, the calculated data were compared with the experimental ones and the error was calculated.

The data obtained in the future will be used as the basis for the development and modernization of ethyl propionate production processes.

\[
\ln y_i = \frac{\sum_{j=1}^{n} \tau_{ij} G_{ij} x_j}{\sum_{k=1}^{n} G_{ik} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{ik} x_k} \left( \tau_{ij} - \frac{\sum_{l=1}^{m} \tau_{lj} G_{lj} x_l}{\sum_{m=1}^{n} \tau_{mj} G_{mj} x_m} \right),
\]

\[
G_{ij} = \exp(-\sigma_{ij} \tau_{ij}), \quad \tau_{ij} = \frac{\Delta g_{ij}}{RT} = \frac{g_{ij} - g_{jj}}{RT},
\]

Figure 1. NRTL equation

Acknowledgements. Maria Toikka is grateful to Russian Foundation of Basic Research for the support of this study (RFBR project 18-33-20138)
THE STRUCTURE OF GRAPHITE OXIDE AND THE ROLE OF WATER

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Graphite oxide as a promising material is studied widely in experimental field. Structure of graphite oxide remains still unknown exactly. Different methods of synthesis lead to different kinds of material specimens with different composition. A lot of models were suggested since 1959. Nowadays, Lerf-Klinowski model [1] is commonly used. It assumes the existence of hydroxyl and epoxy groups located close to each other in the inner part of carbon layers, and carboxyl and hydroxyl groups at the edges. Based on comparative analysis of theoretical and experimental IR spectra, it was suggested [2] that lactones can also be present in graphite oxide layers.

The model of graphite oxide structure can further be extended based on a more thorough analysis of theoretical IR spectra. The effect of water on IR spectra and its probable interaction with functional groups in graphite oxide layers are studied with a particular attention to the properties of graphite oxide as an individual material and a membrane, through which gases like He, H₂, or CO₂ do not penetrate in a dry state, but do in a wet state [3].

Nonempirical simulations were carried out for clusters of a general composition CₓHᵧ(OH)zOₓ(COOH)₃(SO₃H)ₘ(NO₂)ₙ(H₂O)p, and theoretical IR spectra were constructed. In calculations [4], density functional method with B3LYP hybrid exchange-correlation functional and extended Gaussian basis set was used: DFT/B3LYP/6-31G(d,p). For reliable interpretation, experimental IR spectra, X-ray diffraction patterns, and X-ray photoelectron spectra were recorded for graphite oxide specimens synthesized by Tour method (I-GO) [4].

References
Today, it is a matter of routine to simulate the Raman spectra of organic compounds by DFT calculations of a single molecule in vacuum, but this method is hardly applicable for predicting the surface enhanced Raman scattering (SERS) spectra, which usually differ sharply from the ordinary Raman profiles. To date, our research team has collected a lot of high quality vibrational data (SERS, Raman and IR spectra) for the stilbene derivatives [1]. In this work, we present the results of DFT simulations the vibrational spectra of these compounds for the molecules coordinated to the small silver clusters. In order to find the best model system we studied a dependence of simulated Raman spectrum on cluster size, solvent accounting and charge localization using a similar level of theory, which was applied in the analogous studies [2]. The obtained results show the applicability of this approach.

Figure 1. Top to down: calculated Raman spectra of 4,4'-diaminostilbene (DAS), DAS*Ag₆ complex and experimental SERS spectrum of DAS.

References

Acknowledgements. The Russian Science Foundation (grant № 17-73-10209) supported this work. All experimental spectra were collected in the Center for Optical and Laser Materials Research of SPbU. The DFT calculations were performed in the Computing Centre of SPbU.
PREDICTION OF LIQUID-LIQUID EQUILIBRIUM IN HETEROGENEOUS TERNARY SYSTEMS USING UNIFAC EQUATION

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The study of the liquid-liquid equilibrium (LLE) in systems containing biofuel components is of great interest in the production of alternative energy sources. However, biofuel production is inefficient because it needs an excessive amount of raw materials. Nevertheless, the organization of production can be optimized with the help of scientifically sound methods and taking into account basic thermodynamic and kinetic positions [1]. In addition, prediction of LLE in heterogeneous systems also can be useful for optimization of biofuel production.

The objects of investigation were chosen ternary splitting systems including components of liquid biofuel: acetic acid – n-butanol – water, acetic acid – n-butyl acetate – water, n-butanol – n-butyric acid – water.

The purpose of this research is prediction of LLE in above-mentioned heterogeneous ternary systems by UNIFAC equation. Furthermore, comparison the LLE data modeling by UNIFAC with the experimental data of LLE obtained for the same systems by Gas chromatography method analysis. Experimental data of LLE were obtained in the work [2].

The UNIFAC method (UNIQUAC Functional-group Activity Coefficients) is one of the popular and examined models for describing the thermodynamic properties of heterogeneous systems. The modeling LLE data for ternary systems were presented in triangular phase diagrams.

Calculated LLE data have a good correlation with experimental data from work [2]. It confirms correctness the experiment in work [2] and corroborates reliability of this model.

References

Acknowledgements. Maria Toikka is grateful to Russian Foundation of Basic Research for the support of this study (RFBR project 18-33-20138).
Interest in systems consisting of molten salts is due to their broad application in various fields of industry and chemical sciences. When studying certain characteristics of such systems, it is first necessary to have reliable information about phase diagrams in order to avoid undesirable processes. Therefore, much attention is also directed to the development of theoretical approaches to describe the thermodynamic characteristics and phase equilibria in molten salts.

To carry out correct calculations of phase equilibria in salt systems, polarization interactions between ions must be taken into account. This task is successfully solved using *ab initio* and molecular dynamic modeling. However, within statistical theory, this problem for molten salts has not been solved so far. Within the statistical theory, task associated with polarization interactions is more conveniently to consider using the thermodynamic perturbation theory (TPT), taking into account more complex polarization interactions based on simple model of charged hard spheres (CHS) that have analytical solutions:

$$F_{liq} \leq F_0 + \frac{1}{4\pi^2} \sum_{i,j} \sqrt{x_i x_j} \int_{0}^{\infty} \phi_{ij}^1(k) \left( S_{ij}^0(k) - \delta_{ij} \right) k^2 dk + \frac{\rho}{2} \sum_{i,j} x_i x_j \phi_{ij}^1(0)$$

where $S_{ij}^0(k)$ is the structural factor of the reference system, $\phi_{ij}^1(k)$ is the additive to the pair potential, $F_0$ is the free energy of the reference system of CHS, and other two terms describe the polarization additive to the free energy.

Within this variational TPT-approach, the authors carried out calculations of the polarization contribution to the energies of the molten alkali halides. On this basis, the statistical-thermodynamic model is constructed to calculate phase equilibria in salt systems. In the report, this model will be presented on the example of calculating phase equilibria and thermodynamic properties in halide systems of sodium and cesium.

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VALIDATION OF LIGAND DOCKING ASSAY RESULTS APPLYING ADVANCED DFT CALCULATIONS AND IMPLICIT COSMO-RS SOLVENT MODEL CORRECTION

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According to the theory of the transition state, the energy of the activation barrier can be represented as the sum of the energies of the conformational transformations of the reactant molecules and the repulsion energy between the reactant molecules. The calculation of the energy of the true transition state for large biological systems can only be done by applying extremely costly molecular dynamics modeling methods which are inapplicable for the validation of scanning docking results with a large number of ligands. From the thermodynamics point of view, the possibility of chemical reactions and the stability of conformers is described by the Gibbs free energy functions (see Fig. 1). We translated the ligand molecule into a conformational state corresponding to the docking result geometry (ΔE1), the energy difference between this state and the initial one is indirectly related to the activation barrier of the observed reaction. ΔE2 corresponds to the energy of dispersion interactions and conformational changes in the protein binding pocket and could not be accounted due to the margin of error of the employed methods. ΔE3 is the ligand binding (docking) energy. Neglecting the value of ΔE2, we concluded that the described chemical reaction could run only if ΔE1 + ΔE3 <0.

Figure 1. Possible ways of protein-ligand interaction reaction

We suggested that the activity of ligand molecules may be related to their form of existence in aqueous solution, which is correlated with the significant flexibility of the studied ligand structures and the intramolecular hydrogen bonds formation possibility. The optimization of some large and flexible structures by DFT methods could be extremely computationally expensive. To narrow down the number of possible conformations, the search
for conformers based on the molecular mechanic's approach and geometry optimization based on the PM6 semi-empirical method was consistently applied. For DFT simulations, the composite RI-D3-B97-3c method [1] was used. Obtained structures were used in docking assays and DFT simulations. The energies of the most profitable ligand conformations obtained by DFT calculations were taken as reference values for the subsequent comparison with the docking energies. On the next step, ligand conformations, obtained after successful docking assays, were optimized using the DFT method. The reaction energy in the gas phase was calculated as the sum of the energies of the conformational transformation and the protein-ligand interaction. To account the influence of an aqueous solution on the ligand energy, the implicit solvent model COSMO-RS [2] was applied.

The described pipeline could be extremely useful for complex pharmacological search especially in combination with the QSAR approach. It was successfully applied in structural bioinformatics project, related to the nodulation (Nod) factors recognition mechanism by Pisum sativum protein heterodimer. Calculated solvation energies clearly show the large effect of water on the ligand conformational stability, which leads to a significant stabilization of the desired Nod factors in protein dimer and can serve as indirect evidence of the docking results. On the contrary, the results obtained for inappropriate Nod factors indicated a sufficient energy barrier that can impede the protein-ligand interaction.

References:
VESICLES AND STOMATOSOMES SELF-ASSEMBLED IN MIXED SURFACTANT SOLUTIONS: MOLECULAR THERMODYNAMIC MODELING

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Perforations which are known to spontaneously occur in flat bilayers, lamellae, and vesicles are important both for living matter and technology. Studying regularities of pore formation in a vesicle membrane seems to be promising as it may shed light on a mechanism of rupturing of cell membranes. Furthermore, vesicles are used in micellar catalysis and for synthesis of nanoparticles. Up to now, stable perforated lamellae as well as perforated vesicles, called stomatosomes, have been detected by SANS or cryo-TEM in a diversity of amphiphilic solutions including lipids, block-copolymers, surfactants and their mixtures [1 - 3]. A reliable theory of pore formation in self-assembling membranes is needed.

The classical molecular thermodynamic model [4, 5] is used to predict the most stable aggregate's shape and size basing on the aggregate's molecular parameters and temperature. In the present work we propose an extension to this model describing formation of stable vesicles and stomatosomes using our previous result for the mechanism of pore formation in lamellae [6]. We chose catanionic surfactant mixture C_{16}TAB (cetyltrimethylammonium bromide) - SOS (sodium octyl sulfate) in aqueous salt solution as a model system. To calculate an electrostatic term into the free energy of aggregation we derived an equation for electrostatic potential which allows inner part of the vesicle not to be electrically neutral. We obtained the equation showing that transmembrane potential depends on the geometrical parameters of the vesicle, compositions of both vesicle leaflets and the ratio of electrical permittivities in the solution and hydrocarbon membrane.

As a result, our model predicts temperature and solution salinity which stabilize vesicles or stomatosomes as well as optimal geometrical parameters and compositions of these aggregates. The obtained results are in agreement with experimental data for mixed surfactants [7].

References

Acknowledgements The financial support of Russian Foundation for Basic Research (project # 18-03-00698).
Taxifolin (TAX) exhibits pleiotropic effects including anti-oxidant activity [1]. This compound produced industrially as an active pharmaceutical ingredient, however it has a low bioavailability. Recently 191 metabolites of TAX were identified [2]. P-glycoprotein (P-gp) is multidrug transporter. The study objective is to investigate the ability of interaction TAX and its metabolites with P-gp via molecular docking. The structure of P-gp (6C0V) was used as a biotarget [3]. MarvinSketch 19.8 (ChemAxon, Hungary), AutoDock Tools 1.5.6 (TSRI, USA), AutoDock Vina 1.1.2 (TSRI, USA) [4] were used. The results were validated by redocking of the native ATP. Figure 1 demonstrates the docking TAX in ATPase site. Figure 2 shows a positive correlation between the molecular weight of ligands and this affinity energy. TAX and ATP bound with P-gp via the same amino acids residues, also they have a similar binding energy (9.8 kcal/mol and 9.9 kcal/mol respectively). TAX demonstrated good affinity energy, so the design of new TAX forms with higher bioavailability may be useful for new complex cancer therapy development.

Figure 1. The types of interactions between TAX and P-gp.  
Figure 2. Comparable analysis of docking results.

References

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AB INITIO STUDY MOLECULAR CATIONS Rg₂H⁺

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The discovery of the argonium ArH⁺ compound in the spectrum of the Crab nebula [1], and the recent detection of the molecular cation HeH⁺ [2], stimulated the investigations for other compounds of noble gases, which supposedly may exist in the interstellar medium (ISM). The purpose of the study of this work were complexes of the general formula Rg₂H⁺ (Rg = He, Ne, Ar), since it is known that complexes of this type have bright vibrational modes corresponding to the displacement of the proton between the atoms of the noble gases, which somewhat simplifies the task of detecting these molecular cations in ISM.

This work is dedicated to a quantum-chemical study of the mentioned molecular cations, including, preliminary geometry optimization, calculation frequencies of complexes. Further steps were aimed at obtaining the potential energy surface (PES) of the presented triatomic molecules. Using the resulted PES, also were calculated energy levels and rovibrational spectra. The calculations presented in the work were carried out using the method of coupled clusters of the CCSD(T) level. As previously assumed, the investigated complexes are stable and have a linear structure, corresponding to the available literary data [3].

It is expected that the results obtained in this work, in particular, the calculated frequencies of vibrational-rotational transitions, will be of use to eliminate the existing shortage of experimental information about the spectra of cations, and may also contribute to their identification in the ISM.

References

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ENERGY OF ISOMERIC FORMS OF N,N-DIMETHYLBIGUANIDE MOLECULE: QUANTUM CHEMICAL CALCULATION

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Metformin (N,N-dimethylbiguanide, BG) is an antidiabetic drug. The structure and energy (in Hartree units) of possible tautomeric forms of the N,N-dimethylbiguanide (BG) molecule are calculated using the Jaguar program using the DFT/B3LYP-D3/6-31G**++ method. Tautomeric forms were obtained using the Epik program. Typically, the structure of the BG molecule is depicted as Cis 1 or Cis 2. The calculations have shown that the Tauto 1 form, which is in equilibrium with the Trans form, has the minimum energy. The calculations explain the existence of BG in the form of monohydrochloride (protonation of the form of Tauto 1), and not of dihydrochloride (protonation of the form of Cis 1 or Cis 2) and the possibility of the formation of stable BG complex with metal cations (Trans form). The formation of complexes is accompanied in this case by the closure of the chelate cycle.

<table>
<thead>
<tr>
<th>Form</th>
<th>Energy (Hartree)</th>
</tr>
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<tbody>
<tr>
<td>Cis 2</td>
<td>-432.85009933538</td>
</tr>
<tr>
<td>Tauto 2</td>
<td>-432.85772848497</td>
</tr>
<tr>
<td>Antitrans</td>
<td>-432.85094510760</td>
</tr>
<tr>
<td>Cis 1</td>
<td>-432.84958924092</td>
</tr>
<tr>
<td>Tauto 1</td>
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</tr>
<tr>
<td>Trans</td>
<td>-432.85635091027</td>
</tr>
</tbody>
</table>
Presently, a lot of effort is required for associated petroleum gas (APG) utilization [1]. Large volumes of gas are flared due to high dew point temperature which leads to inexpediency of gas transportation to gas processing plants. Using of gas as a fuel to generate electricity comes across certain difficulties as well because of unstable gas composition, detonation risks and coke formation. Thus, a method of gas treatment which would allow obtaining normalized gas mixtures is necessary. Low-temperature steam conversion of light hydrocarbons (LTSC) represents a perspective method of APG treatment. The process occurs at 250-320 °C over Ni-based catalysts and results in increasing methane content. The brutto-reaction is as follows:

$$4C_nH_{2n+2} + 2(n-1)H_2O \rightarrow (3n+1)CH_4 + (n-1)CO_2\quad (n > 1).$$

Process conditions depend on initial gas composition, catalyst activity and gas requirements to be satisfied.

This work represents the results on mathematical simulation of the LTSC process. An array of experimental data on the reaction kinetics was obtained which included effective reactions orders and activation energies. The LTSC of realistic APG over an industrial Ni-based catalyst was simulated using a two-step macrokinetic model suggested. The areas of reaction conditions (GHSV and temperature) which would allow one to obtain normalized gas were determined. The calculations took into account such parameters of the produced gas as dew point temperature, methane number, net calorific value and Wobbe index. The macrokinetic model proposed can be used to predict optimal reaction conditions of the LTSC process for various applications thus being of much importance in terms of actual gas processing.

References

Acknowledgements. The reported study was funded by RFBR project 18-29-24015_mk.
Carboxylic [1] and phosphoric acids can form different anionic complexes with strong hydrogen bonds. In this work the complexes of homoconjugated anions for phosphinic and phosphoric acids with different substitutes have studied by quantum chemical calculations (DFT method). In complexes with more than one hydrogen bonds there is a cooperativity between these bonds. Thus in complex 1:2 length of hydrogen bonds decrease on 0.07 Å and energy increase on 3.52 kcal/mol per bond than hydrogen bond in complex 1:1 (see Fig.1). As a result $^1$H of bridged protons and $^{31}$P NMR chemical shifts have changed on $\sim$3 ppm and 2 ppm, respectively. In figure 1 in blue, orange and black colors $^1$H and $^{31}$P NMR chemical shifts (ppm) and lengths (Å) of hydrogen bridges are presented, respectively.

![Figure 1. Calculated structures of monomers (a), complexes 1:1 (b) and 1:2 (c) of homoconjugate anions of hypophosphorous acid in vacuum.](image)

References

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X-RAY AND COMPUTATIONAL STUDY OF SOLID OCTAMETHYLCYCLOTETRASILOXANE

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Cyclic oligosiloxanes have attracted a great experimental and theoretical interests due to their wide practical usage. Siloxanes are used in various areas of medical, catalytic and synthetic chemistry. Siloxane monomers usually exist as viscous colorless liquids. Thermodynamic properties are important in computational chemistry and high-quantity physical and chemical calculations. Therefore, the joint usage of quantum chemical and X-ray diffraction studies would help to discover interesting dependences.

One of the most commonly used siloxane monomers is octamethylcyclotetrasiloxane (D4) [1]. At the same time, its physical and chemical properties are still poorly understood. To establish the relation between physical properties and crystal structure the series of X-ray experiments at various temperatures were carried out (Figure 1). As a result, the structures of high- and low-temperature phases were established (Figure 2). We performed several MD calculations for the unit cells of D4 at various temperatures to found transition state.

It was found that the phase transition is related to the change of molecular conformation. The driving force of the conformational changes is inharmonic low-frequency vibration of siloxane ring.

Figure 1. Dependence of the unit cell volume by temperature of D4.

Figure 2. Crystal structure of low- (left) and high-temperature (right) phases.

References
THEORETICAL ANALYSIS OF BINDING INTERACTION BETWEEN SHORT PEPTIDES AND SOMATOSTATIN RECEPTOR TYPE 2

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Neuroendocrine tumors are characterized by high expression of somatostatin receptors on their surface. For the treatment of such diseases, peptide analogues of the somatostatin hormone are widely used. The lack of peptide hormones is their rapid hydrolysis under the action of protein kinases, therefore the development of shorter somatostatin analogues seems to be an actual task.

In this work we study two short tetra- (P1) and pentapeptide (P2) as potential biological vectors for radiopharmaceuticals (Fig.1), therefore the binding interaction between shorter peptides and somatostatin receptors needs to be shown.

The affinity of the studied peptides to somatostatin receptor type 2 was evaluated using computational methods: homology modeling [1], molecular dynamics simulation [2] and molecular docking [3]. The peptide-receptor binding energies were obtained, and receptor’s amino acids that are responsible for binding were also identified.

Figure 1. Structure of studied tetra- (P1) and pentapeptide (P2).

References

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MULTI-INSTANCE LEARNING FOR PREDICTING PROPERTIES OF MOLECULES

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The development of new drugs, chemicals and materials with desired properties is one of the key tasks of chemistry. Computational chemistry has developed many methods for predicting the properties of compounds. In drug design, the most popular methods for prediction of compound properties are docking, pharmacophore search, similarity search, and QSAR/QSPR modeling. One of the key limitations of conventional structure-property modeling is the requirement that each molecule has to be represented by a single instance with fixed conformation, protonation state, tautomeric form, etc. However, a molecule is a dynamic object and simultaneously exists in many forms/instances (conformers, protonated states, tautomers, mixtures of stereoisomers, etc) in equilibrium.

To overcome these limitations we propose the methodology based on multi-instance learning (MIL) method. The main idea of the approach is that an object (molecule) can be represented as a set of instances which may simultaneously exist, in our case, different molecular forms, which are encoded by their own vectors of descriptors. The property of the object is associated with one or more instances from the entire set, but it is not known which one. Thus, each object is characterized by a set of instances represented by vectors of descriptors and a single property value. The task is to build a model that finds the correlation between the set of vectors corresponding to the object instances and the property value.

We have developed and implemented the new algorithm for multi-instance learning based on special neural networks that will enable to train regression and classification models on large The MIL approach was compared with classical QSAR techniques based on application of features of 2D molecular descriptors and features of lowest energy 3D structure. We use proposed approach to model the biological activity of chemical compounds. Molecules were represented by several conformations (instances). The model, built on several instances (conformations) within convolutional MIL architecture shows better results than models based on one instance (conformation). The study shows that MIL approach, based on neural networks are very promising for modeling chemical object properties.

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5 section

COST-EFFECTIVE ANALYTICAL METHODS
Energy Dispersive X-ray Fluorescence (EDXRF) is a nondestructive analytical method which is very important for the determination of elements in a large variety of matrices. The advantages of EDX are simple sample preparation, non-destructivity, multielemental capabilities and short analysis time. Because of that the method has found broad application in material and environmental science, biology, chemistry, industrial process monitoring, etc. Nevertheless, most of the serial production EDX spectrometers cannot provide quantification of the elements with atomic numbers below 11 (sodium). This makes EDX hardly applicable for analysis of organic materials. The EDX spectrum contains not only the fluorescence lines of the elements composing the sample, but also the signal from reflected X-ray tube radiation which consists of deceleration radiation and elastic/inelastic scattering of cathode radiation. The intensity of scattered radiation is influenced by average mass absorption coefficient of the sample, which in turn depends on elemental composition. In this way, scattered radiation can be employed as a source of information on integral properties of the samples as determined by its “average” molecular mass. A general feasibility of studying various light elements through the analysis of scattered radiation was explored in the previous studies but the lack of selectivity was the reason for significant imprecision. In this study 46 samples of various plastics were measured with EDXRF. The resulting spectra were processed with principal component analysis (PCA) in order to explore the clustering of the samples. Moreover, using partial least square (PLS) it was possible to construct predictive models relating EDX signals with the content of organic elements C% and H% and integral physical properties (density, mass per atom and others). The derived performance metrics of the models have shown the general applicability of the approach. The use of redundant chemical information hidden in the scattering spectra can be done through chemometric modeling and can provide for novel interesting opportunities in EDX application.
VOLTAMMETRIC DETERMINATION OF THYROXINE ON ELECTRODES MODIFIED BY GOLD NANOPARTICLES AND CARBON NANOTUBES IN DRUGS

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The development of fast and simple methods for determining thyroxine concentrations is of great interest. Being the main thyroid form of thyroid hormones thyroxine plays an important role in the body. The content of this compound depends on the rate of metabolism, the supply of body tissues with oxygen, the work of the heart. Therefore, it is necessary to control the content of this compound to identify pathology and conduct drug therapy. Voltammetry with chemically modified electrodes (CME) is a promising method of analysis, because it is characterized by high sensitivity and selectivity in the determination of organic compounds.

In the present study the catalytic activity of gold nanoparticles immobilized on the surface of a carbon paste electrode (Au-CPE), bare and modified by single-walled carbon nanotubes (SWCNT) during electrooxidation of thyroxine was studied.

A small signal of thyroxine oxidation is observed on the bare CPE in an alkaline medium. It was found that immobilized gold nanoparticles show catalytic activity during the thyroxine oxidation, which is exhibited in an increase in the oxidation current of the modifier in the presence of the substrate and a decrease in the oxidation potential of the substrate in comparison with the unmodified electrode. The using of the CPE modified by gold nanoparticles immobilized on carbon nanotubes leads to a significant increase of the oxidation signal of thyroxine. It is established that functionalized SWCNT exhibit greater catalytic activity than unfunctionalized SWCNT. Oxidation of thyroxine on the Au-SWCNT-CPE occurs at the potential E_0 = 0.65V.

The method of voltammetric determination of thyroxine on Au-SWCNT-CPE is proposed. Calibration graph is linear in the concentration range from 1×10^{-9} to 1×10^{-3} M. The developed method was used to determine thyroxine in drugs.

Acknowledgements. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.
A smoking technology is widely used for the production and preservation of meat products. It assumes the penetration of smoking substances into the smoked meat products during the thermal destruction of wood [1-2]. As a desired consequence of smoking, phenolic substances are generated. Though phenol and phenolic substances are of considerable importance to the organoleptic properties of smoked meat products, they cause potential toxic and carcinogenic effects on humans [3]. According to this fact, there is a need to control the quality of smoked foods to detect the excess content of phenols, which threatens the health and life of the consumer. Taking into account the complexity of sample matrices, sample preparation plays an important role during the analysis. Thus, in this research a new simple and effective scheme of phenols extraction for its following determination was developed. According to this scheme at the first step phenols generation and sorption on magnetic nanoparticles in specially developed vessel equipped with external magnetic field was performed. At the second step, the phenols were eluted from the magnetic nanoparticles, and finally, the analytes were determined by HPLC-UV. The magnetic nanoparticles based on Fe₃O₄ were used as a sorbent for phenols gas sorption for the first time. Large adsorbing surface, high magnetic properties and stability to oxidizing can explain the choice of magnetic nanoparticles in this research.

References
Nowadays, the quantitative determination of glutathione is of great interest. Silver based electrochemical sensors can be used for determination of glutathione.

We present the template electrochemical synthesis of an array of micron silver particles on a solid substrate developed by our scientific group, based on the application of a template obtained by the sol-gel method using a structure-forming polymer dopant [1]. The final material is a polished titanium coated with an array of silver microparticles separated by a dielectric xerogel of titanium oxide. The resulting material was used as an analytical electrode: a method was developed for determining glutathione in aqueous solutions in the range from $10^{-9}$ to $5*10^{-7}$ M, based on the removing of cyclic voltammograms.

![Figure 1. Electron micrograph of the sample made in pulse mode.](image1)

![Figure 2. Dependence of the difference between the maximum current densities in the background electrolyte and with glutathione additives.](image2)

References

The team of authors thanks the Science Park of St. Petersburg State University for their invaluable research assistance.
Greenhouse hydroponic experiments were carried out to examine the impacts of citric acid on Zn uptake and phytoextraction potentials of sorghum (*sorghum bicolor L.M*). Two-week-old seedlings transplanted in hydroponic solutions were treated with different doses of Zn in the concentration range of 5, 25, 50, 100 and 200 mg/L alone or in combination with 10 mM citric acid. After 21 day of culture, the plants were harvested, separated into roots and shoots and then dried. Fresh and dry weights, Zn uptake, translocation factor (TF), bioconcentration factor (BCF), proline, ascorbate and pigment contents were determined. The results indicate that Zn uptake, fresh and dry weights, TF, BCF, proline and ascorbate contents were concentration dependent with more significant increase (P < 0.05) after application of citric acid. Pigments and protein contents were however, severely decreased with increasing Zn concentrations and appreciated gradually with the addition of citric acid. Thus, citric acid efficiently increased phytoextractability of Zn and *Sorghum bicolor LM* was non-hyperaccumulator of Zn; but may be used for phytoremediation of Zn contaminated environments with assistance of citric acid.

References
An important condition for the effective development of agriculture is the justified and controlled use of drugs in veterinary medicine. To control the quality of the products obtained, simple, fast, efficient and environmentally friendly methods of chemical analysis are needed.

To solve this problem, within the framework of this study, a simple and effective method was proposed for isolating drugs of the sulfonamide group from chicken meat samples using a new type of effective extractants - deep eutectic solvents (DES) [1]. This type of extractants is a mixture of hydrogen bond donor and acceptor, the formation of which leads to a lower melting point of the system.

The developed method includes the extraction of analytes into DES synthesized from natural substances, such as choline chloride, glycerin, ethylene glycol, acetic and formic acids. The sample preparation procedure is a liquid extraction of analytes into the DES phase with their subsequent HPLC-UV detection. The developed method allows to determine analytes at the level of mg / kg and could be used to control the quality of meat products. The developed approach made it possible to eliminate the use of toxic organic solvents at the sample preparation stage without losing the efficiency of analyte extraction.

References

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IN-SOURCE DERIVATIZATION: AN EXPRESS METHOD FOR ALCOHOLS DETECTION BY DART MASS SPECTROMETRY

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Fast growing popularity of ambient ionization mass spectrometry methods is caused by the ability of these techniques to provide express qualitative and, sometimes, quantitative analysis without or with minimal sample preparation. At the same time, all of these approaches inherited mainly such ‘soft’ ionization processes as protonation, cationization and deprotonation. Thus, analytes, which are not capable of these processes, have high detection limits or cannot be analyzed by such methods at all. Furthermore, some compounds readily eliminate leaving groups after ionization. Some of these problems can be overcome by using the chemical modification approaches providing the permanent charge derivatization or yielding the readily ionizable derivatives. The main requirement for probable derivatization methods involved in analysis by ambient ionization mass spectrometry is the application of extremely simple and fast reaction procedures. Herein, we describe the first example of such approach for analysis alcohols by ‘direct analysis in real time’ (DART) mass spectrometry. The proposed method is based on reaction of alcohols with pyridine directly in DART sample gap yielding fixed-charge derivatives.

![Figure 1. Gas-phase reaction of alcohols with pyridine in DART ionization gap.](image)

This approach has been tested on linear and branched fatty alcohols, cyclic alcohols and sterols. It was shown that the process proceeds only at rather high helium flow temperatures and is suitable only for relatively high-boiling alcohols. The registered DART mass spectra contain only the peaks of the cationic part of the derivatives. The resulting salts have a high ionization efficiency, and the detection limits of the corresponding compounds are reduced by two orders of magnitude.

The proposed method was applied for profiling of sterols in complex food matrices. It was shown that the obtained results are identical to gas chromatography / mass spectrometry data. At the same time, the latter approach requires much longer sample preparation and analysis times.

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Fe$_3$O$_4$ NANOPARTICLES MODIFIED BY SURFACTANTS AS NOVEL SORBENTS FOR MAGNETIC DISPERSIVE MICRO-SOLID PHASE EXTRACTION OF TETRACYCLINES FROM BIOLOGICAL FLUIDS

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A novel magnetic Fe$_3$O$_4$ nanoparticles coated by surfactants were investigated for a magnetic dispersive micro-solid phase extraction of tetracyclines (tetracycline, oxytetracycline and doxycycline) from biological fluids for the first time. It was established that Fe$_3$O$_4$ nanoparticles coating with cetyltrimethylammonium bromide allowed to improve tetracyclines extraction efficiency and nanoparticles stability without deterioration of their magnetic behavior. Moreover, Fe$_3$O$_4$ nanoparticles coating with surfactants is fast and simple. A magnetic dispersive micro-solid phase extraction procedure based on novel nanoparticles was developed for the HPLC-UV determination of tetracyclines in biological fluids. The developed procedure involved the floating of the nanoparticles in a liquid sample phase for extraction of the analytes followed by their elution and determination. The procedure was applied for the determination of tetracyclines in human plasma and serum samples. The reported procedure proves to be fast, simple, and inexpensive.

Acknowledgements Authors gratefully acknowledge The Russian Foundation for Basic Research for financial support (project no. 18-33-01176_mol_a) of this work.
In recent years, methods for early lung cancer diagnosis, based on the measurement of the volatile organic compounds (VOCs) profile in exhaled air are rapidly developing. The advantages of this approach are the simplicity and non-invasiveness of sampling, relatively small matrix effects, the possibility of online analysis [1]. In this work, a new version of VOCs chemical ionization in glow discharge was developed.

The Lumas-30 time-of-flight mass spectrometer with pulsed ionization source and copper hollow cathode was used. All measurements were carried out using air or a mixture of VOC with air. The several compounds, which belong to different classes of VOCs, such as acetonitrile, benzene, toluene, o-xylene, p-xylene, m-xylene, heptane were analysed. Ionization processes in glow discharge were studied. The VOCs ionization mechanism of efficient VOCs association reaction with metal ions (from auxiliary cathode material) was discovered. Also, efficiency of electron ionization mechanism [2] was shown for determination of VOCs. Additional mechanisms such as Penning ionization, a proton transfer reaction were also used to increase the reliability of VOC identification and increase the informative value of the analysis. The optimal parameters of discharge (pulse duration, repelling pulse delay time, pressure and voltage) were determined for each mechanism. It has to be noted, that in this case it is possible to implement all mechanisms, as well as each of them separately by optimizing the operating parameters. The detection limits of the compounds studied were determined; the values were about ppm level. Moreover, the mixtures containing two organic compounds were analyzed. The mutual influence of the compounds and the ability to control this effect are shown.

References

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Norepinephrine (NE) is an important catecholamine neurotransmitter in the mammalian central nervous system. It mediates increase in heart rate, blood pressure, pupil dilation, and dilation of the airways, and the constriction of blood vessels. NE is critical for attention and focus, learning, memory, and the sleep-wake cycle. Alteration in its level is related to many diseases and other complications in body functions.

For measuring NE use HPLC, gas chromatography, spectrophotometry, fluorometry, chemiluminescence. Most such methods are complicated, requiring derivatization and suffering from low sensitivity and high cost. These drawbacks have been overcome though the use of electrochemical methods with various modified electrodes, simplifying the fabrication with the desired composition, in turn improving their sensitivity. But NE on the indicator electrodes oxidizes with high overvoltage. However, the effects of overvoltage can be reduced by using of modifiers. Thus voltammetric methods of analysis based on the use of chemically modified electrodes (CME) with electrocatalytic properties are of interest.

In this work, the catalytic activity of gold, cobalt, palladium, copper and bimetallic systems of gold (Au-Co, Au-Pd and Au-Cu), electrodeposited on carbon screen-printed electrodes (SPE) at the electrochemical oxidation of NE is established. Catalytic properties are appeared in a multiple increasing of peak current compared with the oxidation modifiers current and in decreasing the overvoltages of the oxidation of the NE compared with unmodified electrode.

The linear dependence of the analytical signal on the concentration of NE is observed in the ranges from $5 \times 10^{-7}$ to $5 \times 10^{-3}$ M on the SPE modified by bimetallic systems of gold particles. CME with electrodeposition bimetallic system Au-Co, distinguished by the best analytical and operational characteristics in the oxidation of norepinephrine, were used in the analysis of drugs.

Acknowledgements. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.
Polyphenols antioxidants activity plays an important role in the prevention of chronic diseases such as cardiovascular and neurodegenerative disorders, cancer, type 2 diabetes, and osteoporosis. One of the main sources of polyphenol antioxidants are tea and coffee. Main tea polyphenols are catechins and in coffee are hydroxycinnamic acids. So, the content of polyphenols in tea and coffee is one of the criteria for analytical quality control of these beverages. Along with target analysis, a promising approach is to obtain characteristic profiles of sample components with subsequent chemometric processing to determine the suitable identification criteria and the quality of the analyzed samples. These tasks are set and solved in this work. Polyphenol antioxidants (catechins, gallic acid, chlorogenic, caffeic, ferulic acids, etc.) were selectively separated by reverse phase (RP) HPLC with photodiode array in various samples of tea and coffee. Caffeoyl-, feruloyl- and dicaffeoylquinic acids (chlorogenic acids) in infusions from roasted coffee beans were identified by RP HPLC with MS detection in negative ionization mode. Chromatographic profiles of polyphenol antioxidant in tea and coffee were obtained. Their chemometric processing was carried out using multivariate classification techniques including principal component analysis (PCA). It allowed identification of a variety of marker compounds responsible for differences among green teas and coffee of different origin and processing methods. Gallocatechine, gallocatechine gallate, epigallocatechine gallate and epicatechine gallate were contributing to most variances in tea samples. The special task of the research was the investigation of polyphenol composition in varieties of tea obtained from the Institute of Floriculture and Subtropical Crops of the Russian Academy of Sciences (Sochi). The chemometric processing of its characteristic profiles will provide an independent classification criterion for new varieties of tea.

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One of the fundamental problems of modern analytical chemistry is a non-invasive diagnostics of pathologies in the human body. The assessment of the condition of the oral cavity of electronic cigarettes smokers is one of the illustrations of medical diagnostic tasks. The lack of sufficient information about the effects of smoking electronic cigarettes leads to various pathologies (diseases). The markers of the state of the oral cavity can be the content of anions of mineral acids in the oral fluid (OF), such as chloride, sulfate, fluoride, nitrite, and nitrate ions. The most appropriate method for their determination is capillary electrophoresis.

Experimental instruments: ‘Kapel-104-T’ capillary electrophoresis system (Lumex).

A technique of sample preparation of OF and optimal capillary electrophoresis conditions for determination anions in OF have been developed.

Overall, there are observed underestimated values of the content of anions in the electronic cigarettes smokers with nicotine OF compared with the OF of smokers of electronic cigarettes without nicotine.

The maximum values of the linear correlation coefficients (values are in brackets) between the content of anions and cations in the case of smokers of electronic cigarettes without nicotine show a linear relationship between the contents of: chloride ions and cations potassium (0,85), magnesium (0,95), manganese (0,73), sodium (0,93); phosphate ions and magnesium (0,87).

In smokers’ of electronic cigarettes with nicotine OF, there is a linear correlation between the contents of: strontium and chloride ions (0,89); potassium and sulfate ions (0,83); fluoride anions and cations of calcium (0,96), potassium (0,94); phosphate anions and cations of calcium (0,81), potassium (0,77).

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The creation of national standards for the quality of medicines based on objective methods is a guarantee of the effectiveness and safety of drugs. Determining the quality of drugs to regulated standards involves the use of various analytical methods. At the same time, the final conclusion about the quality of drugs largely depends on the quality of the method itself, which must meet certain requirements. Generally accepted worldwide recommendations for the production of medicines in the form of GMP rules — good manufacturing practices — contain test method requirements that are used to assess the compliance of pharmaceutical products with established specifications for accuracy and reliability.

The purpose of this work is to select the optimal conditions for determining the content of framycetin sulphate in the preparation of eye and ear drops “Framidex” using HPLC.

Studies were performed using an “LC-20 Prominence” chromatograph with a spectrophotometric detector (manufactured by Shimadzu Corporation, Japan). As a mobile phase used three-component mixtures: acetonitrile for HPLC : 1 N sulphuric acid solution: tris (hydroxymethyl) aminomethane buffer solution. Considered the effect of the amount of the organic modifier, and the eluent supply mode on the retention time and separation of framycetin sulphate from other components of the investigational medicinal product, such as gramicidin and dexamethasone.

The developed method for the quantitative determination of framycetin sulphate, validated as required by EP (European Pharmacopoeia) and BP (British Pharmacopoeia). According to the results of the laboratory experiment, it was found that the metrological characteristics of such validation parameters of the methodology, such as convergence, linearity and internal laboratory precision, do not exceed the validation criteria. The stability of the technique can be reproduced in the laboratory, the deviation of a single value is 100.2% with a confidence level of 95%.

Thus, in the chemical laboratory of the quality control department of “ASEPTICA” LLC (Republic of Uzbekistan), methods were carried out to develop and improve for determination of framycetin sulphate in the eye drops and ear drops “Framidex” using the HPLC method.
Deep eutectic solvents (DES) are a mixture of two or more components capable of self-association, most often through the formation of a hydrogen bond, with the formation of a eutectic mixture, the melting point of which is significantly less than the melting point of the individual components [1]. In analytical chemistry, DES have proven to be effective extractants, with the stage of preliminary synthesis of DES.

In this study, we demonstrated a new approach for the extraction of nonsteroidal anti-inflammatory drugs (NSAIDs), based on the in situ formation of DES. The procedure includes two stages. First: extraction of the analyte from the sample into the acetate buffer solution. Second: extraction of the analyte into the pre-melted menthol to form DES in-situ. The resulting DES is easily separated from the matrix and used for HPLC-UV detection of analytes. This technique was used for determination of diclofenac and ketoprofen in beef liver samples. The detection limit was 0.7 mg / kg for ketoprofen and 1 mg / kg for diclofenac. At the same time, this approach completely eliminated the need to use organic solvents during the sample preparation procedure and allowed the use of natural menthol as an extractant.

References

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Hydrophilic anions both organic and inorganic are of a wide interest for analytical chemists since they are abundant species in industry and environment. Although a lot of methods for sensing of hydrophilic anions have been proposed over decades including chromatography and various optical methods [1], potentiometry might have the biggest advantages, such as low cost, suitability for field-based experiments, and miniaturization. Potentiometric membrane sensors have attracted a lot of attention as simple and effective tools for anion quantification.

Developing sensitive and selective potentiometric sensors for such ions as carbonate, phosphate and sulfate may be a hard nut to crack. The reasons for this are low charge-to-radius ratio, variability in geometry, dependence of anion form on pH of a solution, as well as low permeability of target analyte into the sensing membrane matrix. These challenges lead to development of new anion carriers [2] later used as ionophores in electrochemical sensors.

In this study a set of perfluorinated diketones with various chemical structures was used as ionophores to prepare membranes for potentiometric sensors. Substances which bear fluorine atoms or CF₃ substituents are considered to be the most highly effective anion carriers [3]. They provide effective complexation of hydrophilic anions via hydrogen bonding. The prepared PVC-plasticized sensor membranes were studied for selectivity and sensitivity towards variety of anions. It was found that sensitivity patterns of these new sensors deviate from Hofmeister series. This shows a good promise for development of a new class of anion-selective ionophores with high potential in selective quantification of hydrophilic anions.

References

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POLARIZED TWO-PHOTON EXCITED FLUORESCENCE IN NADH IN WATER/METHANOL SOLUTIONS.

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The biological coenzyme NADH plays very important role as an electron carrier in oxidize-reduced reactions in cells [1]. As known, total fluorescence intensity in NADH can be presented as a sum of three exponents with lifetimes $\tau_1$ and $\tau_2$, and rotational diffusion time $\tau_{rot}$ [2]. However, the nature of the multiexponential decay as well as the correlation of decay parameters on NADH microenvironment are so far not known enough. In the present work, the effect of solvent viscosity and polarity on the decay parameters of polarized fluorescence of NADH have been studied. Two-photon excited fluorescence decay in NADH has been determined and analyzed in water-methanol solutions.

Based on the polarized fluorescence signals obtained, we determined decay times $\tau_1$ and $\tau_2$, rotation diffusion time $\tau_{rot}$, a fluorescence anisotropy $r_0$, and the ratio of pre-exponential factors $a_1/a_2$. It was found, that rotational diffusion time $\tau_{rot}$, the absorption anisotropy $r_0$, and the values of and $a_1/a_2$ depended nonlinearly on the methanol concentration. The decay time $\tau_2$ increased with increasing methanol concentration. A theoretical model has developed showing that the fluorescence parameters are influenced by both the solution viscosity and energy exchange between two NADH chromophores, adenine and nicotinamide. As known, there are two conformers of NADH related to folded and unfolded geometrical configurations [3]. We believed that when the concentration of methanol in solution changed, relative concentrations of these conformers changed also resulting in the changes of rotational diffusion time $\tau_{rot}$, fluorescence anisotropy $r_0$, and the ratio of pre-exponential factors $a_1/a_2$. The data obtained suggest a new way of investigation the processes of denaturation of NADH in solutions and cells.

References
DETERMINATION OF MUSCLE STRESS MARKER 3-METHYL-L-HISTIDINE IN BIOLOGICAL FLUIDS USING DNA APTAMERS

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Determination of the 3-methyl-L-histidine content in human body fluids (urine and blood) has an important diagnostic value in the clinic and sport medicine since this compound serves as a biochemical marker for the degradation of myofibrillar proteins. Thus, it can be utilized for example to monitor the Duchenne disease or muscle stress during intensive trainings. Existing methods for 3-methylhistidine determination have a number of disadvantages: low expressiveness, high cost of analysis, high interferences caused by the presence of other compounds in the analyzed sample.

A new approach based on the use of aptamers - short-chain DNA molecules (sequences up to 80 nucleotides) which have high affinity for the target compound was applied. A key advantage of using aptamers to develop express test systems is the high sensitivity of detection in the presence of other compounds. Currently, there is no information on the use of aptamers for express detection of 3-methyl–L-histidine in available literature.

SELEX (Systematic Evolution of Ligands by Exponential Enrichment) procedure was used for the selection of aptamers specific to 3-methyl-L-histidine from the DNA-aptamer library. Seven rounds including two counter rounds were carried out. Selected aptamers were amplified by PCR procedure after each round. The enriched pool of aptamers after the seventh round of selection has been cloned into cells of the E. coli strain and identified after sequencing. The physico-chemical parameters of the aptamer-target binding were measured. Dissociation constants of aptamer-target complex were in low µM level, which is sufficient to effectively apply these aptamers as specific binding agents in biosensor systems for determination of 3-methyl-L-histidine in biological fluids. The test system developed using oligonucleotide aptamers to 3-methyl-L-histidine can be the basis for new generation methods in clinical and laboratory diagnostics for medicine and sports.

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TiO$_2$ catalysts for the purification of sulfur-containing gases are used in gas and oil treatment processes, chemical industry and metallurgy enterprises. At the same time TiO$_2$ and impregnated sorbents were employed to remove hazardous ions and applied in analytical chemistry.

The goal of this work was to obtain highly efficient and inexpensive inorganic solid-phase sorbents from spent catalyst (TiO$_2$) manufactured by the Shurtan Gas Chemical Complex (Uzbekistan). The catalyst TiO$_2$ matrix was thermal treated (500°C) and impregnated by different organic ligands like 2-amino-1-methylbenzimidazole (MAB), benzohydroxamic acid (BGK), 5-sulphosalicylic acid (SAL), dithizone (DTZ).

The metal complex formation with the surface of the impregnated matrix increases the sorption capacity (mmol L$^{-1}$) of prepared impregnated sorbents.

Figure 1. Effect of impregnation on sorption

References
ELECTRICAL BOUNDARY POTENTIAL AS AN INSTRUMENT FOR CONTROLLING THE CHARACTERISTICS OF THE POLYMERIC ION-SELECTIVE SENSORS

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Ion-selective sensors are widely used in routine analysis. Their response mechanism is based on equality of the electrochemical potentials of all the species in the sensor and sample phases. Therefore, the boundary potential at the sensor/sample interface plays a crucial role in the signal formation both for potentiometric sensors (ion-selective electrodes, ISEs) and for optical chemical sensors (optodes). The possibility of controlling the electrical boundary potential would open broad prospects for tuning the sensor characteristics.

Herein, we report on theoretical and experimental investigation of the mechanism of the boundary potential formation. The potential at the polymeric sensor/solution interface was simulated numerically. The effect of the lipophilic electrolyte partition [1, 2] between the two phases was quantified. Furthermore, strong influence of the co-extraction of the solution anion on the interfacial potential of the cation-selective sensors was predicted theoretically and verified experimentally.

The obtained results allowed developing and quantifying a strategy for tuning and stabilization of the boundary potential at the sensor/solution interface. The latter is strongly required for obtaining optodes that respond to individual ionic activity [1], liquid junction-free reference electrodes for all-solid-state potentiometric devices [2], color standards for digital color analysis [3], and calibration-free optode arrays [4].

References

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A CLOUD POINT MICROEXTRACTION APPROACH FOR THE SEPARATION AND PRECONCENTRATION OF PESTICIDES IN FOOD

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Pesticides are widely used during the cultivation and the post-harvest storage of crops to prevent the destruction of crops by agricultural pests, fungi and weeds [1]. However, pesticides misuse can result in unacceptable high levels of the compounds in the food products can it cause potential harm to human health [2]. Therefore, the pesticide residue monitoring in foods is an important challenge of analytical chemistry. In the current study, a novel cloud point microextraction technique for pesticides determination has been developed. The new approach assumes the addition of extraction mixture consisting from water, fatty amine and carboxylic acid to the sample followed by phase separation using salting-out reagent and centrifugation. The developed approach is rapidly, simple, high sample throughput, low cost and environmentally-friendly, which can be used for simultaneous pretreatment of a large number of samples without any specific equipment. The proposed technique was successfully applied to the GC-MS determination of pesticides in vegetables.

Figure 1. Schematic representation of the developed procedure.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project No 18-33-01176_mol_a).
The problem of pollution in the Arctic has been discussed for more than a decade, and it becomes obvious that the economic activity of countries around the world leads to man-made pollution of Arctic ecosystems. The Arctic nature is extremely vulnerable to the contamination, which in the future may lead to irreversible worldwide ecological processes. This region is under an ever-increasing man-caused impact of both local industrial centers and changing transportation ways of pollutants by air masses, water flows and sedimentary material of arctic rivers. The main contaminates of the Arctic territories along with persistent organic pollutants (POPs) are heavy metals (HM) and petroleum products. Among the prevailing pollutants, a special place is occupied by heavy metals which concentrations must be controlled.

Thus, the purpose of this work was to study the prevalence of xenobiotics in this region and to assess the pollution level and accumulated environmental damage.

In this work, we studied the soil, water and vegetation samples from the Arctic meteorological station located on the Yamal Peninsula. Analysis of the level of oil pollution showed the presence of strong oil pollution of the soil on the territory of the station, the depth of oil penetration reached \( \geq 20 \) cm. Also experiments were conducted to determine the content of such xenobiotics as heavy metals and organic pollutants.

Analysis of the experimental data showed that the soils of the Arctic region were subjected to anthropogenic man-made impact. On the territory of the station there are abandoned radio-relay communication lines, a number of household buildings for their maintenance, destroyed equipment and fuel and lubricant storage sites. The likely sources of oil pollution were the storage facilities for fuel and lubricants needed for the operation of the station.

A number of heavy metal accumulations were obtained. The possible sources of this pollution could be, as well as destroyed buildings, equipment, etc., and transboundary transport. The presence of higher plants intensifies the processes of biomediation, the root system contributes to the loosening of bituminized / oil-contaminated soils, and also plants are able to accumulate xenobiotics.
ANTIOXIDANT ACTIVITY STUDY OF THE 2,6-DI-TERT-BUTYLPHENOLS WITH PYRIDINE MOIETIES USING CYCLIC VOLTAMMETRY

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The search for novel antioxidant express assays as well as for polyfunctional antioxidants is still of great interest [1]. Novel ligands 1-6 and their hydrochlorides 1a-6a containing N-donor pyridine rings and 2,6-di-tert-butylphenols fragments were synthesized and the electrochemical properties of these compounds were studied by cyclic voltammetry (CV) method. The feasible schemes of redox-transformations were proposed.

Antioxidant activity of 1-6 and 1a-6a was measured using electrochemical method [2] based on the reaction with stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) rate measuring. It was shown that the redox behavior of phenols as well as antioxidant activity strongly depends on the structure of pendant in para-position and the length of hydrocarbonyl linker. The compounds 4-6 and hydrochlorides 1a-6a demonstrated high activity. The correlation of redox-properties and antioxidant properties was demonstrated. The data of electrochemical study are in accordance with the results obtained spectrophotometrically in CUPRAC test thus proving the efficiency and reliability of approach proposed.

References

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Determination of organic acids such as ascorbic acid (AA) and malic acid (MA) in fruit juices is an important task, because these compounds are responsible for the taste characteristics and organoleptic quality, and may also effect the stability of the product. Quantification of organic acids in juice is a way to identify the product authenticity. Thus, the development of fast, simple, and selective methods for the determination of AA and MA in juice is of great interest.

For quantitative determination of AA and MA various physical-chemical methods are used, such as titrimetry, spectrophotometry, chemiluminescence, high performance liquid chromatography (HPLC). Along with advantages, these methods have some limitations. Low sensitivity and selectivity are disadvantages of spectrophotometry and titrimetry. In conditions of HPLC one can determine several components but after preliminary preparation of samples, frequently including preliminary derivatization. Besides, these methods are complicated in conduction, time, and cost taking. Therefore voltammetric method with chemically modified electrodes (CME) that have the advantage of simplicity in experiment conduction, high analytical characteristics, and non-expensive equipment represents interest.

Gold-cobalt binary system electrodeposited on the surface of screen printed electrode exhibit catalytic activity during AA and MA electrooxidation. It is exhibited in decreasing of overvoltage of substrate oxidation and in increasing of oxidation current of modifier. The method of voltammetric simultaneously detection of organic acids at the screen printed electrode with two working electrodes modified by gold-cobalt binary system was suggested. The linear dependence of analytical signal from the analyte concentration is observed in the range from $5 \times 10^{-7}$ to $5 \times 10^{-3}$ M of AA and from $5 \times 10^{-7}$ to $5 \times 10^{-3}$ M of MA. This method was used in the analysis of fruit juices.

Acknowledgements. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.
INVESTIGATION OF ASSOCIATION OF TRIS-PILLAR[5]ARENE WITH PHENOTHIAZINE DERIVATIVE: COLOMETRIC RECOGNITION OF ANIONS

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Due to pillar[n]arenes capability to recognize anions through forming supramolecular complexes, creating sensors based on them is attractive concept for modern chemistry. Pillar[n]arenes are also able to form inclusion complexes and associates with aromatic compounds, which makes them suitable structure blocks for receptor systems working on the dye-displacement principle for inorganic anions and biologically relevant anion substrates, e.g., adenosine triphosphate.

We have developed a synthetic procedure to functionalize TREN with three terminal pillar[5]arene terminal fragments linked to the core by amide linkers. UV-spectrophotometry titration was used to study complexation of tris-pillar[5]arene with phenothiazine dye. The structure of the complex is discussed and supported by NMR $^1$H spectrometry, amide fragment of TREN participates in a hydrogen bond with imino group of phenothiazine dye resulting in significant red shift of the absorption band. Anion binding leads to dye displacement with the attendant color change from blue (complex) to pink (free phenothiazine dye). Taking into account electrochemical activity of phenothiazine and polyphenothiazine derivatives this approach might be also promising for further applications in electrochemical sensors.

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NOVEL APPROACHES TO ELECTROCHEMICAL SENSING WITH IONOPHORE-BASED MEMBRANES

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Ionophores: neutral or charged molecules capable of selective complexation with various ions and neutral species are widely used in potentiometric sensors (ion-selective electrodes, ISEs), conductometric sensors and optical sensors (optodes) [1]. These sensors are routinely applied in clinical analysis, agriculture, environmental monitoring and industry. Recently, the family of ionophore-based sensors got new members: voltammetric [2] and ampero-coulometric sensors [3, 4].

In this work, a comparative study of K⁺-selective ISEs was carried out in different measurement modes: potentiometric, voltammetric and ampero-coulometric modes. Sensor membranes were drop-cast or spin-coated on top of PEDOT-PSS layer formed on glassy carbon substrate. The sensor membranes contained polyvinylchloride (PVC) as matrix polymer, bis(2-butylpentyl)adipate (BBPA) as plasticizer, neutral ionophore valinomycin (0.02 m), potassium tetrakis(p-Cl-phenyl)borate (KClTPB, 0.01 m) as cation exchanger, and a lipophilic electrolyte tetradodecylammonium tetrakis(p-Cl-phenyl)borate (ETH 500, 0.01 m).

The ISEs showed linear Nernstian response to K⁺ over the range from 10⁻¹ to 10⁻⁶ M with the slope of 56.8 mV/log(aK) and high selectivity over Na⁺ and other interferences. In voltammetric mode clear oxidation/reduction peaks were registered. Most interesting results have been achieved in ampero-coulometric mode. The existing response model [3] was generalized, and this allowed for a dramatic improvement of the fitting of the experimental curves to the theory. Importantly, for the first time, ISEs in coulometric mode were successfully applied for K⁺ quantification in blood serum samples.

References

Acknowledgements. The resource center “Innovation technologies of composite nanomaterials” is greatly acknowledged for spin-coating of the membranes.
VOLTAMMETRIC DETERMINATION OF CAFFEINE IN ENERGY DRINKS USING AN ELECTRODE MODIFIED BY COMPOSITE BASED ON NAFION AND BIMETALLIC SYSTEM OF BISMUTH–IRIDIUM


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Caffeine (1,3,7-trimethylxanthine) is an alkaloid from xanthine group that is widely found in plant products and beverages. The popularity of caffeine-containing products is connected with her physiological effects, such as stimulation of the central nervous system and gastric secretion. However, high amounts of caffeine can cause trembling, nausea and nervousness. For these reasons, it is very important to control the concentration of caffeine in its different sources.

In this work, we developed a method of voltammetric determination of caffeine using a glassy carbon electrode (GCE) modified by composite based on Nafion film (NF) and bimetallic system of bismuth–iridium (Bi-Ir) for analysis of energy drinks.

Bimetallic system Bi-Ir electrodeposited at the GCE show catalytic activity in the electrooxidation of caffeine. It is exhibited in decreasing of overvoltage of substrate oxidation and in increasing of oxidation current of modifier. When the NF is applied to the surface of the electrode Bi-Ir-GCE, a two-fold increase of caffeine oxidation current has been achieved compared to its oxidation on the modified electrode without the NF. It is due to the accumulation of the substratum in the polymeric matrix. The signal height is linearly related to the caffeine concentration in the solution.

The procedure was verified by the introduced-found method. The relative standard deviation $S_r$ does not exceed 5% in the whole range of concentrations studied.

Developed method was used for detection caffeine in energy drinks. The determined values of caffeine contents in energy drink samples are in good agreement with a content declared by manufacturer as well as with results obtained by HPLC as independent method.

The results obtained using both methods were statistically compared by the paired t-test. Its results indicate that there are no important differences between the obtained results at the 95% confidence level. On the basis of these results it can be stated that the proposed procedure can be applied successfully for caffeine determination in pharmaceutical formulations and beverage samples.

Acknowledgements. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.
Hydroxyapatite is the main mineral component of teeth, bones and one of the most common minerals in pathologic masses in human body. The solubility of hydroxyapatite has been the subject of extensive studies for several decades and many works devoted to this topic were published, but the reported data poorly fit together. One of the reasons for this may be the incongruent dissolution of hydroxyapatite. Difficulties of study of hydroxyapatite solubility are also caused by extremely low solubility and long duration of the setting of chemical and phase equilibria. Therefore, until now, no studies of influence of electrolyte and protein composition of body fluids on the solubility of hydroxyapatite have been carried out.

Low solubility of hydroxyapatite complicates the study of phase equilibria, because even a small sampling can shift the equilibrium in the system. In this regard, it is important to provide non-destructive analysis of the composition of a solution that is in contact with hydroxyapatite. This can be done by a direct ionometry with membrane electrode selective to calcium ions. The use of calcium ion-selective electrode (Ca-ISE) allows a continuous measuring the composition of the solution in time, directly in the cell without sampling. This method has an important additional advantage: the signal of the sensor depends on the activity rather than the concentration of calcium ions in solution.

The main goal of the present work was to get reliable data on the solubility of hydroxyapatite as a function of the solution composition. The results demonstrate that the concentration of calcium ions in solution non-monotonously changes over time: the respective curves contain a maximum.
VOLTAMPEROMETRIC DETERMINATION OF GUANINE ON ELECTRODES MODIFIED WITH COMPOSITE FILM FROM NATHION AND OSMY HEXACIANOMETALLATES

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Heterocyclic nitrogenous base - guanine is the initial structural element of deoxyribonucleic acid (DNA), the primary damage to which in the DNA molecule leads to mutations and changes in the genotype. The level of guanine concentration in DNA is considered to be an important parameter in the diagnosis of mutagenic factor and therapeutic treatment of diseases number.

In this work, the electrocatalytic activity of films based on osmium (III) hexacyano-ruthenate (HCRO) and osmium (III) osmium hexacyanocobaltate (HCCO) deposited on the surface of glass-carbon electrode (GCE) covered of nafion (NF) cation-exchange film during electrooxidation of guanine is established. The highest electrocatalytic effect is registered on the GCE with a film of osmium (III) hexacyanoruthenate. Using the composite NF-GCRO leads to registration the larger catalytic currents due to a combination of accumulation stage of protonated guanine molecules in the nafion polymer matrix and principles of electrocatalysis. The optimal conditions for obtaining the composite NF-GCRO, under which the highest catalytic effect are recorded. The mechanism is proposed and the kinetic parameters of guanine oxidation on the NF – GCRO – GCE electrode are calculated.

The method of voltamperometric determination of guanine on GCE with a composite film NF-GCRO was developed. The dependence of the catalytic current from substrates concentration is linear in a wide range. The detection limit of guanine on the NF-GCRO-GCE is 5*10^{-7} M. The relative standard deviation is less than 5%. The developed voltamperic method of guanine determining was tested in sample of salmon sperm DNA.
Switchable hydrophilicity solvents (SHSs) have been recently introduced into sample preparation as an alternative to toxic and environmental polluted organic solvents. The unique facilities of SHSs to switch reversibly between hydrophilic and hydrophobic forms provide formation of large surface area between the extraction solvent (SHS) and the aqueous phase resulting in rapid phase equilibrium, followed by phase separation.

In the present research, we implemented a switchable hydrophilicity solvent rotating membrane disk-based microextraction (SHS-RMDME) strategy for simple and highly-available analytes preconcentration. The SHS-RMDME procedure (Fig. 1) assumed in situ generation of microdroplets of a hydrophobic medium-chain fatty acid (extraction solvent) from homogeneous sample solution containing water-soluble medium-chain fatty acid salt by acidification. A rapid mass transfer of target analytes from aqueous sample phase to extraction solvent microdroplets followed by collecting of extract microdroplets on a rotating membrane disk was obtained. Afterward the analytes were eluted from the disk. The SHS-RMDME strategy was applied for the determination of tetracycline, oxytetracycline and chlortetracycline in urine samples by HPLC-UV.

Figure. 1. The extraction process diagram.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project No 18-33-01176).
INVESTIGATION OF NON-STOICHIOMETRY IN F- AND O-CONTAINING KTP SINGLE CRYSTALS USING PULSED GLOW DISCHARGE TIME-OF-FLIGHT MASS SPECTROMETRY

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The quality control of nonlinear optical materials and the correlation between crystals growth conditions (solvent composition, growth rate, dopant distribution, etc.) and their composition and optical and electrochemical properties are necessary steps in growing of high quality single crystals used in nonlinear optical instruments. However, the direct analysis of dielectric materials including light elements with high ionization energy is a difficult task.

To solve this problem, the method based on time-of-flight mass spectrometry with pulsed glow discharge has been developed [1-3]. Advantages of the method include high sensitivity and accuracy, simple sample preparation and low matrix effects. The method was used to study the stoichiometric composition of KTP single crystals both pure and doped with KF and Rb⁺ as well as its dependence on crystals growth conditions. The effects of growth rate, solvent composition and temperature on the distribution of the components in the crystal were also investigated. Moreover, it has been shown, that the largest concentration differences in one crystal were observed along the crystal growth axis and in different growth faces, such as (011) and (201); (201) and (100). The last effect is due to differences in the growth mechanisms of the faces [4]. The analysis of electrical conductivity along the cross section of the crystal, in different facets of growth and crystals with different concentration of doped components was provided. It was shown that the concentrations of the main and doped components and the electrical conductivity change regularly.

References

Acknowledgements. The research has been supported by a grant from the Russian Science Foundation (grant №. 17-73-20089).
DETERMINATION OF POLYPHENOLS AND STEROID HORMONES WITH IMIDAZOLIUM IONIC LIQUID BY MICELLAR AND MICROEMULSION ELECTROKINETIC CHROMATOGRAPHY

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In recent years, there has been an active interest in the use of ionic liquids (ILs) in methods of separation and concentration due to their unique properties. A promising direction is the application of ILs in electrokinetic chromatography methods (micellar (MEKC) and microemulsion (MEEKC) variants) as components of electrophoretic system. The variety of combinations of cations and anions in the composition of ILs provides their use both as a surfactant and as “oil” in microemulsion or as modifies of background electrolyte (BGE). It will make possible to control the separation selectivity of such hydrophobic compounds to effect on efficiency and prevent the sorption of analytes on the walls of the capillary.

In this work the possibility of using imidazolium ionic liquids (C\textsubscript{16}MImCl, C\textsubscript{12}MImCl, C\textsubscript{6}MImBF\textsubscript{4}, C\textsubscript{6}MImN(SO\textsubscript{2}CF\textsubscript{3})) for the separation of polyphenol antioxidants and steroid hormones by MEEKC were investigated. The influence of various factors on the efficiency and selectivity of separation of analytes was determined: the concentration and the nature of ILs, the type and concentration of the “oil” and co-surfactants in the microemulsion, the nature and pH of the BGE, the component ratios in microemulsion, the various additives that may undergo some additional interactions with the analytes (cyclodextrins, organic solvents). The addition of 15 mM 2-hydroxypropyl-β-cyclodextrin (HP-β-CD) has been found to increase the separation selectivity of steroid hormone. The results are compared with the use of a traditional cationic surfactant, cetyltrimethylammonium bromide.

The use of on-line preconcentration technique (sweeping) made it possible to reduce the limits of detection of analytes upto 50 ng/ml. As a result, a rapid method for determining steroid hormones by the MEEKC method in biological fluids (urine, blood serum) is proposed.

Acknowledgements. We express our gratitude to the Resource Educational Center in the direction of chemistry of St. Petersburg State University for the equipment provided. The current study was supported by RFFI grant № 17-03-01282-a.
MERGING EFFECT OF DEEP EUTECTIC SOLVENTS AND POLYMERS FOR SIMULTANEOUS DETERMINATION OF TRACE CONCENTRATION OF OMEPRAZOLE AND LANSOPRAZOLE IN COMPLEX MATRICES

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Deep eutectic solvents as a subcategory of ionic liquids are showing great potential in many different areas of chemistry, such as separation, polymer synthesis and metal deposition [1]. Conducting polymers (CPs) have been widely applied for fabricating various electrochemical devices such as sensors, actuators or solar cells [2]. In this study simultaneous electrochemical oxidation of omeprazole and lansoprazole is investigated via a modified carbon paste electrode. The modifiers are a polymer and a deep eutectic solvent. Differential-pulse voltammetry is performed as the electrochemical method in Britton-Robinson buffer solution (0.04 M; pH 6.0) and after optimization of several factors such as pH or conditioning time, well-defined peaks are observed in a linear range of 10 to 300 nM for both drugs. In addition to buffer solution determination of both analytes were done in human serum and urine and the results were satisfactory as well quality control for pharmaceutical formulations.

Figure 1. linear range of simultaneous determination of omeprazole (blue) and lansoprazole (red)

References
While cancer surgery is the most common method of solid tumor treatment, there is no convenient tool for accurate real-time tumor margins assessment by a surgeon [1]. Resecting a tumor, the surgeons mostly rely on their experience; a histological analysis of the excised tumor fragments is generally performed after the surgery. Thus, if the tumor was not completely removed, or, in the other words, the tissue fragment margins are positive for cancer cells, a re-excision surgery is inevitable. The lack of fast and reliable tumor margins assessment method results in extra loading on hospital resources and in higher risk of side effects associated with surgery and anesthesia. Besides, a patient’s moral state could be negatively affected; some people tend to choose radical surgery (e.g., mastectomy) as more “certain”, even if organ-conserving treatment is available as an option.

Recently, various spectroscopic methods have been extensively studied for tumor margins assessment [2]. Due to the different metabolic processes, occurred in tumor and normal cells, it is possible to distinguish them by specific spectral features (light scattering, peak intensities, etc.). In our work, a near-infrared (940-1800 nm) fiber optic probe coupled with portable spectrometer has been applied for tumor distinction in vivo and in vitro from normal and pathologically changed benign tissues (e.g., hyperplasia) on various carcinogenesis animal models (skin, brain, and breast cancer) and on tissue fragments obtained from real patients with cancer (gastric and colon cancer). In combination with several multivariate data analysis algorithms, this easy-to-use approach demonstrates promising results in tumor cells distinction.

References

Acknowledgements. This work was supported by Russian Foundation for Basic Research (project #18-53-53016 GFEN_a).
In recent years the development of fast, precise, accurate and sensitive methodologies in chemical analysis has become an important issue. However, despite the use of highly efficient analytical instrumentation for the end-point determination of analytes, sample pretreatment is usually necessary to eliminate the negative effect of matrix components. Homogeneous liquid-liquid microextraction is based on extraction solvent phase formation from homogeneous solution induced by altering ionic strength, pH and temperature as well as an addition of ion-pair agent. This method has been widely applied for sample preparation prior to determination of both organic and inorganic analytes. Its advantages are simplicity, versatility, rapid phase equilibrium achievement and low solvent consumption. Recently, the so-called switchable hydrophilicity solvents (SHS) have been proposed as promising extraction solvents in homogeneous liquid-phase microextraction as their miscibility with aqueous sample can be easily and reversibly changed by pH adjustment. In this report different modes of SHS-based microextraction as well as main drawbacks and benefits are discussed. Various applications to the real sample analysis are described.

Acknowledgements. Authors gratefully acknowledge the Russian Science Foundation (project no. 16-13-10117) for financial support.
THE STUDY OF LOW TEMPERATURE VAPOR-GAS STREAM COMPOSITION USING ICP-AES AND ICP-MS TECHNIQUES

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There are many sources of atmospheric pollution both natural and anthropogenic. Gold mine tailings is the most dangerous anthropogenic one, which can produce a wide range of contaminants such as aerosol, dust and vapor containing the compounds of S, Se, As, Hg and other elements. However, low-temperature transport of volatile metal and metalloid species has not been extensively studied.

The purpose of this work was to study the chemical composition of gaseous and particulate matter in the stream emerging above the solid material taken from the sulfide tailings dump (Ursk, Kemerovo region, Russia) [1].

Atomic emission and mass spectrometry (ICP-AES, ICP-MS) and SEM EDS were applied to characterize the particles of various sizes: d>0.45μm and 0.45>d>0.2μm and the gaseous fractions as well. Metalorganic framework polymer (MOF) UiO-66 was used as gas adsorbent.

For this research, the special installation was designed (Figure 1) to collect gaseous and particulate fraction of low-temperature stream.

![Laboratory set: 1 – water seal; 2 – membrane filter; 3 – blank sample vessel; 4 – waste material; 5 – 2-step filter (0.45 μm and 0.2 μm consistently); 6 – UiO-66 as adsorbent; 7 – laboratory pump (suction mode)](image-url)

It was found that low-temperature vapor stream contains the compounds of As, Hg, Sn and Sb as adsorbed by UiO-66 at the level of 0.4 - 40 μg/g.

References
There is a growing demand for sensing platforms that provide simultaneous detection of various analytes in a single sample, e.g., for obtaining body electrolytes snapshot from a single drop of body fluid such as blood or sweat. Optical chemical sensors (optodes) appear to be ideal tools for developing such multianalyte sensor arrays due to their tunable dynamic range and miniature size. However, the real media impose special requirements on utilization of optical chemical sensors: the problems of the sample background color, biofouling of the sensor surface, cross-sensitivity in a complex matrix must be carefully addressed.

In this contribution, we summarize the design principles of multianalyte sensing arrays for application in real aqueous samples. Optical sensor compositions for detecting ionic analytes ($K^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $NH_4^+$, $Cl^-$) in blood and serum, human sweat, and hydroponics nutrient solutions are suggested. Furthermore, different functional designs of sensing platforms utilizing substrate and protective materials of various natures will be presented, and their applicability in real samples will be demonstrated (Fig. 1).

Figure 1. Examples of optical response of optodes: (A) casted on inert substrate; (B) protected with cellulose acetate from biofouling.

Acknowledgements. This work was supported by the Russian Science Foundation (project No 18-73-00109).
Over the years, the use of fluoride in toothpaste has been highly controversial. Some people argue that fluoride can cause serious health problems, while experts have found that fluoride can significantly improve dental health.

In recent decades, a new field of physical and chemical research – ionometry, the main task of which is the study and development of various types of ion – selective electrodes, is rapidly developing. To create new types of such electrodes, a wide range of electrochemically active substances is used, such as liquid and solid ionites, mono- and polycrystals, synthetic membrane-active complexons and other compounds that exhibit a selective action relative to certain ions.

Fluoride-selective electrode is used for fast, simple, accurate and economical measurements of fluoride ion concentration in aqueous solutions. Ion-selective electrodes are known for the determination of fluoride ions, the membranes of which are made on the basis of fluorides of rare earth elements.

Objects of research: toothpastes of different names: Ftorodent, New Pearl and Colgate. Purpose: to determine the content of soluble fluoride ions in the toothpastes of different manufacturers. The results are presented in the table.

Table 1. The results of the values of the content of fluoride in toothpastes in %

<table>
<thead>
<tr>
<th>№</th>
<th>Toothpaste</th>
<th>Manufacturer</th>
<th>The mass of charge, g</th>
<th>Fluoride content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ftorodent</td>
<td>Russia, Moscow, Savelovsky district, JSC «Cosmetic Association “Freedom”»</td>
<td>0.4090</td>
<td>1.08±0.01</td>
</tr>
<tr>
<td>2</td>
<td>New Pearl</td>
<td>Russia, St. Petersburg, JSC “Neva Cosmetics”</td>
<td>0.3050</td>
<td>0.86±0.03</td>
</tr>
<tr>
<td>3</td>
<td>Colgate</td>
<td>Importer: Colgate-Palmoliv, CJSC, RF, 121614, Moscow, Krylatskaya St.</td>
<td>1.4740</td>
<td>0.87±0.04</td>
</tr>
</tbody>
</table>
Optodes are the sensors that change the color or luminescence intensity depending on the analyte activity in solution. These devices are miniature and easy to use. Their response is determined by the selective chemical interactions between the active components and the analyte inside the sensor phase, typically plasticized polymeric matrix. The sensing layer is usually integrated into the sensing system, which can be divided into three components: the substrate (supporting hydrophobic organic sensing layer), the sensing layer itself (providing selective binding of the analyte), and the shielding layer (protecting against possible fouling) (Fig. 1A). The reported study was aimed at optimization of the substrate material and pretreatment method, as well as of the protective material, for use in optical detectors containing hydrophobic sensors. Combinations of various materials were tested with well-known sodium-selective optodes based on Na ionophore VI and pH-indicator ETH5350.

A number of materials were tested as candidates for using as an array substrate, such as poly(propylene) and polyester films, Teflon sheets, silanized glass slides etc. They were quantitatively compared in terms of optical response amplitude and reproducibility, inertness, mechanical stability and transparency. Different methods of the substrate surface pretreatment for applying optode composition and optode geometries were evaluated in terms of piece-to-piece reproducibility (Fig. 1B). Several materials were tested as shielding layers for protection of the optode array from fouling in real samples, such as polyester hemodialysis filter and 12 kDa cellulose acetate dialysis filter. The effect of the protective film in the array response time was evaluated (Fig. 1C). The optimal
design of the functional multilayer sensing platform demonstrated high reproducibility of the results, reduced the measurement errors and was successfully verified prior and after contact with whole blood.
NEW HIGH-SENSITIVE LATERAL FLOW IMMUNOSENSORIC SYSTEMS FOR CONTROL OF PLANT PATHOGENS

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Lateral flow immunosensoric systems for control of plant pathogens have two clear fundamental advantages: selectivity provided by immune recognition, and simplicity of handling procedures. However, its place among alternate analytical approaches and perspectives of wider application are still disputable. Further use of lateral flow tests in agricultural and food safety control will depend both on the development of new assay formats that allow reaching extremely low limits of detection. This report provides a comparative assessment of the enhancing approaches that their applied in practice for the control of viral and bacterial pathogens of the potato.

We have proposed several schemes for lateral flow immunoassay enhancement. (i) Combination of magnetic nanoparticles and gold nanoparticles (GNPs) as labels. This approach was applied to the detection of potato virus X and was found to be 32 times more sensitive than the conventional immunoassay. (ii) Combination of two (specific and enhancing) GNP conjugates and alkaline phosphatase. The limit of detection was 27 times lower than that of a non-amplified immunoassay. (iii) Enlargement of the size of GNP using catalytic reduction of metal (Ag, Au) salts. The use of the GNP enlargement method resulted up to 240-fold reduction in the detection limit of potato pathogens.

The developed high-sensitive lateral flow immunosensoric systems show significant potential for various analytical tasks due to universal and simple approaches for increased sensitivity. They are highly promising for the routine and non-laboratory assay.

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THE CREATION OF NEW VARIANTS OF HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY FOR DETERMINATION OF POLAR DRUGS IN BODY FLUIDS

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Hydrophilic interaction liquid chromatography (HILIC) has been actively developed in the last decade driven by the increase in the development of polar drugs within the pharmaceutical industry. The growing interest in HILIC is due to the release of special columns for the determination of polar compounds. Such stationary phase can be obtained by the dynamic modification with the hydrophilic reagents. We propose to apply the imidazolium ionic liquids (ILs) as a hydrophilic coating of C18 stationary phases for HILIC. The influence of the length of the alkyl radical (C4, C6, C8, C12), the nature of the counter-ion (Cl-, BF4-) and IL concentration (1 - 60 mM), the pH of the mobile phase and the organic additive on the efficiency and selectivity of separation of polar drugs had been studied. The possibility of determining drugs (p-aminosalicylic acid and antibiotics levofloxacin, sparfloxacin) by HILIC in blood plasma was demonstrated.

In this study was supposed mode of simultaneous determination of zoledronic acid (ZA) and creatinine in biological fluids by HILIC. ZA belongs to class of bisphosphonates. These drugs have become the therapy of choice for the management of various skeletal disorders such as several types of osteoporosis, malignancy metastatic to bone. However, despite the benefits of bisphosphonates, it may cause also the disruption of the kidneys, which is controlled by the content of serum creatinine. The major factors influencing the retention of ZA in HILIC such as the type of the stationary phase (amino- and amide- phases), the percentage content of water in eluent, the concentration, pH and type of the aqueous solution of the salt were investigated. ZA as strong chelator is capable to interact with the metals of the liquid chromatographic system. This required a series of experiments with the addition of complexing agents (tartaric, citric acid and EDTA) to the mobile phase. The possibility of determining ZA and creatinine by HILIC in serum was demonstrated. The high selectivity of the separation of analytes makes it possible to use the technique for obtaining chromatographic profiles in the evaluation of drug therapy.

Acknowledgements. This work was supported by the Russian Science Foundation, project No. 19-13-00370. Results were performed at the Resource Center of Chemical Analysis and Materials, Research Park, Saint Petersburg State University.
Fluoroquinolones (FQs) are a class of antibiotics which are widely used for the prevention and treatment of various diseases in animal husbandry [1]. The excessive use of these substances can result in the presence of its residue in animal tissue, which contributes to the long-term health effects, including microbial antibiotic resistance and allergic reactions [2]. Thus, there is an important analytical task to control the residue levels of these analytes in various animal products to provide food safety and protect health of consumers.

In the current study, a novel approach for effective solid-liquid microextraction of hydrophobic analytes based on in situ formation of deep eutectic solvent (DES) was proposed for the first time. The developed microextraction procedure assumed dissolution of a hydrogen bond acceptor of DES into a solid-phase sample phase followed by heating with a hydrogen bond donor of DES. The heating the mixture promoted in situ formation of hydrophobic DES, effective analytes microextraction and final phases separation. In this procedure tetrabutylammonium bromide acted as the hydrogen bond acceptor and long-chain alcohol acted as the hydrogen bond donor promoted mass-transfer of fluoroquinolones from solid-phase sample phase to DES phase. The developed approach was coupled with high-performance liquid chromatography with fluorometric detection for the determination of ofloxacin and fleroxacin in meat samples. The limits of detection, calculated from a blank test based on 3σ, were 10 μg kg\(^{-1}\) and 15μg kg\(^{-1}\) for ofloxacin and fleroxacin respectively.

References
Homogeneous liquid-liquid microextraction (HLLME) is a powerful preconcentration method which assumes an extraction of target analyte from a homogeneous solution into an organic phase formed due to phase separation phenomenon. HLLME is a very simple method and requires a reagent addition to decrease a solubility of an organic solvent in aqueous phase resulting in phase separation. Polar, water-miscible organic solvents such as monohydric alcohols or acetonitrile are the most frequently used in HLLME as extractants. Nevertheless, the main drawback of methanol or acetonitrile utilization is the necessity to perform the extraction process at the ratio 1:1 (v:v) between aqueous and organic phases resulting in low enrichment factor values.

In the present research, it was found that the primary amines can also be utilized for HLLME. The homogeneous isotropic solution was observed when primary amine was mixed with an aqueous phase. Phase separation was achieved by simple addition of salting-out agent to the extraction mixture. It was investigated that tetracyclines (tetracycline, oxytetracycline, doxycycline) could be extracted into primary amines.

The parameters such as type of primary amine, the volume of extractant, the phase separation agent and its concentration were optimized. The developed procedure has been utilized for the determination of tetracyclines in biological fluids followed by HPLC-UV determination. The limit of detection, calculated from a blank test based on 3σ, was 0.17 mg L⁻¹ for tetracycline, oxytetracycline and doxycycline.
STRUCTURAL-GROUP ANALYSIS OF OIL SOURCE ROCK ORGANIC MATTER

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Fourier transform infrared spectroscopy (FTIR) has been used for many years to evaluate the mineralogy of rocks [1] and structural group analysis of organic matter (OM) in extracted bitumoids and isolated kerogen [2, 3]. However, the traditional approaches in studies of OM require long and time-consuming sample preparation (extraction of bitumoids in the Soxhlet apparatus, acid dissolution of minerals). In addition, the extraction of kerogen by dissolving mineral rock makes it difficult to completely remove pyrite and quartz.

In this paper the possibilities of IR spectroscopy for structural group analysis of OM directly in source rocks (Table 1) using the example of low-permeable carbonate sediments of the pre-Jurassic basement (Paleozoic) were shown.

It was also shown that IR spectra of kerogen, recorded in the transmission mode using KBr pellets, had more absorption bands, which characterize vibrations of aliphatic and aromatic fragments, than IR spectra obtained in the attenuated total reflectance mode.

Table 1. Parameters of structural group composition of organic matter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aromaticity², S₁₆₀₀ ± ⁴₀₀</th>
<th>Aliphatic factor², (S₂₈₅₀+S₂₉₂₀)/(S₂₈₅₀+S₂₉₂₀+S₁₆₀₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock</td>
<td>0.64 ± 0.04</td>
<td>0.75 ± 0.05</td>
</tr>
<tr>
<td>Rock after extraction of bitumoids</td>
<td>0.26 ± 0.02</td>
<td>0.67 ± 0.05</td>
</tr>
<tr>
<td>Kerogen</td>
<td>1.02 ± 0.23</td>
<td>0.64 ± 0.09</td>
</tr>
</tbody>
</table>

*²S – peak area in IR absorption spectrum

References

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It is essential to monitor the presence and movement of impurities in various water streams used in the power generation process using nuclear power reactors. Chloride content in nuclear reactor water is the necessary parameter. Chloride has proved to destroy intensively the anticorrosive coating of constructive materials of the equipment and tubes at concentrations greater than 100 μg/L. As a result of that, these equipment components are significantly exposed to oxygen corrosion.

The existing analyzers in-situ demand a regular calibration procedure and are very expensive. We suppose that the chloride potentiometric analyzer in-situ using Hg₂Cl₂/HgS and AgCl/Ag₂S electrode pair will demonstrate stable measurements (more half-year) and will not require calibration process during exploitation.

Technological equipment corrosion products are in technological water constantly. We assume that the corrosion products can poison the electrode pair and lead analyzer failure.

In order to simulate electrode poisoning with corrosion products, we have placed them into the experimental stand which can corrode. Electrode characteristics, background solution and deposition elemental composition were determined using direct potentiometry, inductively coupled plasma optical emission spectrometry (ICP OES), and energy dispersive X-ray fluorescence spectrometry (ED XRF) and anodic stripping voltammetry, respectively during the test.

It has been found out that:

- the redox reactions involving electrode and stainless steel components do not affect electrode quality;
- iron, nickel, and zinc as stainless steel and brass corrosion products do not cause electrode pair lifetime diminishing.

Acknowledgements. ICP OES and ED XRF measurements were performed using the facilities of “Chemical Analysis and Materials Research Centre” of St. Petersburg University Research Park.
FRACTAL ANALYSIS OF LYOPHILIZED DRUGS

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Fractal analysis is a new cost-effective analytical method. Previously we demonstrated that there is a correlation between the fractal dimension of dihydroquercetin lyophilizates and their water solubility [1]. The aim of this work was to investigate the possibility of fractal analysis using for quality assay of biotechnology-derived medicinal product, such as bifidumbacterin.

The accelerated storage for bifidumbacterin was modeled by keeping its samples at 50 °C for 5, 15, 30, 60, 120, and 240 min. The fractality of sample’s surfaces was determined by computer analysis of photomicrographs. Fig. 1 demonstrates a logarithmic dependence between the fractal dimension of samples surface and exposure time ($R^2 = 0.9599$). The pH-value of bifidumbacterin suspension is one of the quality parameters. There was a linear dependence between the pH-value and exposure time ($R^2 = 0.9751$). Apparently the fractal analysis is more sensitive for determination of improper storage than potentiometry. So the fractal analysis could be recommended for quality assay of lyophilized active pharmaceutical ingredients.

![Graph showing fractal dimension (Fd)/time and pH-value/time relationships.]

Figure 1. The fractal dimension (Fd)/time and the pH-value/time relationships.

References

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AUTOMATED SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM (VI) IN FOOD PRODUCTS WITH PRELIMINARY ON-LINE MICROEXTRACTION EXTRACTION

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A modern direction in analytical chemistry is the search for new, environmentally friendly solvents as analogues of widely used organic toxic substances. Such solvents can be deep eutectic solvents (DES) that have recently appeared in analytical practice. These substances are analogs of ionic liquids, obtained by mixing the donor and acceptor of hydrogen bond. Such systems have melting points substantially low the melting points of the initial components. These solvents have several advantages, such as environmental safety, high dissolving ability, and compatibility with most analytical instruments. In addition, most DESs mix well with water, but they are capable of dissolving non-polar organic solvents. This property can be effectively used to use DES as an effective dispersant in dispersive microextraction, instead of widely used organic solvents.

In our study, we demonstrated the application of DES as an effective dispersant in fully automated spectrophotometric method for the determination of chromium 6 in food products and natural waters. The detection limit was 50 µg/l, the performance of the method was 4 analyses per hour.

Figure 1. Graphical Abstract.

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DETERMINATION OF URANIUM IN NATURAL WATER WITH THE USE OF GLOW DISCHARGE MASS SPECTROMETRY AND OXIDIZED NANOTUBES

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Pollution of the environment with uranium dictates the need to control the concentration of this element in natural waters to the permissible limits for the stability of ecosystems and public health. Uranium enters the environment with effluents from natural sediments, with emissions from industrial enterprises and uranium enrichment plants. The presence and accumulation of uranium in the industrial effluent of these enterprises has a toxic and carcinogenic effect on living organisms. Uranium affects all human organs and tissues, causes health problems, because it is a general cellular poison. Uranium bioaccumulates and remains for many years in bones, kidneys and liver. In 2011 WHO set maximum permissible concentration of uranium in water – 0.03 ppm, due to the strong toxicity and radioactivity of uranium in water. Therefore, continuous monitoring of uranium content is an important task for the safety and health of citizens.

To determine the low uranium content in natural waters, conservation of the studied solutions is necessary. However, this method of storage and transportation is not always simple. In this paper, as a convenient method of concentrating uranium, preserving the sample and transporting it, we used the method of sorbing uranium on sorbents. Single-layer carbon nanotubes were used as sorbents. Their surface was modified using wet chemical oxidation and synthesis with Aerosil A-380 silica.

Two schemes for concentrating uranium on the surface of the sorbent are considered: individual carbon nanotubes and nanotubes modified with silica. Direct analysis was used to determine the content of uranium in the sorbent, namely, time-of-flight mass spectrometry with pulsed glow discharge (GDMS). The most effective approach to the determination of uranium in water is the sorption of uranium on a tablet consisting of oxidized nanotubes modified with silica. The limit of detection in this case was 0.2 ppb.
Due to rare earth elements (REEs) special properties, these elements have a wide range of applications. REEs are used as catalysts in petrochemical processes, as an additive to the structural materials in the space industry, in the production of semiconductors, magnets, detectors and many others [1]. The increasing consumption of these materials leads to the increased risk to the health of workers occupationally exposed to REE. The human health effect of rare earth elements is not well studied. REEs inhibit calcium metabolism enzymes, disrupt the metabolism of proteins and nucleic acids, and cause fatty degeneration of the liver [2, 3]. Therefore, it is necessary to control the content of these elements.

Determination of rare earth elements in biological media was performed for the workers of the metallurgical plant, producing chemical and rare metals products for high-tech industries. REEs concentrations were determined in whole blood using a mass spectrometer with inductively coupled plasma Agilent 7500cx. The obtained concentrations of 14 REEs were evaluated by comparison with the reference levels [4]. Exceedance of 14 rare earth element concentrations in some blood samples was found. The multiplicity of exceedance varied from 1.32 times for yttrium to 38.5 times for europium.

References
Bisphenol A (BPA) is a polyphenol compound used in the manufacturing of polycarbonates-based plastic packaging. It is known, that BPA as a carcinogen can be found in food products stored in the plastic packaging. Therefore, monitoring of BPA's content in foods and drinks is an important task for analytical chemistry. Recently, deep eutectic solvents (DESs) are presently getting increased attention from researchers in analytical chemistry as high-efficiency extraction solvents. DESs are formed by mixing two or three cheap components that are capable of interacting through the formation of hydrogen bonds, to form a eutectic mixture with a melting point lower than that of each individual component. DESs are regarded as a cheap alternative to ionic liquids. DES is easy to be produced and cheaper due to lower cost of the raw materials.

In this work, deep eutectic solvents were investigated as a new kind of dispersive solvent for effective dispersive liquid–liquid microextraction (DLLME) for the first time. After optimization of extraction conditions, the proposed approach was compared with the DLMME procedure using conventional polar, water-miscible organic dispersive solvents. The obtained results shown that polar, water-miscible organic dispersive solvents increase solubility of BPA in an aqueous phase. The developed procedure was used for the determination of BPA in three beverages samples (still water, sparkling water and Orange juice). The limit of detection of proposed procedure was 0.0003 mg L$^{-1}$.

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APPLICATIONS OF METAL-ORGANIC FRAMEWORKS FOR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AND SOLID-PHASE EXTRACTION

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Metal-organic frameworks (MOFs) are a new promising class of materials. These materials have found several applications including storage and separation of gases, sensors, catalysis and functional materials, but in the last decade, they have also attracted interest as stationary phase in separation technologies [1]. Their key properties are high porosity, large pore volume, high surface areas, uniform structured cavities and uniform pore size, wide possibilities of direct design of polymers. Due to this properties MOFs can be regarded as promising materials for use in gas chromatography (GC), high performance liquid chromatography (HPLC), and solid phase extraction (SPE) as a stationary phase. Impressive progress has been made in research into utilizing MOF stationary phases in HPLC and SPE during recent years [2]. The utilization of functionalized MOFs as stationary phases in both HPLC and SPE will offer well opportunities for analytes in complex matrixes.

This work is aimed to investigate the possibility of using the UIO-66 family of MOFs as a stationary phase in HPLC and solid-phase extraction, particularly for element speciation.

References

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RESEARCH ON THERMODYNAMIC PROPERTIES OF COMPLEX OXIDE NdBaCo$_2$O$_6$-$\delta$

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Perovskite-like oxide NdBaCo$_2$O$_6$-$\delta$ (NBC) has a significant oxygen nonstoichiometry and quantitative determination of thermodynamic characteristics of the processes connected with change of oxygen content is very important. The aim of this work was to determine the standard enthalpies of formation of complex oxides of NdBaCo$_2$O$_6$-$\delta$ at different values of $\delta$, partial molar enthalpy of oxygen dissolution in the lattice of complex oxide and enthalpy of the process of Co$^{3+}$ disproportion. Samples of NdBaCo$_2$O$_6$-$\delta$ were synthesized using standard ceramic technology. The single-phase nature of the samples was confirmed by x-ray phase analysis. Samples with different oxygen content were obtained by quenching after holding at a given temperature and partial pressure of oxygen. The quantitative oxygen content in the samples after quenching was determined titrimetrically. Enthalpies of formation of prepared and attested NBC oxides were determined by measuring the heat of dissolution of the oxide samples in 4M hydrochloric acid with the addition of hydrazine dihydrochloride in the amount of 1 g per 200 ml of solution. The enthalpies of dissolution of Nd$_2$O$_3$, CoCl$_2$·2,2H$_2$O and BaCO$_3$ in a solvent of the same composition were also measured to make a thermodynamic cycle for the calculation of the enthalpy of NBC formation. On the basis of the obtained results enthalpies of formation of NBC oxides were determined. It was found that the function $\Delta H_f$ (NdBaCo$_2$O$_6$-$\delta$) = f($\delta$) can be divided into two sections, each of which is well approximated by a straight line. The difference between the angular coefficients of these lines allowed us to determine the enthalpy of the Co$^{3+}$ disproportion process, which was 16.6 kJ/mol Co$^{3+}$. To verify the correctness of the results obtained, the enthalpy of formation of complex oxide SmBaCo$_2$O$_5$,$\delta$ was similarly measured and the function of the enthalpy of formation of complex oxide of the composition LnBaCo$_2$O$_5$,$\delta$ on the number of lanthanide in Periodic table was made, which is well approximated by a straight line.
Precise calculations of the isotope shifts of X-ray transitions in heavy few-electron ions and in heavy neutral atoms are performed. The calculations include all contributions to the isotope shifts, namely, the contributions of the nuclear recoil effect (mass shift), the contributions of the finite nuclear size effect (field shift), and the related quantum electrodynamic (QED) corrections. The relativistic calculations of the mass and field shifts are based on the large-scale configuration-interaction Dirac-Fock-Sturm (CI-DFS) method [1]. The QED corrections to the field shift have been evaluated using approximate analytical formulas obtained in Ref. [2]. The contributions due to the nuclear polarization and nuclear deformation effects have been also estimated. The obtained theoretical results, in combination with the corresponding experimental data, can be used to determine the nuclear charge radius differences, and also for tests of QED in a new region: strong coupling regime beyond the external field approximation (i.e. beyond the Furry picture). The corresponding experiments with heavy few-electron ions are currently under preparation at GSI/FAIR facilities (Darmstadt, Germany). It is expected that with the new FAIR facilities the experimental accuracy of the isotope shift measurements will be improved by an order of magnitude, compared to the present one [3]. From the theoretical side, to meet this accuracy, one needs to evaluate all the contributions mentioned above.

References

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