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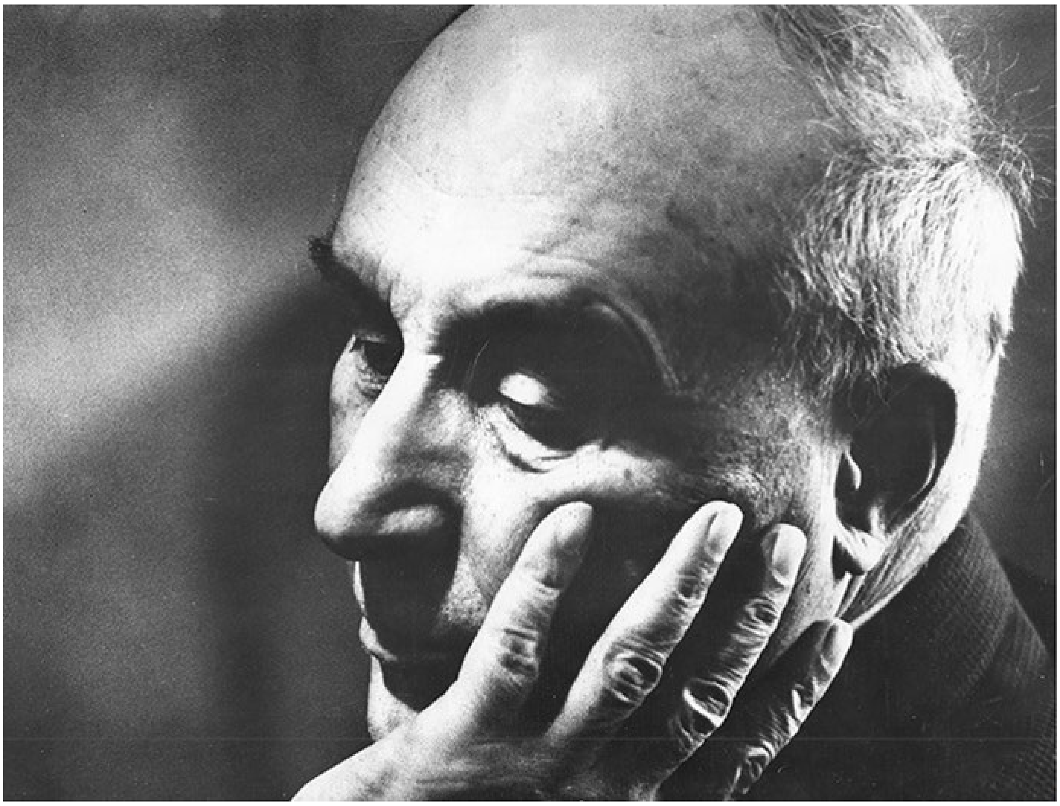
THE INTERNATIONAL CONFERENCE «CHEMISTRY OF ORGANOELEMENT COMPOUNDS AND POLYMERS – 2024»

BOOK OF ABSTRACTS

18–22 NOVEMBER 2024, MOSCOW



Academician Alexander N. Nesmeyanov

INEOS RAS

The international conference «Chemistry of Organoelement Compounds and Polymers – 2024»

BOOK OF ABSTRACTS

The conference is dedicated
to the 70 th anniversary of INEOS RAS
and the 125th birth anniversary of its founder
academician Alexander N. Nesmeyanov

18-22 november 2024
Moscow

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Proceedings of The international conference “Chemistry of Organoelement Compounds and Polymers –2024”, held from November 18 to 22, 2024. The conference will cover both fundamental and applied aspects of organoelement and polymer chemistry. The conference program will include invited lectures, oral and poster presentations. The topics will include:

- Organoelement and coordination chemistry
- Homogeneous and heterogeneous catalysis
- New trends in polymer synthesis
- Organoelement polymers
- Physical chemistry of polymer systems
- Organoelement and macromolecular compounds for biomedical applications
- Supramolecular chemistry and MOFs
- Organoelement and macromolecular compounds for material chemistry

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CONTENT

PLENARY LECTURES

WILL ARTIFICIAL INTELLIGENCE (AI) REPLACE CHEMISTS?

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The advent of artificial intelligence (AI) in chemistry has raised a crucial question: will AI replace chemists, or will it act as an empowering tool for accelerating scientific discovery? This presentation explores the transformative role of AI in chemical research, emphasizing its potential to enhance rather than replace human expertise. As experimental data proliferate and the complexity of molecular phenomena grows, AI-driven approaches provide chemists with powerful tools for designing new synthetic pathways, analyzing vast datasets, and uncovering intricate reaction mechanisms[1,2]. Cutting-edge developments in AI applications for the creation of next-generation chemical technologies are discussed, with particular attention to the integration of AI in process design[3], experimental data analysis[4], and the development of highly active catalysts[5]. The presentation also highlights the role of AI in creating universal photocatalysts6, demonstrating how these systems can offer unprecedented precision and efficiency, complementing the chemist's role in innovation. Ultimately, the collaboration between AI and human intelligence represents a pivotal step forward in the advancement of chemical science.

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POLYPHENYLENE SULPHIDE COMPOSITE MATERIALS FOR ADDITIVE AND FILM TECHNOLOGIES

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Polyphenylene sulfide (PPS) is a semi-crystalline thermoplastic widely used in industry, especially in the manufacture of heat-resistant products operating under high loads and in contact with aggressive environments. The global polyphenylene sulfide market volume was $1.41 billion in 2022 and is projected to be $2.77 billion in 2030, with an average annual growth rate of 8.8%.1

In the laboratory "Synthetic polymeric materials and composites" of the Kazan Federal University, new thermostable cross-linking reagents, plasticizers, sizing agents (lubricants) for glass and carbon fiber have been developed, allowing the production of a wide range of materials for injection molding, extrusion and additive technologies using polyphenylene sulfide: filament, adhesives, films. A testing base and pilot industrial line for the extrusion of filament and film (up to 40 cm wide) from polymer materials and composites with a processing temperature of up to 450°C and a productivity of 10 kg/hour have been created.

To develop low-energy-intensive processes for baromembrane fractionation of oils of various origins, as well as technology for the purification of waste oil, thin films based on polyphenylene sulfide and its composites with washable polymer fillers, were obtained by the extrusion method.

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Acknowledgements

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FLUORINE-SUBSTITUTED DERIVATIVES OF Γ-CARBOLINES AND CARBAZOLES AS A PROMISING DRUG CHEMOTYPE FOR THE NEURODEGENERATIVE DISEASES TREATMENT

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The search of effective drugs for the treatment of neurodegenerative diseases such as Alzheimer's disease, amyotrophic lateral sclerosis (ALS), Parkinson's disease is an extremely complex challenge. It is explained by both the multifactorial nature of most such pathologies and the difficulties in modeling CNS diseases in vitro and in vivo. The main modern trends in finding drugs for the neurodegenerative disease treatment are the targeted search for drugs that directly affect the pathogenesis of diseases, the creation of multi-target structures, and the repositioning of already known drugs[1].

Previously, neuroprotective activity of the domestic drug Dimebon (γ-carboline derivative) was discovered[2]. This compound has pronounced therapeutic properties in the 2nd phase of clinical trials in Alzheimer's disease patients. We carried out a targeted modification of the parent γ-carboline structure to find new neuroprotective properties in various cellular and animal models of neurodegenerative disorders[3-6]. Pronounced antiaggregatory properties were found in a group of fluorinated derivatives in ALS models. Moreover, structures representing conjugates of fluorine-substituted carbazoles and aminoadamantanes demonstrated unique antimitotic properties, which allows them to be considered as promising neuroprotective agents.

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COBALT, RUTHENIUM, CHROMIUM AND PALLADIUM IN THE SYNTHESIS OF HETEROCYCLOALKYNES AND ENEDIYNES

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8-, 9- And 10- membered rings containing triple bonds play an important role in biomedical chemistry. In the case of enediynes the presence of (Z)-3-ene-1,5-diyne moiety incorporated into the strained ring leads to spontaneous Bergman cyclization at human body temperature and makes these systems the most potent, highly active antitumor agents. As for cycloalkynes, Strain-promoted azide-alkyne cycloaddition, (SPAAC) to date is the most sought-after bioconjugation reactions.

Our efforts in this area have been concentrated on the molecular design of 10-membered heteroenediynes and heterocyclononynes fused to heterocycles[1-3]. Searching for convenient synthetic methods for constructing strained cyclic systems fused to a heterocycle, we have investigated several technics such as Ring-closing metathesis[4] the Nozki–Hiama–Kishi reaction[5] and the Nicholas-type cyclization[6-8]. The scope and limitation of each synthetic approach will be discussed.

In both cases, synthesis of all acyclic precursors is based on a combination of electrophilic cyclization of functionalyzed acetylens or butadiynes and subsequent palladium-catalyzed Sonogashira coupling of resulting iodoheterocycles. In this regard, the development of catalytic systems based on acyclic diaminocarbene palladium complexes is also related to these studies and will be discussed.9,10

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PHOTOCATALYSIS IN ORGANIC SYNTHESIS

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POLYMERS BASED ON NORBORNENE DERIVATIVES FOR MEMBRANE GAS SEPARATION PROCESSES

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Rapid development of technologies and tightening of environmental requirements for industrial production increase the importance of effective separation on molecular level. The monomers based on norbornene derivatives can be considered as attractive molecular design platform that enables to synthesis tailor-made glassy polymers, and membranes with desired transport and separation performance. Thus, the polynorbornene-based membranes can be used for gas separation, separation of organic compounds from wastewater, and separation of enantiomers from the corresponding racemic mixtures. This talk will cover the recent advances in the synthesis of membrane materials based on norbornene derivatives, including optically active ones, in comparison with other groups of polymers being developed for similar purposes (Figure 1).

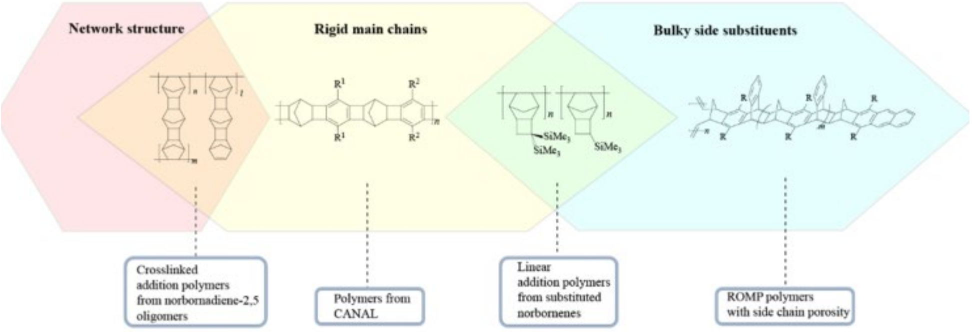

Figure 1. Basic approaches to the design of porous and membrane materials based on norbornene derivatives.1,2

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RECENT TRENDS IN CARBONYLATION AND MULTI-CARBONYLATION REACTION

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Carbonylation reactions represent a significant class of transformations in organic and organometallic chemistry, wherein carbon monoxide (CO) is utilized as a carbonyl source to convert various organic substrates into compounds containing carbonyl groups. This process has emerged as a powerful tool in the synthesis of pharmaceuticals, agrochemicals, and fine chemicals, owing to its efficiency and versatility. In this context, carbonylation reactions catalyzed by transition metals have been extensively studied[1]. Among them, those catalyzed by noble metals (such as Pd, Rh, Ru, and Ir) stand out, featuring well-established catalytic systems including carbonylated C–C coupling reactions, carbonylated Heck, Sonogashira, and Suzuki reactions, as well as carbonylation of alkyl halides employing nucleophilic reagents like alcohols and amines. Recently we developed some efficient strategies involving nickel as an earth-abundant 1st-row transition metal-catalyzed carbonylation reactions. Additionally, some strategies involving low-toxic and environmentally friendly CO surrogates (carbon monoxide sources) such as *N*-formylsaccharin, $Co_2(CO)_8$, phenyl formates, formic acid, CO_2, DMF, etc., as CO sources for the synthesis of fine chemicals, have been developed recently. Moreover, multi-carbonylation reactions, which entail the successive incorporation of multiple carbonyl groups into organic molecules, have garnered increasing attention in recent years[2]. These reactions provide unique synthetic pathways for constructing complex molecular architectures with multiple carbonyl functionalities. Various strategies, including sequential carbonylation, tandem reactions, and cascade processes, have been developed to achieve efficient multi-carbonylation transformations. These methodologies hold promise for the streamlined synthesis of highly functionalized molecules with potential applications in medicinal chemistry, materials science, and beyond. In this context, over the past two decades, double carbonylation reactions have been gaining interest for synthesizing complex molecules, utilizing two carbonyl molecules in a single step. Very recently we have developed a novel methodology involving the unusual oxidative adjacent triple carbonylation of tertiary amines towards oxomalonamide synthesis using a Palladium catalyst for the first time[3].

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SYNCHROTRON RADIATION SOURCE OF THE «SKIF» COMMON USE CENTER AS A TOOL FOR CONDUCTING ADVANCED X-RAY RESEARCH

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NEW ORGANOMETALLIC REACTIONS IN ORGANIC SYNTHESIS

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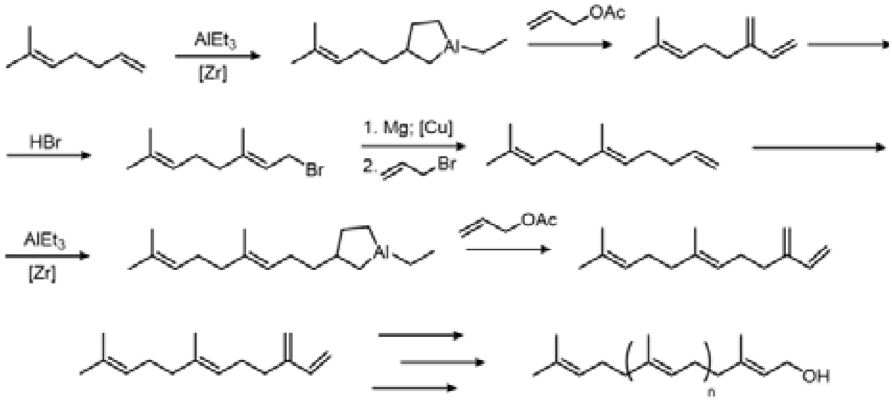
The report presents new organometallic reactions catalyzed by transition metal complexes, the introduction of which into synthetic practice has contributed to a change in the organic synthesis strategy. This topic has been widely studied over the past 15-20 years by domestic and foreign researchers around the world.

Much attention will be paid to the consideration of original organometallic reactions such as catalytic cyclometallation of olefins, 1,2-dienes, and acetylenes using alkyl derivatives of non-transition metals (Mg, Al, In, Ga) to obtain previously undescribed small, medium, macrocyclic and bulky metallocarbocycles.

Our studies on the above-mentioned reactions application, as well as the well-known organometallic reactions of E. Negishi, A. Suzuki and D. Stille in the synthesis of important natural metabolites, drugs and other valuable substances are of particular interest and practical value. For example, the application of catalytic cycloalumination reactions in the synthesis of industrially important regular *trans*-isoprenoids is given below.



LUMINESCENT METAL-ORGANIC FRAMEWORKS FOR NANOMOLAR DETECTION OF ENVIRONMENTAL POLUTANTS

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An important task related to ensuring the safety of life and health of humans is the development of fast and simple methods for detection of biologically active substances and pollutants in environmental objects (water, soil, air), and then in food products, tissues and human fluids. Metal-organic frameworks (MOFs) with their crystalline nature, structural diversity, permanent porosity, and adjustable functionality stand out as a unique type of sensors compared to other traditional luminescent materials. A relevant area of research is the development of highly sensitive/highly selective and easy-to-use luminescent sensors based on MOF based materials. The report discusses our recent results [1-6] on the synthesis of new MOFs based on the ligands modified with chromophores - 2,1,3-benzochalcogenadiazoles, as well as conformationally flexible polycarboxylate ligands. Such compounds are of interest from the point of view of their sensory properties, since their photophysical properties change in the presence of various analytes. The development of simple and reliable methods for detecting biologically active substances and pollutants is of great social importance.

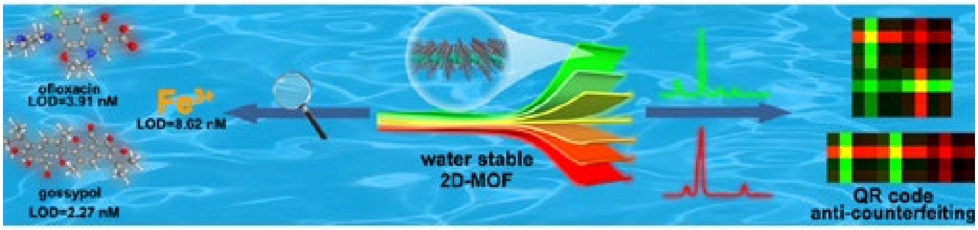

Figure 1. A highly emissive Ln(III) MOFs exhibits excellent sensing properties with exceptionally low detection limits towards iron(III), ofloxacin and gossypol in water. A novel anti-counterfeiting QR-coding scheme based on unique and tunable emission spectra of Ln-MOFs was designed.

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1,3-DIAZA-2-METALOLS

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Reduction of 1,4-diaza-1,3-dienes ArN=C(R)–C(R)=NAr with metals, e.g. Li, Mg, Al, Ga, Sn, affords five-membered heterocycles – 1,3-diaza-2-metalols (DAMs). Conjugation of p_z orbitals of the five ring atoms in these compounds provides for the formation of 6e π system. The properties of DAMs differ significantly of those of acyclic metal bisamides, $(R_2N)_2M$, as well as of metal-free imidazols. In contrast to the bisamides, all the DAMs (**A**, **B**, **E** and **F**) are intensively colored. Some of them, e.g. **E** and **F**, reveal also absorption in the IR region. A characteristic reaction of DAMs is (2+4) cycloaddition. In the course of this process the conjugation within the cycles is destroyed. As a result the products, e.g. **C** and **D** are only little colored.

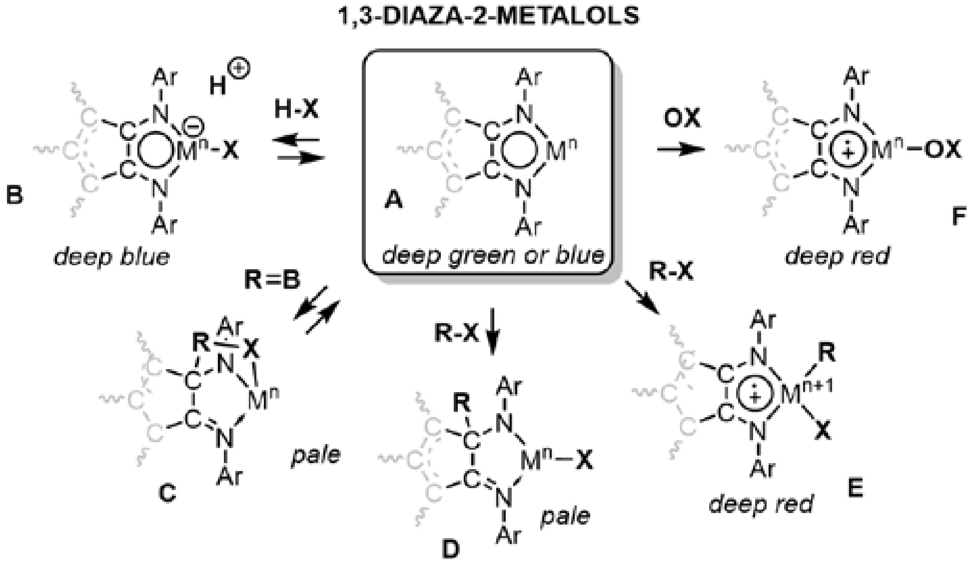

Figure 1. All the DAMs represent highly reactive species.

Acknowledgements
The study has been supported by the Russian Science Foundation, project 24-13-00369.

COPPER(I)-CATALYZED PROTO/CARBOBORATION OF 1,3-DIYNES: AN EASY AND SUSTAINABLE ACCESS TO BORYLATED ENYNES AND DIENES

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Targets with high structural complexity can be easily assembled using small, modular building blocks similar to a 'Lego' construction using Iterative chemistry.[1-3] Organoboron compounds have been in the spotlight as versatile building blocks in natural product synthesis. Here, we present a sustainable, glovebox-free regioselective protoboration of 1,3-diynes using a stable diboron source and CuI/phosphine as a catalyst to access stable enynyl and dienyl boronate esters in a single operation. Then, we developed the first copper-catalyzed carboboration of 1,3-diynes, in which a simultaneous C−B and C−C bond formation was achieved in a single operation using a CuI/NHC catalyst. The methodology provides easy access to highly sterically encumbered penta- and hexasubstituted dienes. A wide range of electrophiles have been successfully employed. The introduction of allyl moiety provided access to skipped diene-yne boronate ester with excellent regioselectivity. DFT studies supported the regioselective incorporation of electrophiles.[4,5]

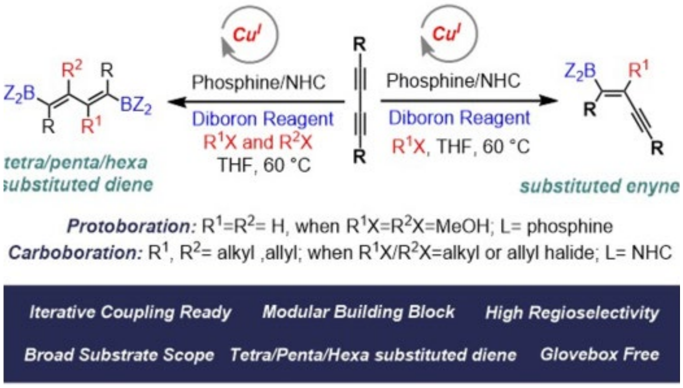

Figure 1. CuI-Catalyzed Proto/Carboboration of 1,3-Diynes

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CHIRAL C,N-PALLADACYCLES BASED ON TERPENE LIGANDS

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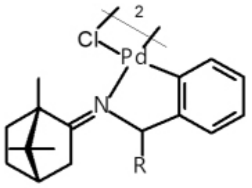
Palladium compounds containing a metal-carbon bond intramolecularly stabilized by a donor heteroatom are called cyclopalladated compounds or palladacyls (PCs). PCs are relatively easy to synthesize and exhibit high thermal, oxidative, and hydrolytic stability. Currently, PCs of various types have been obtained and described, which have found application in various fields of chemistry, including medical chemistry.

We have studied various nitrogen-containing derivatives of natural terpenoids as ligands for obtaining chiral PCs. Bornane and pinane derivatives of benzylamine are universal platforms for the synthesis of PCs of various types. The report discusses the problems of selectivity of terpene ligand cyclopalladation, provides numerous examples of the synthesis of new palladium complexes, as well as the results of studying the antitumor and antimicrobial activity of the obtained compounds. In particular, it was found that, depending on the choice of the palladating agent, cyclometallation can proceed in different directions - either along the aromatic ring of the benzylamine fragment (complexes of type I), or along the terpene substituent (complexes of type II, III).

The results of the study of the biological activity of palladium complexes of various types allow us to conclude that binuclear PCs containing a Pd-C bond and a labile chloride bridge can be considered as the most promising structures in the design of metal-containing drugs.



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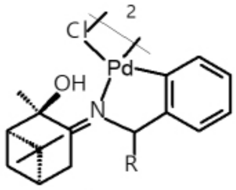

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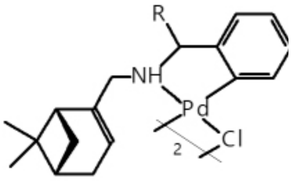

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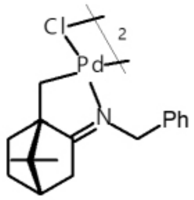

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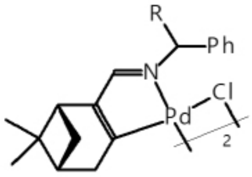

III

Acknowledgements

The research was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation (State Assignment, Reg. No. 122040600073-3).

"STIMULI-RESPONSIVE" LUMINESCENT SYSTEMS BASED ON CYCLIC PHOSPHINES AND ARSINES FOR BIOMEDICAL APPLICATIONS

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An effective strategy of design of biocompatible nano-sized luminescent systems based on transition metal complexes of tailor-made phosphine and arsine ligands have been developed within the last decade. The tailor made phosphine and arsine ligands with exocyclic chromophoric pyridyl-, pyridylethyl-, thienyl-, thienylethyl- and biphenyl-groups on phosphorus[1] or arsenic[2-4] atoms have been obtained. The wide range of luminescent mono-, bi-, tri-, tetra- and hexa-, homo- and heteronuclear complexes of gold (I) and copper (I) based on novel ligands has been designed.[1]

Core-shell nano-particles of the complexes stabilized by polyelectrolyte shell have been created in order to improve stability of complexes in bioenvironment and their cytotoxicity. [1,3]

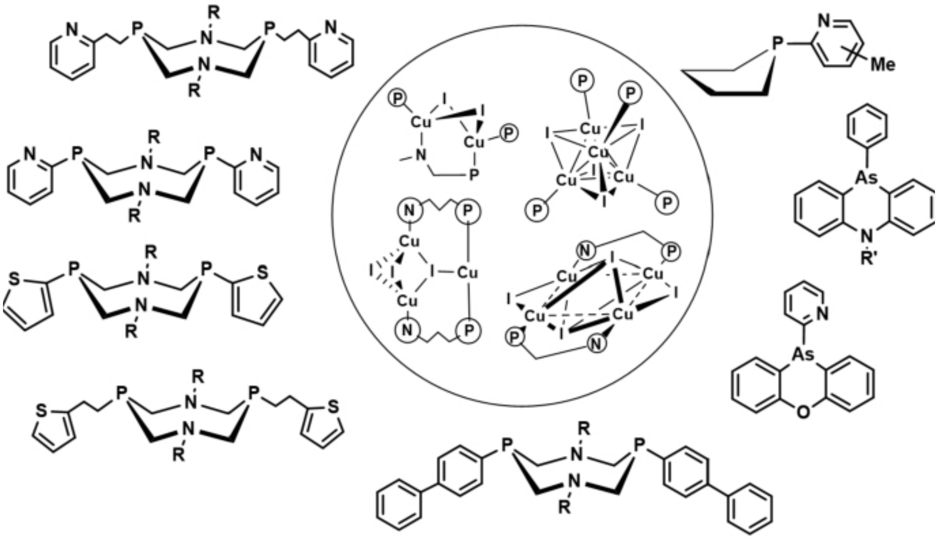

Figure 1. Main types of P - and As- ligands and polynuclear cores of luminescent complexes

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Acknowledgements
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POLLUTION OF THE PLANET WITH MACRO-, MICRO-, AND NANO-PLASTIC: EMOTIONS AND SCIENTIFIC APPROACH

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Contamination of the environment with polymer waste has recently acquired the features of a global challenge to humanity. During a hundred years of development of polymer science and the polymer industry, about 10 billion tons of waste from used polymer materials have accumulated in the world, which degrade extremely slowly in natural conditions. A particular danger is associated with the pollution of water environments - rivers, lakes, seas and oceans.

To solve this problem, some environmental scientists propose a radical reduction in the global production of polymer materials. This cannot be agreed with, since these materials are an integral part of modern world civilization. Instead, scientists working in the field of polymer science should offer their own approaches that are not associated with reversing global scientific and technological progress.

The report will provide an overview of the main areas of scientific research in the field of polymer science, which will ensure the evolution of the polymer industry towards the creation of environmentally friendly production and minimal impact on the environment.

Sorting waste for their subsequent use can only delay littering the environment. Polymer material can be recycled at best several times. Eventually, it will end its life cycle in a landfill or be incinerated. Therefore, the key issues are: (a) thoughtful design of landfills; (b) effective catalysts that prevent air pollution during combustion of polymer materials.

The problem of micro- and nano-plastics (i.e., polymer waste particles smaller than 5 mm) will be discussed separately. The harm from micro- and nano-plastics to living organisms is probably overestimated. Only particles smaller than 5 μm can penetrate the blood, and only objects smaller than 50 nm can pass through cell membranes. In natural aquatic environments, these particles will be covered with a layer of surfactants, so that the immune response to these particles will be similar to that for small dust/sand particles, with which many organisms have coexisted for many millions of years.

VISIBLE LIGHT-INDUCED CATIONIC POLYMERIZATION: SYNTHESIS OF FUNCTIONALIZED POLYISOBUTYLENE AND POLYISOBUTYLENE-BASED BLOCK COPOLYMERS

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The use of photocatalysis in polymer synthesis is emerging and intensively developing area of research during the last decades.[1] Benefits from this method include low energy and solvent requirements with high reaction rates and spatiotemporal control, creating relatively safer reaction conditions to handle. Although the photo-induced living radical photopolymerization was well developed during last decade, the cationic visible light-induced polymerization is still at its infancy. Furthermore, the photo-mediated mechanistic transformation from one polymerization method to other, i.e. from cationic to radical polymerization is also very challenging.

In this work, we report for visible light-induced cationic polymerization of isobutylene (IB) via radical oxidation/addition/deactivation mechanism using initiating system consists of $Mn_2(CO)_{10}$ and diphenyl iodonium salt ($Ph_2I^+PF_6^-$). This initiating system induced controlled catalytic chain transfer cationic polymerization of IB proceeded with some induction period at -30 ºC in CH_2Cl_2/n-hexane affording *exo*-olefin-terminated polyisobutylene (exo content >85%) with Mn up to 3000 g mol^{-1} and relatively low polydispersity (Đ < 1.7). The Mn could be efficiently controlled from 2,000 to 30,000 g mol^{-1} by the concentration of diphenyl iodonium salts.[2] The effect of diphenyl iodonium salt nature, temperature, solvent and initiator as well as the mechanism of the polymerization will be also discussed in details.

In addition, the strategy for the synthesis of block copolymers of isobutylene with styrene and methyl methacrylate via $Mn_2(CO)_{10}$-triggered photo-induced radical polymerization in bulk will be also briefly discussed. The proposed strategy consists of the preparation of difunctional PIB-based macroinitiator via consecutive cationic polymerization, in situ functionalization followed by acylation of phenol-terminated PIB by 2-bromo-2-methylpropanoyl bromide. In the second step, the photo-induced radical polymerization of styrene and methyl methacrylate from PIB-based macroinitiator results in the formation of corresponding block copolymers. Finally, the possibility of polyisobutylene functionalization via photo-induced radical addition will be presented.

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This work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation under grant agreement № 075-15-2024-633 (Sechenov University). In part, this work was also supported by State Program for Scientific Research of Belarus "Chemical processes, reagents and technologies, bioregulators and bioorganic chemistry" (project 2.1.01.03).

FROM PROTEINOGENIC TO NON-PROTEINOGENIC AND ARTIFICIAL ALPHA-AMINO ACIDS: PAST AND PRESENT…

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The 20 α-amino acids (AAs) in the L-form are known to be the building blocks for peptides and proteins in mammals. These AAs are encoded by genes and play a crucial role in protein formation. Most of these AAs enter the human body through food, but due to the increasing global population, there has been an increasing trend towards producing proteinogenic α-AAs synthetically.[1]

Non-proteinogenic α-AAs, on the other hand, are components of antibiotics and pharmaceutical compounds. They serve as building blocks for drugs and drug candidates today. With the development of humanity, artificial AAs become more prominent due to their ability to modify and fine-tune the structure and physicochemical properties of peptides and proteins. This is done with the goal of improving their bioactivity and stability. They also actively apply in the field of asymmetric catalysis as organocatalysts and ligands.[2]

At INEOS RAS, a lot of effort has been put into this direction, and a versatile and reliable metal-template approach has been developed for the asymmetric production of various α-AAs on demand.[3-5] For this reason, the topic of developing artificial synthetic methods to produce enantiopure α-AAs will be discussed.

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PROTOTYPES OF THE CRYOGENICALLY-STRUCTURED BIOMEDICAL MATERIALS DEVELOPED BY THE LABORATORY FOR CRYOCHEMISTRY OF (BIO)POLYMERS IN INEOS RAS

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Cryogenically-structured macroporous polymeric materials known as cryogels and cryostructurates[1] are of scientific and also of significant practical interests.[2,3] Cryogels are generated when the gel-formation occurs exactly in the frozen system, and upon its thawing, the formed 3D polymeric network becomes swollen in the defrosted solvent. The nodes of the three-dimensional polymer network of such cryogels can be stabilized by covalent, ionic, coordination and non-covalent bonds or by their combination. Cryostructurates are macroporous polymer matrices, the formation of which is accomplished via freezing a molecular or colloid solution of non-gelling precursors, followed by removal of the frozen solvent by the techniques of freeze-drying or cryo-extraction. If required, additional tanning (cross-linking) of the sponge-like matrix thus prepared has to be done to make the material insoluble. Polycrystals of the frozen solvent perform as porogens upon the formation of both cryogels and cryostructurates, and macropores within the resultant polymer matrices are interconnected. In general, this approach to the preparation of similar materials is termed "cryostructuring of polymer systems", and scientists from INEOS RAS were among the pioneers in this area of polymer science, especially with respect of research related to the mechanisms of chemical and physico-chemical processes occurring upon the formation of the respective cryogenically-structured materials.[4] One of the intensively developing fields of application of various polymeric cryogels and cryostructurates is the biomedical practice.[5] Among these biomaterials are diverse innovative prototypes elaborated in the INEOS RAS by the Laboratory for Cryochemistry of (Bio)Polymers in collaboration with biomedical professionals. Relevant examples include macroporous carriers for the immobilization of enzymes and cells, bioaffinity adsorbents for the isolation and purification of biological molecules and particulate matter like viruses and whole cells, sponge-like scaffolds for culturing animal (including human) cells for the tsks of tissue engineering, biodegradable and non-degradable macroporous covers on wounds and burns, hemostatic materials, drug-delivery carriers for the so-called "depot-forms" of medications, drug-containing temporary implants, drainage systems, etc.

Currently, the studies on cryostructuring processes and the development of novel polymeric biomedical materials are intensively continuing in many countries.

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METAL-BASED DUAL-POTENCY DRUGS CANDIDATES

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Metal-based drugs represent a relevant sector of the pharmaceutical market with potential development in the treatment of incurable diseases. Metal compounds might offer biological and chemical diversity that is distinct from that of organic substances.[1] The presentation will focus on novel approaches to constructing physiologically active metal-based drugs candidates based on target-oriented design, new synthetic methods and extensive biological screenings. This study is focused on the design of hybrid compounds possessing in one molecule a known organic drug and metal atom with a confirmed pharmacological activity ((Pt, Sn, Au, Fe, Co, Ni, Cu, Zn, Ga, In, Ce, La). [2-4]

Figure 1. Metal-Based Dual-Potency Agents

For construction of new multitargeted substances we synthesized several organotin compounds combined with non-steroidal anti-inflammatory, anti-tumor and antioxidant drugs. Results of 1H, 13C, 119Sn NMR, IR, ESI-MS DPPH, CUPRAC, NBT, LOX, and MTT methods as well as *in vitro* and *in vivo* screening demonstrated that the combinations of metal compounds with pharmacologically active organic agents are a perspective road to new drugs candidates. [5,6]

As a result, several lead compounds have been selected for further in-depth preclinical investigation.

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SOME ASPECTS OF MODERN CHEMISTRY OF PENTACOORDINATED PHOSPHORUS DERIVATIVES

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Penta- and hexacoordinated phosphorus derivatives (phosphoranes and phosphorates) are key intermediates in phosphorylation and dephosphorylation reactions under the action of kinases occurring in a living cell and playing an important role in its energy, activation of the action of various signaling cascades, recording information in the form of DNA and RNA and other processes [1]. To correctly assess the mechanism of these reactions, knowledge is needed not only about the thermodynamics and kinetics of processes, but also about the structure and reactivity of pentacoordinated phosphorus derivatives, which also act as key intermediates of many reactions important for organic synthesis, for example, the Wittig, Mitsunobu, Evans reactions, oxaphosphorane condensation, various rearrangements, etc. To obtain phosphoranes, as a rule, reactions of oxidative addition to derivatives of P(III) of various organic reagents are used (for an overview, see [2]).

The report summarizes and analyzes current trends in the chemistry of pentacoordinated phosphorus, such as the effect of stabilization by the Martin ligand, new types of optical activity of hydro- and hydroxyethylphosphoranes, synthesis of phosphoranes with an antiapicophilic arrangement of substituents in trigonal bipyramide, an unusual type of chirality in compounds with phosphorus(V) atom, leading to the formation of enantiomers ($\mathit{\Lambda}$P, $\mathit{\Delta}$P); reaction of P,P,P-trihalobenzo-1,3,2-dioxaphospholes with aryl- and alkylacetylenes. Among the new synthesis methods, intramolecular cascade-type processes in a number of the cyclic P(III) derivatives carrying a carbonyl group, an imino group or an alkenyl fragment in the exocyclic substituent initiated by the activated unsaturated systems are considered. Among them, it is possible to note the obtaining of 5-carbaphosphatrane derivatives bearing a four–membered cycle [3]; synthesis of cage phosphoranes with a P–C or P–O bond [4]; spontaneous rearrangement of bis(2-benzylidenaminophenyl) phenylphosphonite into spirophosphorane; intramolecular cyclization of naphthylidenaminoaryloxy phosphines into derivatives with a P–C bond, PCO/POC rearrangement in a series of cage phosphoranes [5-7], rearrangements in a series of the cage phosphoranes themselves [8]. For P–C- or P–O-cage phosphoranes, the directions of hydrolysis, characterized by a high chemoselectivity, are considered.

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MULTISTEP CATALYSIS IN THE SYNTHESIS AND TRANSFORMATIONS OF HIGHER OLEFINS: FROM THE MECHANISTIC INSIGHTS OF THE PROCESSES TO THE DEVELOPMENT OF VALUABLE LIPOPHILIC AND AMPHIPHILIC PRODUCTS

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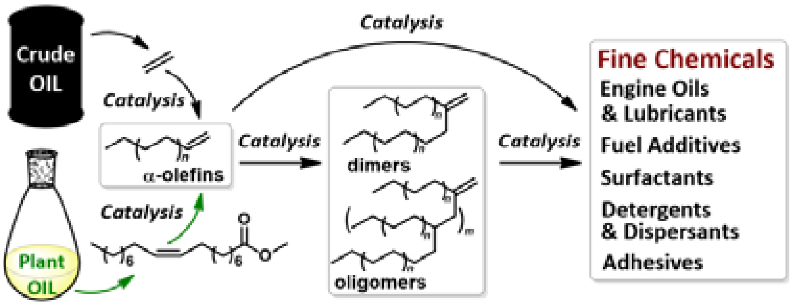
Russian Federation has huge reserves of oil and gas. One of the most important goals of Russian industrial policy is the achievement of the technological sovereignty in the petrochemical business. In this respect the role of Russian chemists including the specialists in catalysis and in material science in a sustainable development of the national chemical industry cannot be overestimated. Ethylene is the first and most mass oil processing product, and currently the development of efficient catalytic technologies of the ethylene conversion into valuable products is of particular importance. Various lipophilic and amphiphilic compounds make up the considerable part of the fine chemicals market, and their production includes two logical stages. In the beginning the ethylene should be oligomerized with a formation of α-olefins with desirable chain length. Optionally, these α-olefins could be further dimerized or oligomerized. In the second step, α-olefins, their dimers or oligomers should be functionalized. Different catalytic approaches are used at both stages, and advanced chemical technologies are often based on multistep and tandem catalytic processes. The higher is the scientific level of catalytic solutions the greater are the prospects of industrial implementation of these processes.



The experience of our Laboratory in the development of commercially feasible processes of the production of in-demand fine chemicals, including synthetic oils, fuel additives, surfactants and adhesives, will be presented in this report. The synthetic availability of α-olefins derived from the plant oil will also be addressed.

Acknowledgements
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SYNTHESIS OF CHIRAL BORANES BY RHODIUM CATALYZED ASYMMETRIC INSERTION INTO B-H BONDS

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Compounds with chiral carbon atoms play a vital role in modern organic chemistry. On the other hand, similar compounds with chiral boron atoms have started to attract a lot of attention several years ago.[1] In this talk we will discuss the insertion of carbenes into B-H bonds, which provides unique chiral boranes.[2,3] Design of the chiral rhodium catalysts for this reaction and the asymmetric poison approach will be also discussed.4

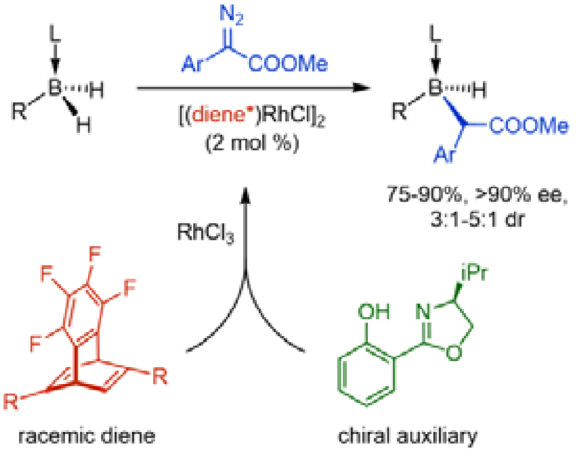

Figure 1. Conceptual synthesis of chiral boranes

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SULFUR-CONTAINING HETEROAROMATIC BUILDING BLOCKS FOR EFFICIENT ORGANIC LUMINOPHORES AND SEMICONDUCTORS

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Nowadays various sulfur-containing heteroaromatic building blocks are successfully used in the synthesis of conjugated organic molecules (Figure 1). Thiophene is a promising structural unit of various linearly conjugated, annulated and branched molecules for organic electronics and photonics.[1] Oligothiophenes are known as efficient organic semiconductors for organic field-effect transistors (OFETs), while thiophene-phenylene co-oligomers (TPCO) possess high luminescence in the films, the field-effect mobility of which can be tuned by their terminal substituents.[2,3] It was shown that a six-ring TPCO with trimethylsilyl end groups is promising for not only for OFETs, but also for light-emitting and photoelectric devices.[4] The highest field-effect mobility can be obtained by annulated structures such as dialkyl derivatives of benzo[b]benzo[4,5] thieno[2,3-d]thiophene (BTBT).[5-7] Annulated thieno-thiophene and thieno-pyrrole fragments are constituents of various non-fullerene acceptors used in efficient organic photovoltaics.[8-10] 2,1,3-Benzothiadiazole is the other very popular sulfur-containing heteroaromatic building block, peculiarities of which include strong accepting ability and high stability. It was used for the synthesis of a number of very efficient linear and branched organic luminophores for various applications.[11-15]

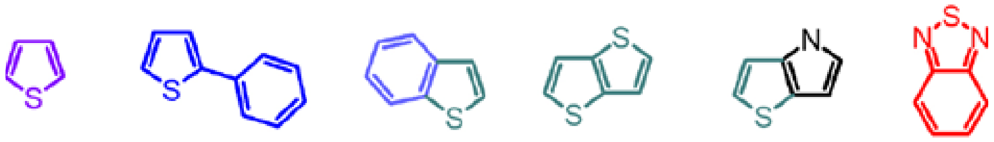

Figure 1. Examples of sulfur-containing heteroaromatic building blocks under consideration.

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DENDRIMERS: FROM DESIGN TO APPLICATIONS

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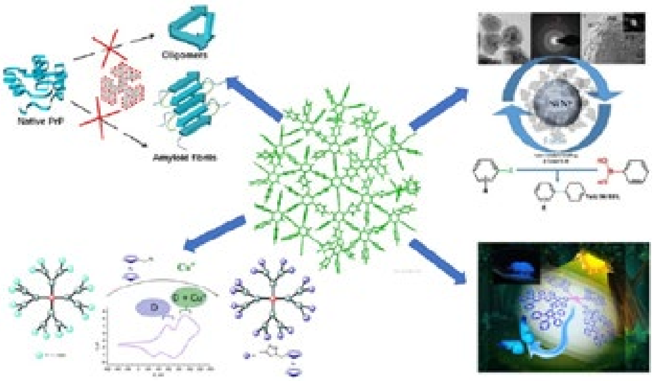
Dendrimers are hyperbranched, three-dimensional macromolecules with pre-cise chemical structures. Their synthesis involves repetitive sequences of chemical reactions, progressively increasing the generation size in a controlled hierarchical manner. Their multifunctional peripheries offer vast possibilities for targeted modifi-cations, making dendrimers suitable for applications where the use of traditional poly-mers is either impossible or impractical. Due to the active centers on the multifunctional periphery and branched architecture denrdimers can form catalytically active nanocomposites that are effective in a variety of chemical reactions.

Dendrimers have been found to have diverse applications in medicine as contrast agents for MRI, drug delivery systems, in vitro diagnostic tools, boron-neutron capture therapy agents, and in mimicking micelles, acting as nanoscale reactors. Their multifunctional surfaces and internal cavities can provide controlled release of drugs or encapsulation of therapeutic agents.

We have designed rigid functional aromatic dendrimers that serve as versatile platforms for creating various advanced materials. These dendrimers have demonstrated utility in catalysis[1], as electrochemical sensors of ions[2], light-emitting materials[3], drug delivery systems, in the inhibition of amyloid protein aggregation[4]. Here we present recent results in the synthesis and application of aromatic dendrimers developed in our laboratory, along with prospects for the further development of dendrimer chemistry.



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ORGANOSILICON MATERIALS FOR USE IN EXTREME CONDITIONS AND IN THE FAR NORTH

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RARE- AND ALKALINE-EARTH METAL COMPLEXES IN CATALYTIC FORMATION OF C-C AND C-E (E = N, P, Si) BONDS. A NEW APPROACH TO ACTIVATION OF C=C AND C-H BONDS

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The recent achievements in development of new approaches to the activation of multiple C-C, *sp*^{3}- and *sp*^{2}-hybridized C-H, E-H bonds by complexes of s- and f-elements will be reported.

Efficient and selective catalysts for intermolecular reactions of hydroamination, hydrophosphination, hydroarylation, hydrobenzylation of olefins and acetylenes, hydrosilylation/dearomatization of nitrogen-containing heterocycles of the pyridine series, stereoselective migration of the double bond C=C in α-olefins and allylbenzenes, as well as dehydrocoupling of hydrosilanes with arenes, amines and phosphineshave have been developed. Heterobimetallic ate-complexes $\{[(p\text{-}t\mathrm{BuC_6H_4})_2\mathrm{CH}]_3\mathrm{M}\}\mathrm{K}$ (M = Yb(II), Ca(II)) demonstrated unprecedented catalytic activity and 100% regioselectivity in intermolecular olefin hydroamination allowing to involve into the reaction a broad scope of substrates including ethylene (1atm), internal C=C bonds and a variety of primary and secondary amines. Complex $\{[(p\text{-}t\mathrm{BuC_6H_4})_2\mathrm{CH}]_3\mathrm{Ca}\}\mathrm{K}$ allowed for the cascade NH_3 alkylation with styrene and hydroaminoalkylation involving one of styryl fragments to afford N,N-diphenethyl-1,4-diphenylbutan-2-amine.A synergistic effect of ions of two different metals, consisting in concerted activation of each of the substrates on different metal centerswas discovered.

Complexes $\{[(p\text{-}t\mathrm{BuC_6H_4})_2\mathrm{CH}]_3\mathrm{M^1}\}\mathrm{M^2}$ (M^1 = Ca, Sr, Ba, Yb; M^2 = Li, Na, K) in the combimnation with amine (1:10 molar ratio) perform high catalytic activity in the migration of the terminal double bond of allylbenzenes and α-olefinsat room T providing high reaction rates and quantitative conversions, achieving E-stereoselectivity 90-98%.

Coordinatively unsaturated hydrides $\{[\mathrm{tBu_2CarbAr_2}]\mathrm{MH(THF)}\}_2$ and $\{[\mathrm{tBu_2CarbAr_2}]\mathrm{MH}(\eta^6\text{-}\mathrm{C_7H_8})\}_2$ (M = Ca, Yb) catalyze the reversible addition of hydrosilanes to nitrogen-containing heterocycles at room T. Dearomatization of pyridines and quinolines proceeds easily with exceptional regioselectivity and yields the 1,2-addition product.When the reaction T increases to 90°C, the same complex catalyzes the reverse reaction: release of the initial silane and restoration of the aromaticity of the pyridine system.Using the DFT method, it was found that due to the entropic contribution, the formation of reaction products becomes unfavorable at higher temperatures.

Acknowledgements
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AMPHIPHILIC BLOCK-COPOLYMERS AS A MATRIX FOR PREPARATION OF PT(II) AIEGENS

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Aggregation of chromophores containing developed aromatic systems may afford two principally different effects: Aggregation Caused Quenching (ACQ)[1] and Aggregation Induced Emission (AIE)[2]. In the last decade the latter attracts growing attention because of unique photophysical properties demonstrated by the AIE chromophores (also called AIEgens). The AIEgens commonly give a strong increase in emission intensity, very often from zero to nearly quantitative quantum yield, due to strong blocking of rotational and vibrational channels of emissive excited state relaxation, which usually are the major reasons of emission quenching. These characteristics form the basis for a wide range of AIEgens applications in electroluminescence, advanced analytics, and especially in medical diagnostics and theranostics.

The major part of studies in this area is related to fluorescent AIEgens, which have been discovered first and investigated in detail. However, aggregation of some types of phosphorescent transition metal complexes such as square-planar Pt(II), Pd(II) and Au(III), which tend to form metallophilic bonding between metal centers in addition to π-stacking of the ligands' aromatic systems, may result in transformation of emissive excited state from the typical ligand centered (^{3}LC) and metal-to-ligand charge transfer (^{3}MLCT) characters, or their mixture, to that determined by the formation of M-M bonds either in ground or excited states.[3] The transformation results in a strong bathochromic shift of emission into red and NIR areas of spectrum to fall into so called "window of transparency" of biological tissues without a crucial loss in emission intensity that is of particular importance for the application of these emitters in biomedical research.

It is worth noting, however, that the AIE phenomena are typically observed in solid state where AIEgens are additionally stabilized by rigidity of the chromophore environment. Quite naturally, these emitters are not soluble in water and physiological media that strongly limited their application in biomedicine. In our research group, recently a few methods of solubilizing of the Pt(II) AIEgens have been elaborated, which are based on the use of amphiphilic block-copolymers either as an outer stabilizing matrixes for this type of AIE chromophores or by copolymerization of the platinum complexes with biocompatible polyvinylpyrrolidon using RAFT methodology. Detailed description of the research results will be presented in this lecture together with the analysis of the photophysics of the obtained AIEgens.

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ACCOMPLISHMENTS OF ACADEMICIAN A.N. NESMEYANOV IN TODAY'S ASSESSMENTS

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The name of A.N. Nesmeyanov takes a special place among the names of outstanding chemists and statesmen of the 20th century, which are remain in the history of world science. He became one of the founders of a new chemical discipline - the chemistry of organoelement compounds to made also an outstanding contribution to the development of organic and inorganic chemistry. For many years he was a recognized leader of the entire scientific community of the Soviet Union heading Soviet science as President of the USSR Academy of Sciences (1951-1961). This time became a period of outstanding achievements in Soviet science and technology. He created one of the largest scientific schools in his country and in the world. The scientific contribution of A. Nesmeyanov and his students received wide international recognition. He was a man of many talents possessed a rare combination of human qualities: a quick analytical mind and developed intuition, irreconcilability in upholding basic principles and the ability to find compromises, high demands on himself and on people, strictness in assessments and soft benevolent humor, precision and imagery of the mind. This report examines the principles of organizing chemical education and scientific research that he laid down, as well as the most important achievements of his work, which continue to have a beneficial effect on the development of science and education in our country.

ORAL PRESENTATIONS

HOW TO INCREASE THE EFFICIENCY OF CATALYTIC REACTIONS

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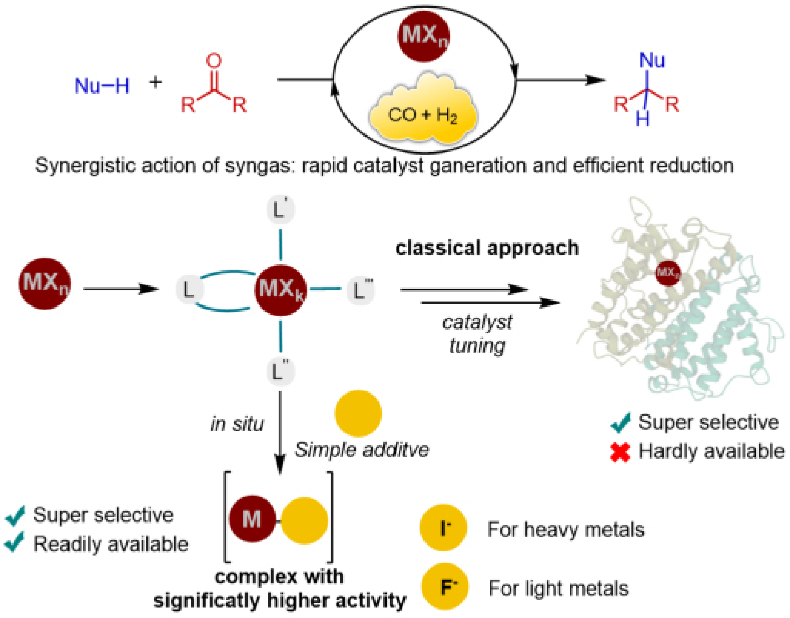
Catalytic reactions represent a highly attractive approach towards the complex molecules construction. The standard way to develop a selective transformation implies the fine-tuning of the catalyst structure to ultimately fit the substrate. This results in highly efficient catalytic reactions. However, the catalyst preparation becomes very time and resource consuming and the process versatility decreases.

This talk covers alternative ways to achieve high efficiency in the catalytic reactions. Instead of the catalyst fine-tuning, we suggest the activation of the simple organometallic catalysts by the low molecular weight additives like fluorides or iodides. This allows increasing TON by two orders of magnitude in the reductive amination, asymmetric Michael addition, asymmetric cyanation and cyclic carbonates synthesis. Another way implies the use of non-classical reagents with standard catalysts to achieve both stabilization of catalytically active species and efficient reaction. For example, application of syngas instead of hydrogen in the reductive addition allowed to strongly increase TON and reduce temperature of the process.



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AMMONIA IS A UNIVERSAL SYNTHETIC MEDIUM FOR OBTAINING SILICONES WITH A DEFINITE MOLECULAR STRUCTURE

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The main task solved by modern polymer chemistry is the creation of macromolecular systems with a set of specified useful properties with minimal impact on the environment both at the stage of production and at the stage of operation and disposal. At the same time, the need to improve performance characteristics (mechanical and thermal stability, high hydrophobicity, radiation resistance, etc.) is constantly growing. It is well known that the structure of the macromolecule determines the properties of the polymer. The development of a targeted and simple method for the synthesis of polymers of various molecular structures, in particular silicones, is a relevant area of the chemistry of high-molecular compounds.

The use of ammonia as a reaction medium for the synthesis of organosiloxanes is a unique and promising area of research. This is due to such properties of ammonia as good solubility in it of many organic and inorganic compounds, low viscosity and density, the possibility of removing it from the reaction zone by decompression.

This work will present the results of the synthesis and study of the properties of: narrow-dispersed homo- and heterofunctional polyorganosiloxanes[1], functional star-shaped PDMS, ladder polyphenylsilsesquioxanes[2,3] obtained in an ammonia environment. Approaches to the processing of siloxane rubbers with various fillers will be considered separately.

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HETEROCYCLIC TETRYLENES STABILIZED BY LIGANDS WITH ACCESSORY DONOR CENTERS. FEATURES AND CATALYTIC ACTIVITY

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Recent research in the chemistry of main group elements has emphasized the importance of using specifically low valence element compounds for catalysis. The unique electronic nature of the heavy analogs of carbenes makes it possible to mimic the characteristics of transition metals. Compounds of this type are used as organocatalysts for numerous transformations, such as cyanosilylation, hydroboration and hydrosilylation of carbonyl compounds and unsaturated hydrocarbons [1].

A transition to tetrylenes with increased nucleophilicity of the low valence center is required to increase the catalytic activity. This can be achieved by the extention of bidentate ligand systems to polydentate ones stabilizing tetrylene due to additional donor-acceptor interactions (Figure 1.) [2].

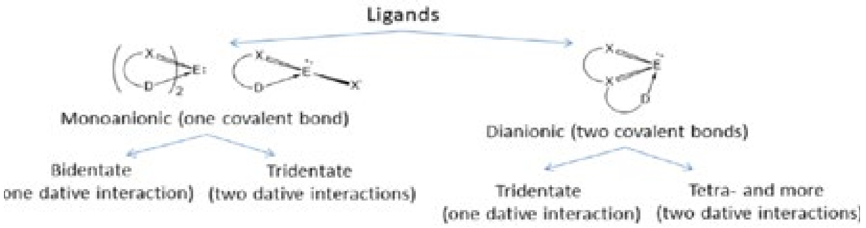

Figure 1.

This work is devoted to the synthesis, peculiarities of structure and catalytic activity of heavy analogs of carbene based on ligands capable of additional chelation of the metal center.

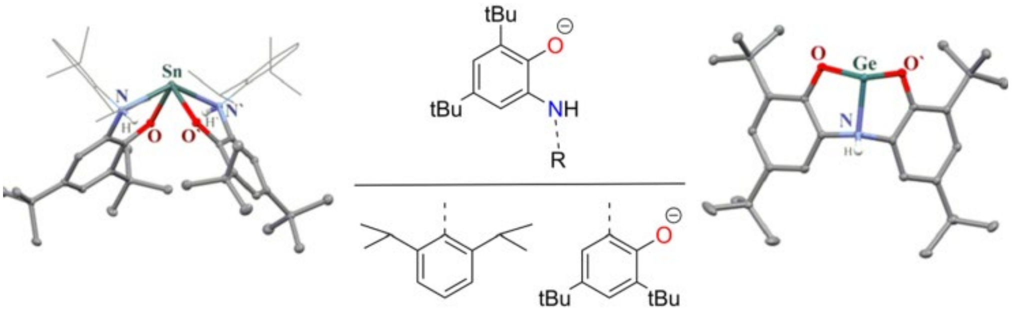

Figure 2. Aminophenolate derivatives of low valence group 14 elements (Sn and Ge)

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CATALYTIC APPROACHES FOR SYNTHESIS OF FUNCTIONAL ORGANOSILICON COMPOUNDS

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Catalysis plays a key role in modern organic chemistry. Catalytic approaches allow to obtain both bio-based and previously unknown complex structures.

Unfortunately, catalytic methods for the synthesis of functionalized organoelement compounds, in particular organosilicon, are less developed, compared to organic ones. At the same time, organosilicon compounds are among the most important, because of their wide applicability.

In this presentation main achievements of our research group will be discussed:

- Catalytic systems for the liquid phase aerobic Si–H- and C–H-functionalization, which allow obtaining a range of silanols,[1,2] p-carboxyphenylsilanes[3,4] etc. Dumbbell-shaped and graft siloxane polymers were obtained based on silanols.[5] A variety of HOFs and MOFs were obtained based on p-carboxyphenylsilanes.
- Catalytic systems for ultra-fast silica-aerogel production. It allows to obtain high quality aerogels within 6-24 hours, compared to previous techniques, which require at least several days.[6]
- [Pt]- and [Mn]-based catalytic systems for hydrosilylation. [Pt]-systems were shown to be recyclable up to 60 times.[7-9] [Mn]-system presents an alternative to expensive [Pt]-catalysts.[10] These catalytic approaches were implemented in microfluidic flow reactors.[11]

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PRODUCTION OF A FILM FROM POLYPHENYLENE SULFIDE BY EXTRUSION

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In order to develop new products and expand the fields of plastics application, it is necessary to increase production and develop new high-strength plastics, on the basis of which composites of special applications will be obtained. A large number of engineering plastics and composites are represented on the world market, the demand and production of which will increase every year. In Russia, until recently, high temperature polymers were synthesized in very small quantities, and in the last 7 years a positive trend has been outlined for the development of synthesis on an industrial scale.

One of the high temperature polymers with excellent chemical resistance is polyphenylene sulfide, which is nonflammable and has high mechanical properties compared to general–purpose polymers. Products made of polyphenylene sulfide and composites based on it are used in various industries such as electronics, automotive components and the aerospace industry.

This polymer is important for strategic areas of industry. Its synthesis was established in Kazan in 2021, in the presented work samples of PPS powder obtained at a pilot plant in the commonwealth of LLC "Injekhim" and "STC "Ahmadullins" were used. Polymer synthesis alone is not enough to master the technology and introduce its products into industry.

The presented work is devoted to the production of products of a higher degree of processing from natural polyphenylene sulfide. Granulate samples and composites were obtained on the Scientific LTE 16 – 40 twin-screw extruder. Film materials were obtained on the Welber EXT-25 extrusion line. Samples for mechanical and thermomechanical tests were obtained by injection molding on the Welber FEL 85. Tensile tests of the obtained samples were carried out on a universal electromechanical testing machine UTS-111 with wedge-shaped grips and with a deformation rate of 5 mm/min. The determination of the heat deflection temperature for the samples was performed on the SMARTEST VHDT 1113 device with a heating rate of 2 ºC/min and a load weight of 250 g (1,8 MPa). Izod impact strength tests without notch were carried out on a TSKM-50 pendulum copra with a pendulum energy of 7.5 J. DMA and DSC tests were also carried out on DMA 242 E Artemis devices with a heating rate of 3 ºC/min and DSC 214 Polyma with a heating rate of 10 ºC/min, respectively.

The developed approaches made it possible to significantly increase the viscosity of polyphenylene sulfide without the introduction of fillers, which ensured its excellent recyclability during extrusion. As a result, it was possible to produce film materials from PPS.

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FLP-LIKE REACTIVITY OF BIMETALLIC TRANSITION METAL COMPLEXES

Belkova N.V.,[a] Sedlova D.V.,[a,b] Gutsul E.I.,[a] Osipova E.S.,[a] Shubina E.S. [a]

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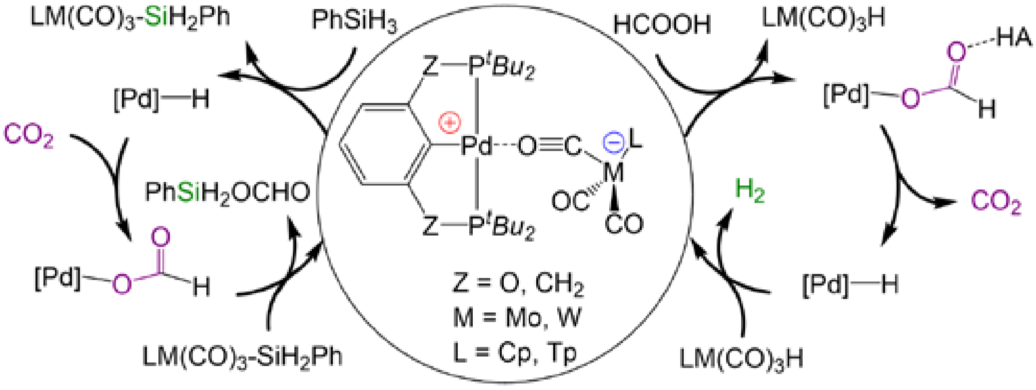
Depending on the polarization of the M–H bond Hydride complexes of transition metals can display both acidic and basic properties.[1] Bimetallic ionic complexes ($(^{tBu}PZCZP)Pd(\mu\text{-}OC)M(CO)_2L$ (Z = CH_2, O; M = Mo, W; L = Cp, Tp (Scheme 1)) formed by the interaction of the acidic tungsten hydride $LW(CO)_3H$ and the basic palladium hydride $(^{tBu}PZCZP)PdH$ feature Lewis acidic $[Pd]^+$ and basic $[W]^-$ metal centers making them a transition metal analogue of frustrated Lewis pairs (FLPs). These complexes effectively dehydrogenate amine-boranes (Me_2NHBH_3, tBuNH$_2$BH) through the cooperative BH/NH bond activation followed by the stepwise proton transfer to $[W]^-$ and hydride transfer to $[Pd]^+$.[2] FLP-like reactivity and cooperative action of these two metal centers are also demonstrated for in formic acid dehydrogenation[3] and carbon dioxide hydrosilylation.[4] In HCOOH dehydrogenation the *hydride abstraction/CO_2 release* step is facilitated by −OCHO···H−A hydrogen bonding (HA = $LM(CO)_3H$ or HCOOH), the reaction being much slower in the absence of $LM(CO)_3H$ or its substitution by organic base.[3] For carbon dioxide reduction, the *step-wise* CO_2 hydrosilylation can be stopped at the formate level in presence of bimetallic complexes $(^{tBu}PZCZP)Pd(\mu\text{-}OC)M(CO)_2Cp$. In contrast, sole $(^{tBu}PZCZP)PdH$ rapidly proceeds beyond this stage, achieving a more extensive reduction. The diffusion-controlled step involves CO_2 insertion into the Pd-H bond, making Si-H bond activation by bimetallic complex in the FLP-fashion the *rate-determining step*.[4]



Scheme 1.

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Acknowledgements
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NOVEL CATALYTIC SYSTEMS FOR THE SYNTHESIS OF HIGHLY REACTIVE POLYISOBUTYLENE: LIQUID COORDINATION COMPLEXES IN THE PRESENCE OF ETHERS

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Polyisobutylene with number-average molecular weight below 2500 g mol^{-1} and content of exo-olefin end group more than 75 mol.% (so-called highly reactive polyisobutylene or HR PIB) is a well-known precursor for manufacturing of motor oils and fuel additives.[1] Nowadays HR PIB is commercially produced by means of conventional cationic polymerization of isobutylene (IB) in the presence of complexes of BF_3 with ethers/ secondary alcohols as catalysts in hydrocarbons at temperatures below 0°C. Considering the high volatility and corrosiveness of BF_3, many efforts have been reported aimed at replacing this catalytic system.[2] Since our discovery of efficient catalytic systems for the synthesis of HR PIB based complexes of Lewis acids ($AlCl_3$, $FeCl_3$, $EtAlCl_2$ etc.) with ethers, acidic imidazole-based ionic liquids in combination with diisopropyl ether ($^iPr_2O$) were shown to be even better catalysts.[3] However, imidazolium salts are strongly hygroscopic, less stable and expensive in comparison to other bases tend to form compositions with Lewis acids.

In this contribution, we present new catalysts for the synthesis of HR PIB based on the combination of liquid coordination complexes (LCCs) such as tri n octylphosphine oxide-$AlCl_3$ ($POct_3O$-$AlCl_3$) or $POct_3O$-$FeCl_3$ and ethers (bis(2 chloroethyl)ether (CE) and $^iPr_2O$). These catalysts allow to synthesize with the high yields low molecular weight PIBs (Mn ≤ 2500 g mol^{-1}) with high content of exo olefin end groups (>80 mol.%) and relatively low dispersity (Mw/Mn<2.0) at high temperature (0°C-20°C) and high monomer concentration ([IB] = 5.2 M) in n-hexane. Among these two catalysts, $POct_3O$–$FeCl_3$/$^iPr_2O$ is more promising due to the affording PIB with lower Mn and higher exo-olefin end group content at lower catalyst concentration as compared to $POct_3O$–$AlCl_3$/CE. The main feature of these new catalysts, similarly to ionic liquid-based counterparts, is the interfacial character of the polymerization process that provides polymers with relatively low dispersity in comparison with homogeneous catalytic systems. In comparison to appropriate ionic liquids LCCs are cheaper, easier in operating and possessing strongest acidic properties.

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The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation under grant agreement № 075-15-2024-633 (Sechenov University). In part, this work was also supported by State Program for Scientific Research of Belarus "Chemical processes, reagents and technologies, bioregulators and bioorganic chemistry" (project 2.1.01.03).

DESIGN OF ONE-COMPONENT CATALYSTS FOR ADDITION POLYMERIZATION OF NORBORNENE DERIVATIVES

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Despite the attractiveness of addition polynorbornenes, which as a rule have high chemo- and thermal stability, transparency and high glass transition temperatures, the application of materials based on them is severely limited. The 'cornerstone' in the applications of addition polymers based on norbornenes is the process by which they are produced. Addition polymerization currently is a poorly understood process for which effective catalysts have not yet been developed, and the involvement of certain monomers, especially those with polar groups, in addition polymerization can sometimes be very difficult. To date the development of highly efficient catalysts for addition polymerization is a very urgent task. In the literature, there have been many attempts to develop single-component catalyst for addition polymerization. Some of them have been quite successful. In this talk, we will present the results on the development of one-component catalysts for addition polymerization based on cationic palladium complexes with carbene ligands, as well as systematic studies on the optimization of the properties of complexes of this type.[1] The developed catalysts made it possible to obtain a series of new promising polymeric materials.

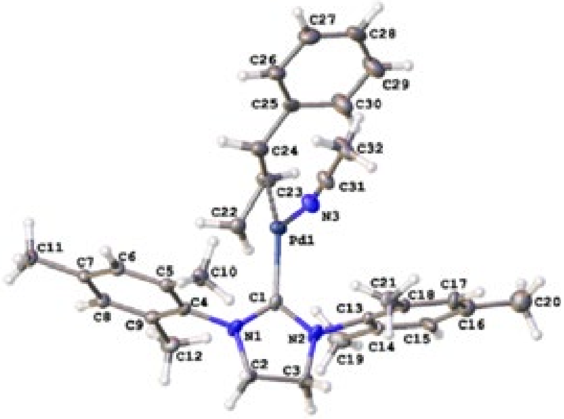

Figure 1. An example of the structure of the synthesized (NHC)Pd-complex according to the X-ray diffraction analysis.

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INTERACTION BETWEEN PARTIALLY BETAINATED CHITOSAN AND ALBUMIN IN ALCALESCENT MEDIA

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Chitosan – a semi natural polyaminosaccharide derived from natural chitin – attracts much attention for biomedical applications due to its biocompatibility, biodegradability, and antimicrobial properties. However, the loss of solubility in neutral and alkalescent media is a limiting factor for its applicability. One of the approaches to solving this problem is quaternization of chitosan. An advantage of *N*-betainated oligochitosans[1,2] among other quaternized derivatives is their high biocompatibility and low toxicity together with high antimicrobial activity in alkalescent media[3].

In the present work, the main features of the interaction of partially *N*-betainated oligochitosan with bovine serum albumin (BSA) is studied in media with pH 7.4 corresponding to the acidity of the main physiological fluids. For this purpose, we perform titrations of chitosan derivatives into protein solutions in two buffers with different heat of ionization using light scattering and isothermal titration calorimetry (ITC). The comparison of ITC curves reported in phosphate buffer with low heat of ionization and in TRIS buffer with high heat of ionization evidences the impact of proton transfer from buffer substances onto chitosan derivatives in polymer-protein interaction[4]. This leads to the conclusion about the participation of primary amino groups of chitosan derivatives along with quaternary ammonium ones in electrostatic binding with BSA. Circular dichroism study shows that the secondary structure of BSA in soluble complexes remains unaltered. An increase of ionic strength to 0.15 M suppresses the electrostatic binding.

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CAGELIKE Mn-, V-, Fe-, Ln-SILSESQUIOXANES: UNIQUE STRUCTURES AND FUNCTIONALITIES

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Cagelike metallasilsesquioxanes is an impressive family of metallacomplexes with various types of (supra)molecular architectures and different applications.[1,2] Structural diversity of metallasilsesquioxanes is explainable by an easy preparation of metallasilsesquioxane complexes with additional organic ligands[3] and/or an application of alternative synthetic methods, e.g. solvatothermal ones.[4] Lecture will discuss actual results of our groups concerning self-assembly of metallasilsesquioxanes as well as investigation of their catalytic, magnetic, luminescent and antifungal properties.

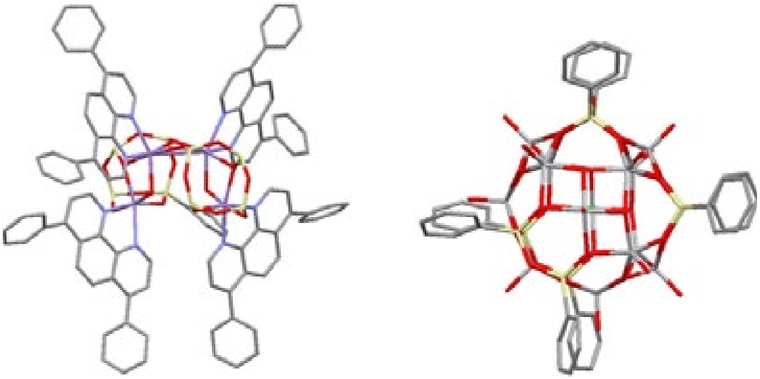

Figure 1. Molecular structures of Mn-silsesquioxane[3] (complex with bathophenanthroline, left) and V-silsesquioxane[4] (right)

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MAGNETIC PROPERTIES OF HYBRID MATERIAL BASED ON GRAPHENE OXIDE WITH ANIONIC IRON(III) SPIN CROSSOVER COMPLEX

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The present work proposes the creation of spin-switchable hybrid film materials based on graphene oxide (GO) with salt **1**, represented by an anionic spin-crossover (SCO) complex $[Fe^{III}(5Cl\text{-}thsa)_2]^-$ (5Cl-thsa – 5-chlorosalicylaldehyde thiosemicarbazone) and the organic tetraethylammonium cation. The $N_2S_2O_2$-coordination anionic SCO complex $[Fe^{III}(5Cl\text{-}thsa)_2]^-$ excludes the possibility of interaction with carboxyl (–COOH) groups on the GO surface, unlike $[Fe^{III}(Ligand)]^+$ cationic SCO complexes.[1]

The film of the hybrid material GO-**1** was characterized by scanning electron microscopy, EDX and XPS analysis, IR, Raman and ^{57}Fe Mössbauer spectroscopy, dc magnetic measurements, and powder X-ray diffraction.

Comparison of the magnetic properties of salt **1** and a film of the hybrid material GO-**1** demonstrated a significant influence of the GO nanosheets matrix on the completeness of spin transition (Fig.1). Therefore, it can be assumed that the cooperativity effect of intercalant Fe (III) complexes is implemented by their interaction through shortened contacts between themselves and with the surface of GO nanosheets.

This result opens up new horizons for the generation of GO-based hybrid materials for switching device applications.

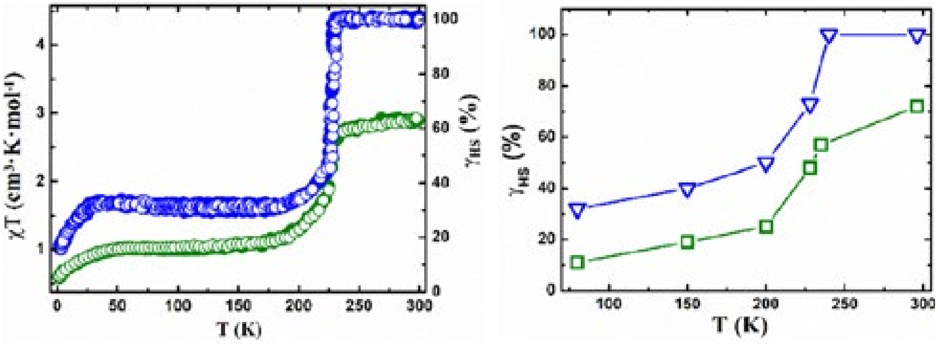

Figure 1. *Left:* Temperature dependences of χT(left axis)/γHS (right axis) in the heating (empty circles) and cooling (full circles) modes for $[Et_4N][^{57}Fe(5Cl\text{-}thsa)_2]$ salt **1** (green) and GO-**1** film hybrid material (blue) according to *dc* magnetic measurements.
Right: Temperature dependences of γHS in the cooling mode of salt 1 (green squares) and GO-**1** (blue triangles) according to Mössbauer measurements in the 80-296 K temperature range

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ELECTROPHILIC CATALYSIS WITH ORGANIC LEWIS ACIDS

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Organocatalysis is an attractive alternative to metal complex catalysis due to the significantly lower harmful effects on the environment and the low sensitivity of organocatalysts toward atmospheric oxygen and moisture. One of the directions in the development of the field of electrophilic organocatalysis is the preparation of analogues of metal complex catalysts featuring a nonmetal element with a kinetically labile coordination vacancy as the central atom. Such catalysts combine high activating ability, environmental friendliness, and high stability toward oxygen and water.

The report will discuss the latest experimental data on the kinetics of reactions in the presence of cationic organochalcogen and organohalogen compounds (Figure 1), xenon derivatives, as well as the results of quantum chemical calculations that reveal the essence of the observed catalytic effects.[1-5] Special attention will be paid to the creation of tandem catalytic systems involving a new type of organocatalyst.

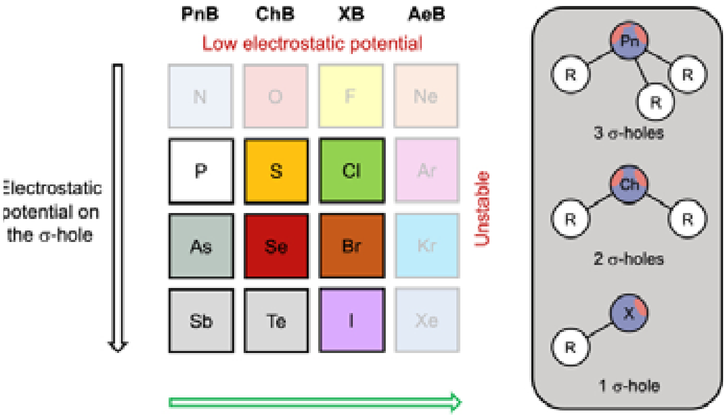

Figure 1. Structures of chalconium and halonium cations utilized for the catalysis.

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DESIGN OF FERROCENE-CONTAINING POLYPHENYLENE DENDRIMERS FOR SENSING APPLICATIONS

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Ferrocene-containing dendrimers, with their potential applications in molecular electronics, catalysis, and ion sensors, have garnered significant interest from researchers.[1,2] These compounds exhibit an enhanced electronic property of the redox center due to the positive dendritic effect. Our previous research has shown that redox-active polyphenylene dendrimers can be effectively used to create modified electrodes.[3,4] However, these macromolecules were found to be insensitive to the presence of ions, attributed to the significant distance between the receptor group and ferrocene termini (Fig. 1, left). To address this, we proposed the synthesis of dendrimers with a closer arrangement of these groups (Fig. 1, right).

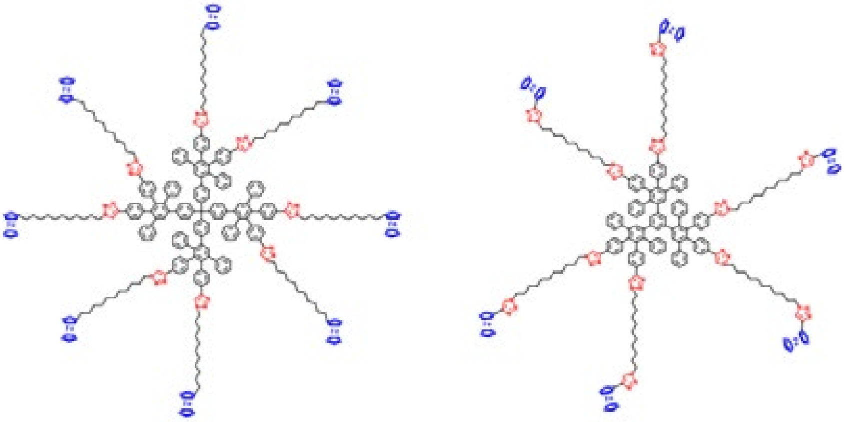

Figure 1. Ferrocene-containing polyphenylene dendrimers

Dendrimers were obtained under mild conditions of Cu(I)-catalyzed azide-alkyne cycloaddition. It was found that the oxidation/reduction process of dendrimers is electrochemically reversible, and modified electrodes are capable of detecting ions.

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THE NICHOLAS REACTION: EXPECTED AND UNEXPECTED WAYS

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The Nicholas reaction is a unique and mild technique for the modification of the propargylic position in $Co_2(Co)_6$-alkyne complexes with nucleophiles.[1] The presence of an appropriate functionality at the propargylic position allows the formation of Co-stabilized carbocations that readily react with various hetero- and C-nucleophiles. This reaction can take place inter- and intramolecularly. Therefore, Nicholas-type cyclization is known as a useful method for the synthesis of strained medium-sized cyclic alkynes.

We have shown that Nicholas cyclization is the method of choice for the synthesis of heterocycle-fused enediynes[2] and cycloalkynes (Fig. 1, A).[3] Thus, only Nicholas cyclization allows the synthesis of 10-membered enediynes fused to 5-membered rings, while other common techniques are insufficient. In addition to high yields, this method allows the synthesis of these classes of compounds and their storage in a Co-protected form that can be subjected to mild decomplexation when needed.

In some cases, however, the Nicholas reaction goes in unpredictable directions (Fig. 1, B). For example, in the case of indole fusion, instead of the expected 10-membered rings, the formation of pyrrolines and dihydrofurans was observed without affecting the proposed cationic center.[2,4] A similar BF3-promoted intramolecular reaction occurred within the already formed benzothiophene-fused thiaenediyne.

The most interesting unexpected type of the Nicholas cyclization was found when DCM (a solvent for this reaction) contained too much stabilizing amylene that was not removed from the DCM prior to the reaction. In this case, a new type of Nicholas cyclization/alkene incorporation (NC-AEI) was discovered. It was shown that this reaction follows the Markovnikov rule and is an attribute of O-nucleophiles. The formation of the corresponding (n+2) cyclic products was found to be thermodynamically controlled. This novel type of the Nicholas reaction demonstrated with enediynes can be applied to the synthesis of cycloalkynes.

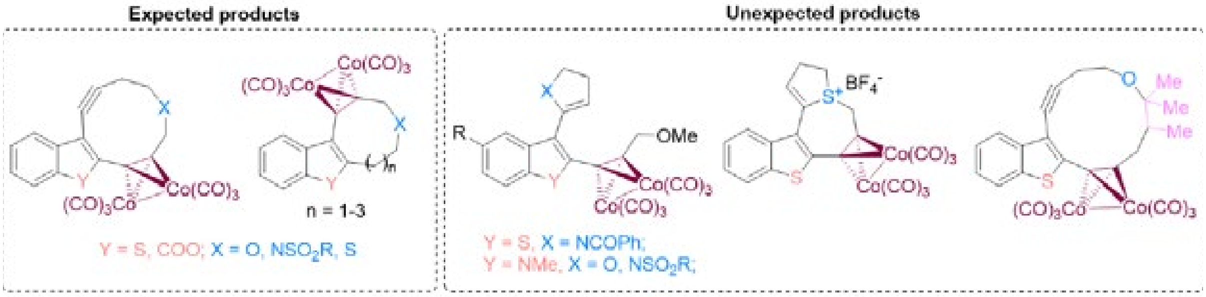

Figure 1. Normal and unexpected products obtained under Nicholas cyclization conditions

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FLUORESCENT POLYHEDRAL BORON HYDRIDES FOR BORON NEUTRON CAPTURE THERAPY

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Currently, the promising area of application of boron compounds in medicine is boron neutron capture therapy for cancer (BNCT). BNCT is a binary method for treatment of cancers, based on the selective accumulation of boron compounds in a tumor followed by its irradiation by a thermal neutron flux. In this presentation the principles of BNCT and main boron-containing biologically active compounds used for BNCT will be shown.[1,2] For successful treatment of tumors using the BNCT method, selective delivery of the boron part to tumor cells is necessary, as well as monitoring the accumulation of boron in them for further irradiation with a thermal neutron flux. One of the ways to solve this fundamental problem is the synthesis of polyhedral boron hydrides containing BODIPY moieties, capable of fluorescing and tracking the accumulation of boron in tumor cells. Therefore, the development of effective methods for the synthesis of new conjugates of polyhedral boron hydrides with BODIPY is an urgent task. The report will present our recent results on the design and preparation of various boron clusters with BODIPY (Figure 1).

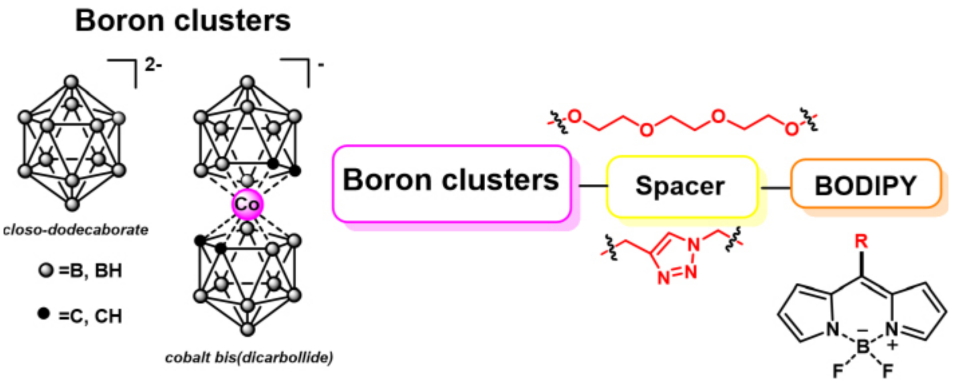

Figure 1. Conjugates of polyhedral boron hydrides with BODIPY

The synthesis of conjugates of polyhedral boron hydrides with BODIPY as potential candidates for BNCT was mainly carried out via the Cu(I)-catalyzed 1,3-dipolar [3+2] cycloaddition reaction of alkynes to azides (“click” reaction) and the ring-opening reactions of the cyclic oxonium derivatives of polyhedral boron hydrides with various nucleophiles.

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CRYSTALLOCHEMICAL CHARACTERISTICS OF COMPOSITES BASED ON CALCIUM PHOSPHATES AND HYALURONIC ACID

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In the last decade, technologies for obtaining polymeric calcium phosphate compositions biocompatible with human bone tissue have been intensively developing. Natural polysaccharides have been widely used as organic components, since they are well resorbed by cells in vivo, without having a negative toxic effect. The paper studies the phase composition and crystallochemical parameters of calcium phosphate low molecular weight hyaluronic acid composites.

The powders were synthesized from a model medium similar to human synovial fluid1, with varying concentrations of low-molecular hyaluronic acid (in the form of sodium salt, 0.1 MDa, Germany), wt. % - powder No.: 0 - 1; 0.15 - 2; 0.30 - 3; 0.45 - 4; 0.60 - 5; 0. 75 - 6. The crystallization time of the precipitates was 7 days. The diffraction patterns of the powders were obtained on a D8 Advance device, Bruker. The powder diffraction database (ICDD PDF-2, EVA, Bruker) was used to decipher the phases. The content of the phases present in the samples was determined by the corundum numbers method (Chang method, Crystallographica Search-Match program). Crystal chemical parameters were determined using the least squares method (LeBayle method, TOPAS 4.2, Bruker).

X-ray studies showed that the unmodified sample is represented by poorly crystallized hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$, JCPDS No. 9-432). It is shown that the composition of the composites is determined by the rheological properties of the mother model media. It was revealed that at low concentrations of the polysaccharide in the synthesis medium, powders containing metastable phases of whitlockite and brushite are formed (samples No. 2 and No. 3). With an increase in the viscosity of the model solutions, the HAP content in the sediments increases. In highly viscous solutions, the precursor phases are completely transformed into apatite.

It was found that the crystallochemical parameters of the powders are close to those of non-stoichiometric calcium-deficient hydroxyapatites (JCPDS No. 46-0905: axes a and c = 9.44 and 6.881 Å). All the composites, compared to the stoichiometric phase of HAP: axes a and c = 9.418 and 6.884), show an increase in the parameter a of the unit cell with an insignificant change in the value of c. High values of the parameter a can be explained by the presence of water molecules in the channels of the HAP powder structure. With an increase in the viscosity of the solutions (samples No. 4-6), the parameter a of the HAP composites decreases and approaches the value for the stoichiometric phase. It is possible that in such environments, water molecules are bound to the hydrophilic matrix of the polysaccharide.

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STRUCTURE DETERMINATION OF MOLECULAR AND POLYMERIC CRYSTALS AND 2D-NANOMATERIALS FROM POWDER X-RAY DIFFRACTION DATA

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Information about crystal structure is highly important for many research areas in chemistry, biology, pharmacology etc. The single-crystal X-ray diffraction allows defining the structure with high accuracy. However, in many cases, it is impossible to obtain a single crystal with suitable quality. Therefore, determining the structure from powder X-ray diffraction (PXRD) data is an extremely significant and pressing issue.

In our work we demonstrated a high potential of PXRD for determination of different crystal structures of organic, organoelement, coordination compounds and layered nanomaterials.[1] Each stage of structure determination (indexing, solving and refining) from PXRD data involves certain difficulties and features, which will be discussed in the report.

In the last years we focused on characterization of active pharmaceutical ingridients[2,3] and applied Kurchatov source of synchrotron radiation for data collection. The almost complete absence of texture in synchrotron experiment with 2D detector increases the probability to find the right structure solution. Moreover, the capability of temperature variation makes it possible to study phase transitions in operando.[4]

Applying synchrotron irradiation, we successfully solved and refined the structure of several drug components, for example, ticagrelor (form III) contained two symmetrically independent flexible molecules (Fig. 1). This is one of the most complex structures defined from PXRD data.

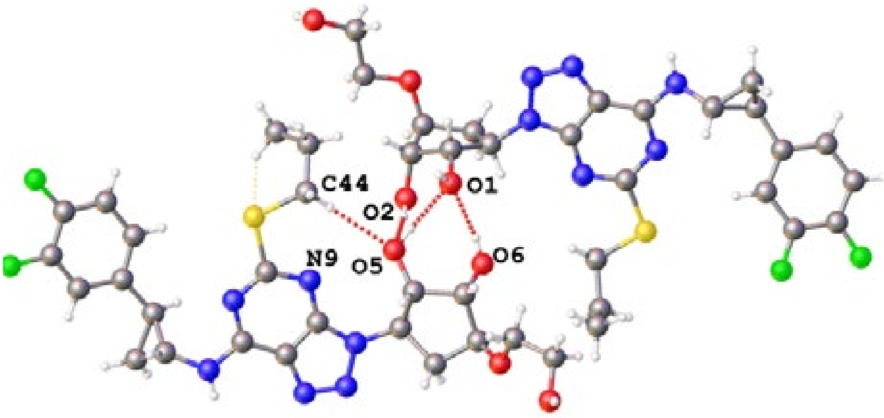

Figure 1. Crystal structure of ticagrelor (form III)

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SYNTHESIS OF 4-(TRIFLUOROMETHYL)-2*H*-CHROMENES, 4-(TRIFLUOROMETHYL)COUMARINS AND THEIR THIOANALOGS

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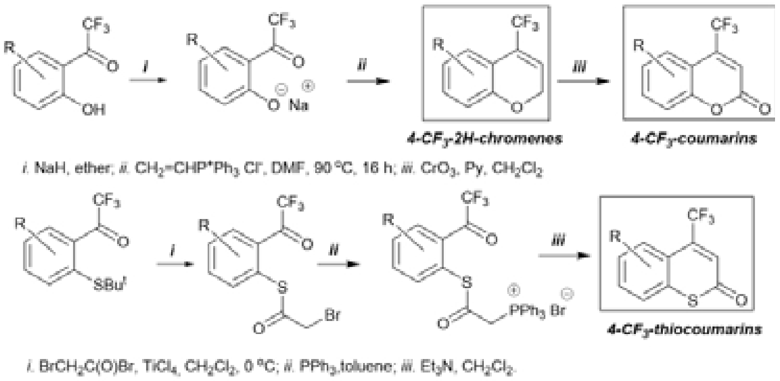
4-CF_3-coumarins (4-(trifluoromethyl)-2*H*-chromen-2-ones) have found a wide application in practice (fluorescent probes in various biological, analytical and photochemical studies) and in medical research. Coumarin-related 4-CF3-2*H*-chromenes are promising as potential drugs.

We have developed a new synthesis of substituted on the benzene ring 4-CF_3-2*H*-chromenes from substituted 2-(trifluoroacetyl)phenols and vinyltriphenylphosphonium chloride via the Schweizer reaction in moderate to excellent yields. The influence of the type and the position of aromatic ring substituents on yields of 4-CF_3-2*H*-chromenes have been investigated. It was found that 4-CF_3-2*H*-chromenes may serve as convenient precursors to 4-CF_3-coumarins.

We have also introduced a protocol that allows synthesis of previously unknown 4-CF_3-thiocoumarins starting from 1-(2-(tert-butylthio)phenyl)-2,2,2-trifluoroethanones. The construction of the thiopyranone core was carried out by the reaction of S-acylation of the latter with bromoacetyl bromide, followed by the formation of a phosphonium salt by treatment with triphenylphosphine and a subsequent intramolecular Wittig reaction (fig. 1).

The presented synthetic methods can lead to the expansion of practical use of these CF_3-containing heterocycles.



i. NaH, ether; *ii.* $CH_2=CHP^+Ph_3$ Cl^-, DMF, 90 °C, 16 h; *iii.* CrO_3, Py, CH_2Cl_2

i. $BrCH_2C(O)Br$, $TiCl_4$, CH_2Cl_2, 0 °C; *ii.* PPh_3,toluene; *iii.* Et_3N, CH_2Cl_2.

Figure 1. 4-CF_3-coumarins, 4-CF_3-2*H*-chromenes, and 4-CF3-thiocoumarins.

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CREATION OF PHOTOACTIVE SUPRAMOLECULAR STRUCTURES, DEVICES AND MACHINES

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Currently a new trend is formed in nanotechnology "bottom-up": supramolecular engineering of supramolecular devices and machines for various purposes. The most convenient means for controlling supramolecular devices and machines is light, which can be easily adjusted both in the wavelength and in the amount.

We propose a new unique class of polyfunctional photoactive compounds: unsaturated (polymethine) dyes functioning as photochromes, fluorophores and ionophores.[1] A large body of research has been performed for their synthesis, determination of their spatial structures, study of self-assembly features to give supramolecular systems, and also study of fluorescent, photochemical and complexing properties.

Resulting from the research, we elaborated for the first time universal supramolecular meccano, allowing one to accomplish building-up, with using a limited number of complementary compounds with participation of metal cations and hydrogen bonds, photoactive supramolecular structures of varied architecture with adjusted properties.[2] Within the same class of compounds one can construct in solution, solid and at the air-water interface new types of photoswitchable supramolecular devices, photocontrolled supramolecular machines (Fig. 1), photoactive monolayers and monocrystals susceptible to all of the key photoprocesses.

The high practical value of these studies deserves attention. They provide a new strategy for the design of materials for supramolecular and nanophotonics, which was demonstrated, first of all, by the creation of practically important sensor[3] and photochromic materials.[4-7]

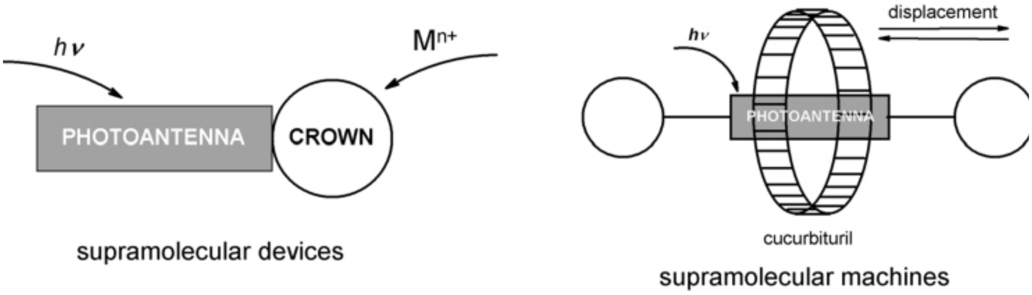

Figure 1. Photoactive supramolecular devices and machines

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INTERMOLECULAR BIMETALLIC COOPERATION IN Mn(I) CATALYZED DEHYDROGENATION OF AMINE-BORANES

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Controlled production of high purity hydrogen by transition metal-catalyzed dehydrogenation of amine-boranes under mild conditions represents a viable solution for chemical hydrogen storage. However, the most active systems for amine-boranes dehydrogenation based on 3d metal complexes are highly sensitive to air and moisture, require catalyst loadings of 0.5–10 mol% and/or additional activation by strong bases or UV light.[1]

We have recently discovered a highly efficient dimethylamine-borane dehydrogenation by bimolecular catalytic system generated in situ from air-stable Mn(I) bromide complex **1** bearing bis(NHC) ligand in presence of NaBPh4 as halide-ion abstractor and traces of base (Figure 1).[2] The combined spectroscopic, kinetic and theoretical data revealed that the activation of N–H and B–H bonds proceeds via unconventional intermolecular cooperative action of Mn(I) cationic and hydride complexes with formation of ternary non-covalent adducts $\mathbf{3\cdots2}^{+}$.[2] The system was found capable to dehydrogenate various amine-boranes with precise control of hydrogen liberation rate. The best performance was achieved for dimethylamine-borane at 0.1 mol% to 50 ppm catalyst charge affording TON up to 18200.

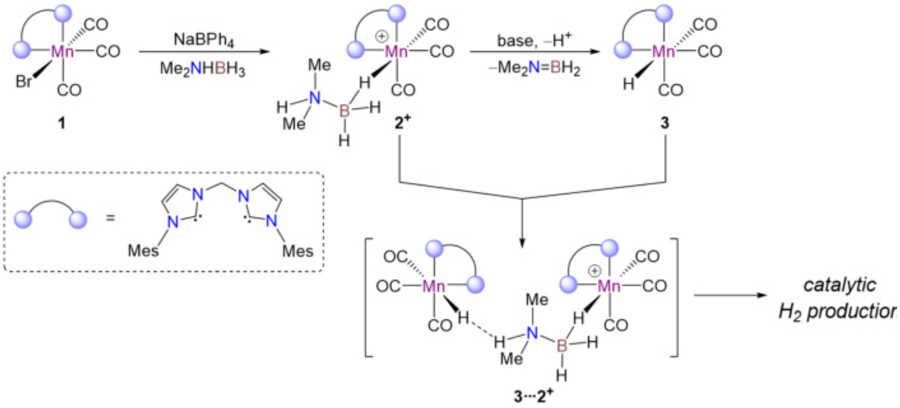

Figure 1. Formation of non-covalent adducts upon Me_2NHBH_3 dehydrogenation by **1**/$NaBPh_4$.

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ISOSTRUCTURAL EXCHANGE AS A TOOL FOR METAL-INVOLVING HALOGEN BOND INVESTIGATIONS

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Halogen bonding (XB) is actively investigated type of noncovalent interactions, which used as a tool for crystal engineering, supramolecular chemistry, and catalysis. In most cases, nonmetal atoms are XB acceptors, i.e. nucleophiles toward covalently bound halogens.

During the investigations[1] of the cocrystals of *trans*-[$PtCl_2(NCNR_2)_2$] (R_2 = Me_2, Et_2, $(CH_2)_4$, $(CH_2)_5$) with iodoform, the C–I···Pt (R_2 = Me_2) and C–I···(Cl–Pt) (R_2 = $(CH_2)_5$) metal-involving XBs were found, but only with molecules of especial shapes and substituents. Using the principle of isostructural exchange, a series of isostructural cocrystals[2] *trans*-[MX2($NCNMe_2)_2$]·$_2$CHX'$_3$ (X = Cl, Br; X' = Br, I; M = Pd, Pt) was obtained, and all of them also contain the C–X'···M (X' = Br, I; M = Pd, Pt) metal-involving XBs.

This principle was also used in the investigation of [M(S2CNEt2)2]·2FIB (M = Ni, Pd, Pt; FIB = *sym*-trifluorotriiodibenzene) with the C–I···M (M = Ni, Pd, Pt) metal-involving XBs,$_3$ [$(Ph_3P)_2N$][$AuCl_2$]·CHX'$_3$ (X'$_3$ = HCl_2, Cl_3, Br_3),[4] and

[(4-X'$C_6H_4)_2$I][$AuCl_4$] (X' = Cl, Br)[5] with the C–X'···Au (X' = Cl, Br) metal-involving XBs.

Thus, the metal-involving XBs can be "cought" in a series of isostructural crystals using halogen-halogen or metal-metal isostructural exchanges.

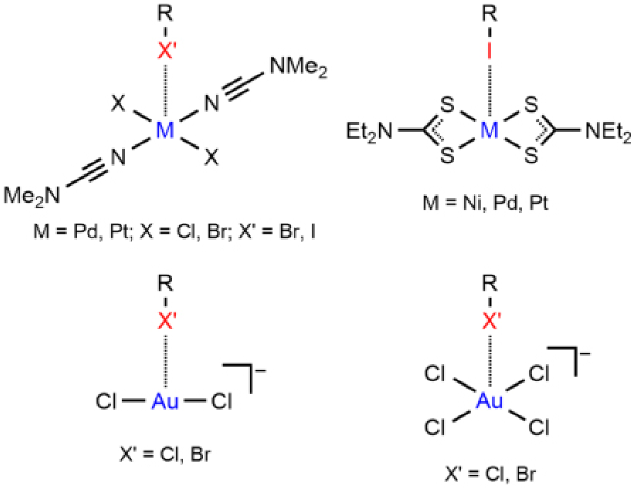

Figure 1. Metal-involving XBs in isostructural crystals

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PORPHYRIN-BASED MOFS ON 2D MATERIALS AS PHOTOCATALYSTS AND ARTIFICIAL ENZYMES

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Porphyrin-based MOFs integrate functionalized porphyrins as organic linkers bonded by metal ions or clusters into the continuously ordered structures. Because of versatile coordination properties and functional diversity of porphyrins, these hybrid structures are most useful for applications in chemically selective sensors, separation membranes and the solid catalysts. However, MOFs assembled by comparatively weak coordination bonds can undergo rapid decomposition in the chemically active environment.

The most potent strategy of stabilizing MOFs is their assembly on planar solid supports maintaining the integrity of the MOF structure in the reactive solutions. There are two different approaches to anchoring MOFs to solid surfaces creating SURMOFs: the intercalation, that is, the binding in the pores or interlayer space of solid particles, and the attachment to their outer surface. Both methods make it possible to integrate the functional properties of SURMOFs with those of supporting solids in a single hybrid structure.

Herein we show how to apply these approaches to create various functional MOF-based hybrids materials through the integration of 2D inorganic matrices such as graphene oxide, molybdenum disulfide and single-sheet rare earth metal hydroxides and zinc porphyrin complexes by using one and the same paddle-wheel coordination motive in the anchoring layer of metal clusters formed by zinc acetate. Due to the mutual stabilization of the components in the reaction media, the synergy in these materials may occur as symbimetic properties, manifesting themselves in the orchestrated conversion of the organic substrate in a manner, similar to that of the mutual-dependent digestive function of the biological symbionts.[1]

Non-covalent structuring the components at the nanoscale also allows effective transfer between organic and inorganic counterparts without contact quenching of emission of the porphyrin. These combinations make it possible to control the photocatalytic activity of the hybrid materials over a wide spectral range through an ambivalent[2] or multimodal switching[3] between different kinds of photoinduced charge separation or energy transfer by altering the excitation wavelength and red/ox conditions.

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MECHANOCHEMICAL MODIFICATION OF BIOLOGICALLY ACTIVE MOLECULES USING POLYMERIC SUBSTANCES FOR VETERINARY MEDICINE

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According to statistics from the World Health Organization, approximately 5 million deaths occur annually in the world as a result of infectious and parasitic diseases. Parasitic diseases affect more than 4.5 billion people in the world, with helminthiasis accounting for 99% of the total number of diseases of this type[1]. It should be borne in mind that in most cases, sources of helminth infection are domestic animals. Therefore, the treatment of animals is put at the forefront when solving health problems related to helminthiasis. For the prevention and treatment of helminthiasis in animals, substances from various classes of organic compounds (benzimidazoles, isoquinolines, salicylamides, etc.) are used, which are mostly poorly soluble substances with low bioavailability[2]. Therefore, the task of improving the solubility of such medicinal substances is relevant in order to create conditions for their further promotion and implementation in medical practice.

There are many different approaches to improve the solubility of drug substances[3], such as wet grinding to reduce the size of crystalline particles, emulsification in an oil-water system with a number of copolymers, co-crystallization, obtaining nanosuspensions, incorporation of drug molecules into dendrimer-like biopolymers, obtaining solid lipid nanoparticles, liquid-phase complexation with polymers, etc. Unfortunately, the above-mentioned processes are often associated with high solvent consumption, partial decomposition of the drug, and are quite complex. Unlike traditional liquid-phase methods for preparing dosage forms, the mechanochemical approach uses fairly simple operations and equipment. The preparation time of the dosage form is significantly reduced, a solvent is not required, solid and liquid waste is eliminated, etc.[4]

The paper will present the results of modification of a number of parasitic substances from various classes of organic compounds using polymeric and auxiliary substances, which made it possible to recommend a number of promising compositions for veterinary medicine, some of which are patented[5]. Work in this direction continues.

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PROMISING POLYMERS AND COMPOSITE MATERIALS FOR MEDICAL APPLICATIONS

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The Kabardino-Balkarian State University named after H.M. Berbekov

Modern medicine and its further development are associated with the emergence of a large number of products of a high molecular weight nature, allowing the creation of materials with predetermined properties.

Solving the problem of the use of polymers in medicine requires a two-way approach: biomedical and physical-chemical.

The report examines promising polymers and composite materials for medical purposes developed at the Center for Advanced Materials and Additive Technologies of KBSU.

It is shown that today high-performance polymers and composites based on them are the most promising materials for use as implants for reconstructive surgery. In combination with 3D and 4D printing, they significantly expand the possibilities for obtaining personalized implants [1,2].

Special attention is paid to the problems that arise during the osseointegration of implants based on high-performance polymers and methods of their solution, regulation of mechanical properties to obtain high-quality products similar in properties to human bone tissue. Examples of new approaches to the modification of polymers and composites to improve osteointegration are given.

Examples of successful application of printed products made of high-performance polymers and composites in medicine are demonstrated.

It is noted that the use of high-performance polymers and composites in 3D printing is limited by a number of complex problems, the solution of which requires a certain scientific and technical reserve.

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4D-PRINTING OF MECHANICALLY DURABLE HIGH-TEMPERATURE SHAPE MEMORY MATERIALS BASED ON POLYBENZIMIDAZOLE

Kholkhoev B.Ch.,[a] **Bardakova K.N.,**[b,c] **Matveev Z.A.,**[a] **Epifanov E.O.,**[b] **Efremov Y.M.,**[c] **Timashev P.S.,**[c] **Burdukovskii V.F.** [a]

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4D printing of high-temperature shape memory polymers (SMPs) has attracted tremendous interest because of its potential application in smart devices for the aerospace field. The challenge of developing shape memory polymers (SMPs) with high thermal and mechanical characteristics as well as radiation resistance remains pertinent.

In this work we developed UV-curable resins based on rigid thermally stable poly-2,2'-(*p*-oxydiphenylene)-5,5'-dibenzimidazole (OPBI), photosensitive solvent (N,N-dimethylacrylamide), and crosslinker (bisphenol A ethoxylate diacrylate or *tris*[2-(acryloyloxy)ethyl] isocyanurate). 4D-printed high-performance SMPs were obtained through UV-thermal dual-curing process (Figure 1), which resulted in materials with high glass transition temperature (155–185 °C) and increased tensile strength (115–144 MPa). The combination of hard segments from OPBI and the crosslinkers, as well as soft segments from N,N-dimethylacrylamide, results in excellent shape memory performance of the materials (average shape fixity and shape recovery ratios both exceed 94%).

Besides, we found that 4D-printed OPBI-based SMPs are resistant to γ-radiation with doses up to 10^6 Gy. After γ-irradiation, the materials maintain high tensile strengths (up to 124 MPa), glass transition temperatures (up to 179 °C) and shape memory behavior. Thus, these new 4D-printed OPBI-based SMPs offer great potential for the aerospace industry.

Figure 1. Digital models and 3D-objects fabricated from developed UV-curable resins.

Acknowledgements
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ELECTROCATALYTIC CARBON DIOXIDE REDUCTION AND HYDROGEN EVOLUTION REACTION USING A COMBINED APPROACH

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In the work discuss the targeted design of efficient catalysts for carbon dioxide reduction (CO_2RR) and the hydrogen evolution reaction (HER). The emphasis will be on strategies that improve the electrocatalytic efficiency and selectivity of these crucial reactions.

This work presents three primary strategies for developing effective electrocatalysts for CO_2RR. First, we will highlight the incorporation of specific functional groups into catalyst structures. These functional groups are carefully selected to enhance the adsorption and activation of CO_2 molecules, thereby facilitating their reduction. Second, we will discuss the creation of specialized surfaces from solutions during the electrochemical reduction process. This method involves engineering the catalyst surfaces at the molecular level to optimize their interaction with CO_2 molecules. The modifications aim to increase the number of active sites and improve electron transfer characteristics, which are essential for the efficiency of CO_2 reduction. Third, we will demonstrate catalytic systems that, due to their unique geometric configurations, enable selective CO_2 reduction. The design of these catalysts focuses on shaping the spatial arrangement of atoms to create selective pathways for CO_2 conversion, minimizing unwanted reactions and enhancing overall catalytic performance.

Additionally, we will explore the synergistic effects of combining catalysts for CO_2RR and HER. By designing catalysts that can effectively perform both reactions, we aim to develop integrated systems capable of simultaneously reducing CO_2 and producing hydrogen, a valuable clean energy carrier. This dual functionality not only enhances the practicality of such systems in sustainable energy applications but also increases the overall energy efficiency of the process.

Acknowledgements
This work was supported by the grant of the Russian Science Foundation, №22-73-10203.

METAL (ACYCLIC DIAMINOCARBENE) COMPLEXES EXHIBIT NANOMOLAR ANTIPROLIFERATIVE ACTIVITY AGAINST CANCER CELLS

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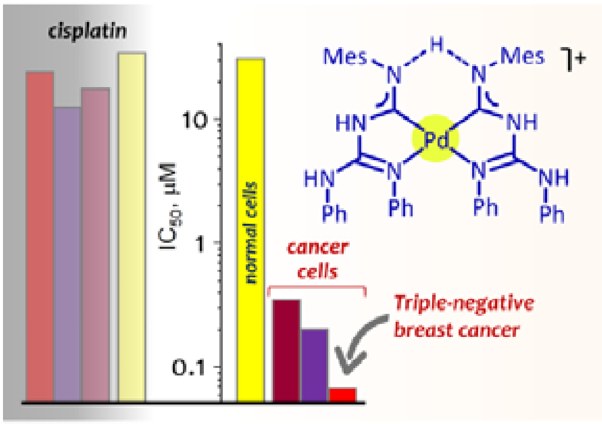
Cancer remains a leading cause of mortality worldwide. Approximately half of the cancer patients are treated with chemotherapy, and most of the protocols include the use of platinum(II)-based chemotherapeutic agents, the easy drug resistance and side effects limit the clinical effect and practical application of platinum chemotherapy. As a result, the discovery and development of new anticancer agents with novel chemical structures and mechanisms to address the unmet demands is of prime interest.

In this context, transition metal complexes with acyclic diaminocarbene (ADC) ligands offer significant advantages for biological applications.[1] The electrophilicity and Bronsted acidity of NH hydrogens, as well as the presence of a lone pair of electrons on the nitrogen atoms of the deprotonated ADC species, ensure the involvement of the N(H) groups in intra- and intermolecular hydrogen bonds with biomolecules. The flexibility of the open structure of acyclic diaminocarbene ligands not only leads to different metal-carbene interactions, but also results in the adaptation to biological targets for efficient binding.

This talk will report the discovery of a novel classes of hydrolytically stable PdII and PtII species with C,N-chelated acyclic diaminocarbene ligands, which exhibit excellent antiproliferative activity for cancer cells in vitro (IC_{50} up to 0.07 μM) together with high selectivity for triple-negative breast cancer.[2] Our lead drug candidate surpasses cisplatin by 300 times in vitro and exhibits superior efficacy in reducing the growth of aggressive MDA-MB-231 xenograft tumors in mice. The critical role of interference with metabolic processes and redox homeostasis in achieving excellent selectivity for cancer cells is demonstrated.



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Acknowledgements
The authors thank Saint Petersburg University for support of this investigation.

HIGHLY ACCEPTING HALOGENACETYLENES – NEW VALUABLE REAGENTS IN ORGANIC SYNTHESIS

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Although a trifluoroacetyl group belongs to the strongest mesomeric acceptors and is extremely promising for further transformation of the cycloadducts, only very few examples of the Diels-Alder reactions of trifluoroacetylacetylenes have been reported up to date. Herein, we describe the simple preparation of 1-trifluoroacetyl-2-halogenoacetylenes and some sorts of their cycloaddition reactions. The unsaturated trifluoromethyl ketones delivering by these reactions appeared to be the useful starting materials for the preparations of complex fluorinated fused heterocyclic compounds.

The first thing we disclosed, the available bis(trimethylstannyl)acetylene **1** easily reacts with trifluoroacetic anhydride to afford the monoacylated alkyne **2**, which in turn can be quantitavely halogenated to form 1-trifluoroacetyl-2-halogen acetylenes **3a-c**. The compounds **2a-b** exhibited the properties of the strongest dienophiles in the Diels-Alder reactions. Furthermore, they entered the unusual orbitally forbidden [2+2]-cycloadditions with simple alkenes under very mild conditions (Figure 1).[1]

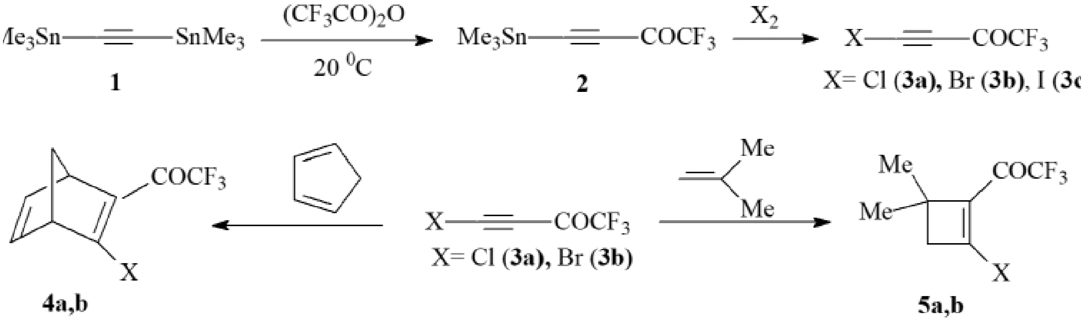

Figure 1. Cycloaddion reactions of 1-1-trifluoroacetyl-2-halogen acetylenes

The cycloadducts **4, 5** thus obtained were found to be the valuable versatile reagents for the preparation of a variety of fluorinated heterocycles fused with the strained carbocyclic moieties.[2] For example, they smoothly react with ammonia to give the corresponding enaminoketones **6**, which serve as a source of trifluoromethylated pyridines **7** (Figure 2).[3]

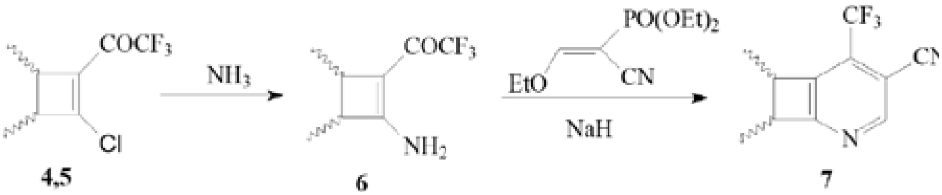

Figure 2. Heterocyclization reactions of trifluoromethyl enaminoketones

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POLY(VINYL ALCOHOL) CRYOGELS FORMED ON THE BASIS OF PVA/DMSO-SOLUTIONS AS NOVEL ADVANCED TOOLS FOR RESTORATIVE CLEANING OF THE WORKS OF ART

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Poly(vinyl alcohol) cryogels are the noncovalent macroporous gels formed as a result of freeze-thaw processing of concentrated PVA solutions. PVA cryogels are widely used as biomedical materials due to their mechanical durability, biocompatibility and also viscoelastic properties similar to those of soft biological tissues. PVA cryogels in the forms of dialysis membranes, wound dressings, artificial skin, cardiovascular devices, drug delivery and spine disc replacements have been applied as functional materials in clinical practice.

Poly(vinyl alcohol) cryogels can be fabricated by “freezing-thawing processing” of water or DMSO solutions of the polymer [1,2]. In the present study cryogels were prepared originating from the DMSO solutions of PVA both with and without low-molecular additives. Rheological and thermal properties of the resultant cryogels, as well as their macroporous morphology have been revaluated.

It was shown that thus prepared PVA/DMSO and PVA/DMSO/additive cryogels turned out to be effective for controlled and non-invasive cleaning, as well as for deletion of contaminants and unwanted layers from delicate surfaces of works of art.

Figure 1. Case study on real samples: removing of unwanted layers from an icon by the DMSO/PVA cryogels (left - before and right – after cleaning).

Restoration specialists consider such gel materials developed at INEOS RAS as highly effective “tools” for controlled and non-invasive cleaning of the objects of cultural heritage.

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MICELLAR FORMS OF HYALURONIC ACID LOADED WITH *CLOSO*-DECABORATE ANION DERIVATIVES

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According to the World Health Organization, the prevalence of cancer and, as a result, mortality from it are steadily increasing. In 2019 cancer was the leading or second leading cause of death for patients under 70 years of age in 112 countries[1]. The development of drugs and methods for treating the malignant tumors is an important and still unsolved scientific problem. One of the promising methods for treating malignant tumors is boron neutron capture therapy (BNCT)[2]. This method involves the selective destruction of tumor cells by accumulating the stable isotope boron-10 in them and subsequent irradiation with epithermal neutrons."

This paper presents a method for obtaining micellar forms of hydrophobized hyaluronic acid (HA-C18) loaded with the imidazolium salts of sulfonium derivatives of the closo-decaborate anion with alkyl *exo*-polyhedral substituents BMIM[$B_{10}H_9SR_2$] (BMIM is 1-butyl-3-methyl imidazolium, R = C_4H_9, C_8H_{17}, $C_{12}H_{25}$, $C_{18}H_{37}$). Micellar structures of HA-C18/CDB were obtained by ultrasonic homogenization followed by evaporation of the solvent until a thin film was formed (thin film method).

The highest loading of closo-decaborate anion derivatives was achieved for BMIM[$B_{10}H_9S(C_8H_{17})_2$]/HA-C18 (87.4%) and BMIM$B_{10}H_9S(C_4H_9)_2$/HA-C18 (77.1%) micelles. According to the results of dynamic light scattering, these micellar structures have a size in the range of 180 to 250 nm, a monomodal distribution by volume, and a narrow range of polydispersity (<0.2).

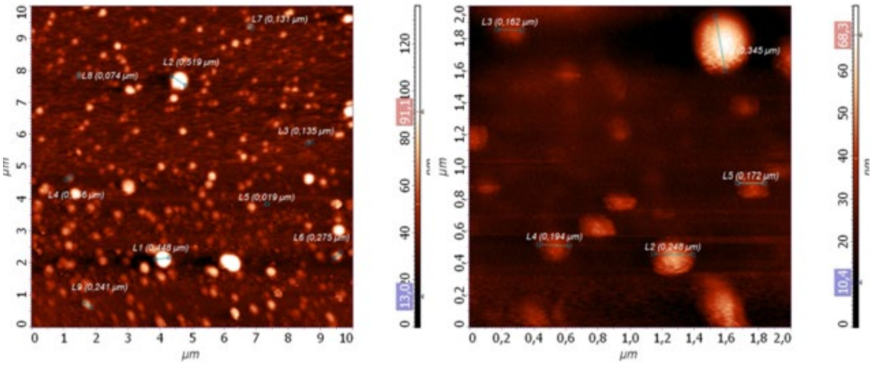

Figure 1. AFM visualization of micellar forms of BMIM[$B_{10}H_9S(C_8H_{17})_2$]/HA-C18 with indication of the sizes of micellar structures

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LUMINESCENCE OF HEAVY DIMERIC ISOCYANIDES

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Compounds with multiple bonds between heavier main group elements attract much attention of organometallic and inorganic chemists due to their unique physical and chemical properties that are strikingly different to those of lighter counterparts.[1] For instance, phosphaalkynes R–C≡P, analogues of nitriles, that remained undiscovered until 1981 and are now widely used as precursors of organophosphorus compounds.[2] Isocyanides, another a well-studied class of organic compounds, are commercially available as reagents for multicomponent reactions and as ligands in coordination chemistry.[3] Meanwhile, no heavier analog of isocyanides R–N≡E (E = Si, Sn, Pb) were isolated so far.

Our approach to the preparation of heavy isocyanide analogues is to use a series of anilines with bulky phenyl substituents ^{H,Me}ArNH2, ^{Me,Me}ArNH$_2$, ^{tBu,Me}ArNH$_2$ (^{H,Me}Ar = 2,6-(Ph)2-C$_6$H$_4$CH$_3$, ^{Me,Me}ArNH$_2$ = 2,6-(p-tol)2-C$_6$H$_4$CH$_3$, ^{tBu,Me}ArNH$_2$ = 2,6-(p-tBuC$_6$H$_4$)$_2$ -C$_6$H$_4$CH$_3$). The reaction between these anilines and M(btsa)$_2$ (M = Sn, Pb) gives imides [ArNM]$_2$, which still remain dimers. These compounds are reducing agents, and their interaction with iodine or benzoyl peroxide leads to the oxidation of only one metal atom. Also, tin imides [ArNSn]$_2$ exhibit a rare phenomenon – photoluminescence in solution and in the solid state, the parameters of which exceed the known tin compounds (Figure 1).[4]

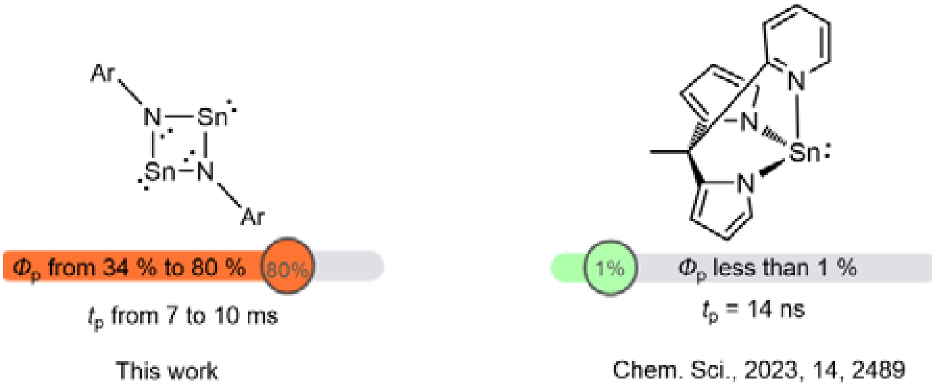

Figure 1. Comparison of luminescence parameters [ArNSn]$_2$ with a known Sn(II) compound.

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MODELING OF GEOMETRIES, ATOMIC CHARGES, AND LMCT SPECTRA OF GROUP IV METALLOCENES

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Modeling of electronic-structural properties of transition-metal compounds is a sophisticated and often unsolvable problem. Group IV metallocenes acquired particular importance in catalytic polymerization of unsaturated hydrocarbons, activation of small molecules, as antitumor drugs, and so on. This class of organometallics possesses the rarest and least studied ligand-to-metal charge transfer (LMCT) phosphorescent states.[1-5] An extensive systematic series of different methods (HF, DFT) was applied in our on-going research to establish the best methodology for studying d0 organometallics of this type.

Recently, we obtained and systematically analyzed a large set of computing (HF, DFT) data using the example of titanocene dicarboranyl $Ti(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ and demonstrated good agreement between most of the simulated structural data and crystallographic data.6 The photophysical and structural characteristics of d^0 metallocene enantiomers were modeled using the example of a triad of structurally complex metallocenes with carboranyl σ-ligands having CMe2< bridges between the π- and σ-ligands: $M(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ (M = Ti, Zr, Hf). Recently, using the example of $Hf(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$, the changes in the structure and electric dipole moment of the metal complex during the transition from the ground state to the ^{1}LMCT were estimated for the first time.[7,8] Much scarce are the methods capable of modeling LMCT excitations with acceptable accuracy. Noteworsy, the current state of TDDFT methods is such that it is impossible to estimate the computational errors and reliability of the methods without comparing the results with other higher-level theoretical calculations and, where possible, with experimental data. In the present work, the state of art of modeling of principle characteristics (molecular architecture, orbital and electronic properties, electronic absorption and excitation spectra) will be overviewed for important organometallic family – group IV metallocenes.

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METALLACYCLIC TRIANGLE GALLIUM CATECHOLATE WITH BRIDGING ANION-RADICAL LIGANDS OF TETRAZINE TYPE

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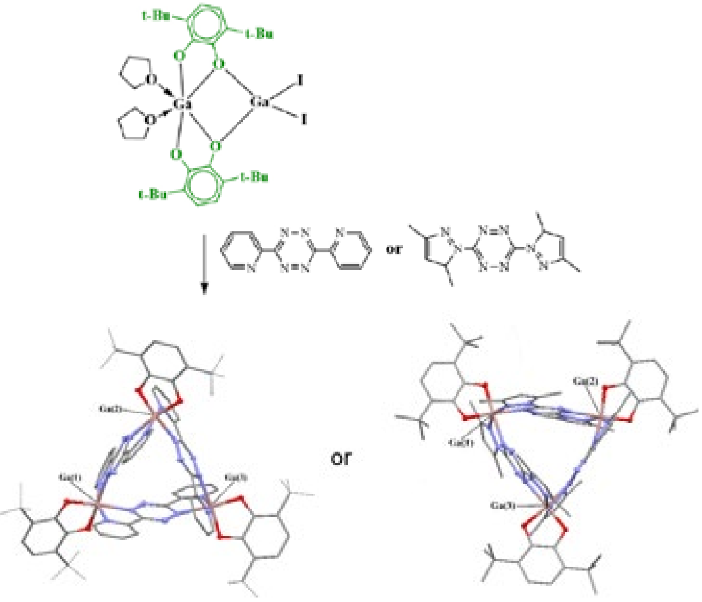
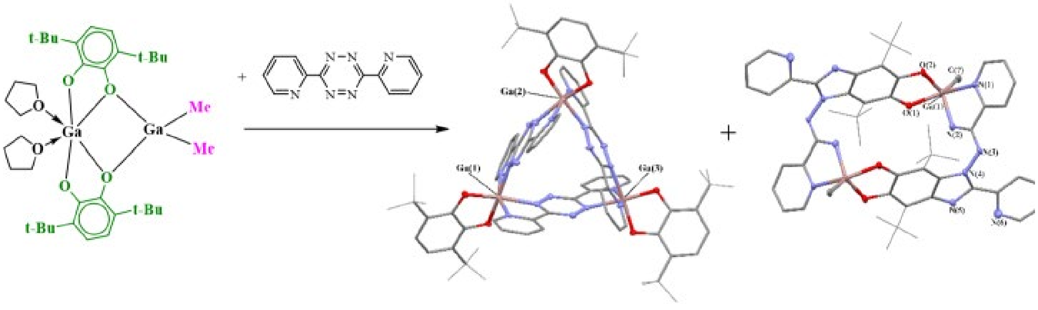
New metallocyclic gallium derivatives containing bridged N-containing ligands in the radical anion form were obtained by reacting gallium catecholate with neutral substituted tetrazines.



In the case of the interaction of methyl gallium catecholate with pyridine- substituted tetrazine, in addition to the cyclic trimeric derivative, it is possible to detect a dimeric derivative with an open form of the tetrazine-type ligand.



Acknowledgements
This work was supported by the Russian Scientific Foundation (Grant № 22-13-00351).

TIN(IV) AND VANADIUM(V) COMPLEXES BASED ON REDOX-ACTIVE TETRADENTATE ONNO LIGAND IN DIFFERENT OXIDATION AND PROTONATION STATES

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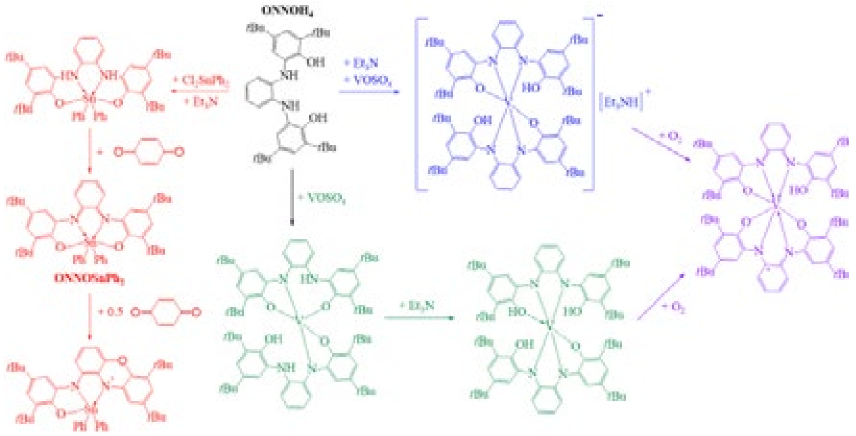
The tetradentate redox-active ONNO ligand, namely N,N’-bis(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-1,2-phenylenediamine, is able to undergo stepwise transformations in the coordination sphere of tin(IV) and vanadium(V). Depending on the chosen conditions, it is possible to obtain complexes containing the ONNO ligand in different degrees of oxidation and deprotonation (Scheme 1). The synthesized compounds have excellent optical and electrochemical properties. In particular, the UV-vis-NIR spectrum of the ONNOSnPh$_2$ complex bearing the ONNO ligand in the dianionic state contains an intense absorption band in the NIR region corresponding to intraligand charge transfer (ILCT) (Figure 1). Moreover, this compound undergoes two successive reversible one-electron oxidations and two successive reversible one-electron reductions, which do not change even after 100 measurement cycles (Figure 1).



Scheme 1. Stepwise transformation of the ONNO ligand in the coordination sphere of Sn(IV) and V(V)

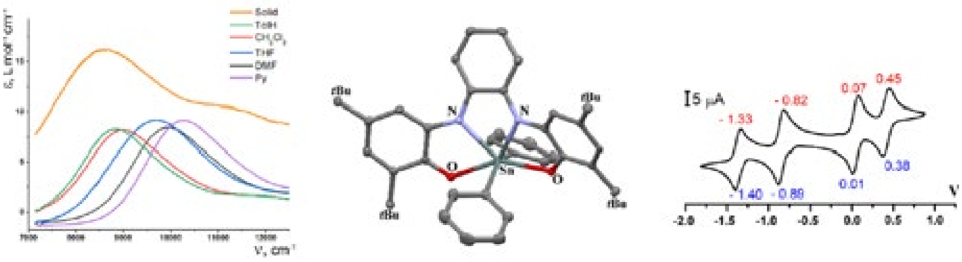


Figure 1. Molecular structure, cyclic voltammogram and electronic absorption spectra of solutions of ONNOSnPh$_2$ complex

Acknowledgements
The study was financially supported by the Russian Science Foundation (Grant No. 24-23-00268)

RING-OPENING METATHESIS POLYMERIZATION OF 5-*N*-ALKYL-2-NORBORNENE IN THE PRESENTS OF 1-HEXENE, ETHYLENE AND DIMETHYLMALEATE. HYDROGENATION OF METATHESIS PRODUCTS

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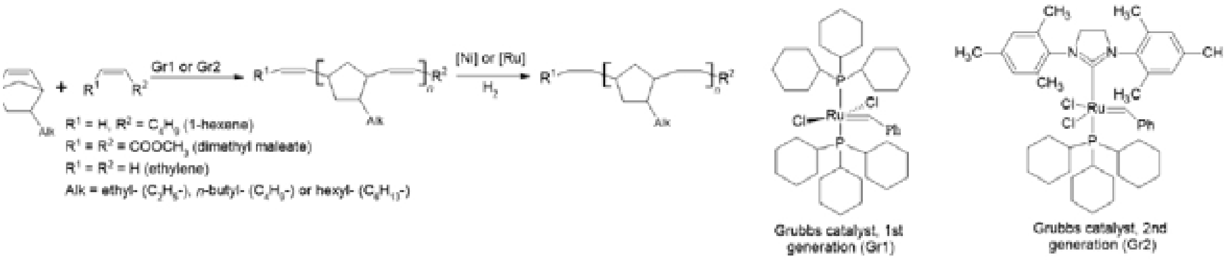
α-Olefin oligomers are used as lubricants, but their synthesis can be complicated by high requirements for the polymerization purity of monomers. Oligomers of alkyl substituted norbornenes are compounds similar in the structure to olefins. They are easily obtained by the Diels-Alder reaction and can be involved in ROMP on the commercially available first (Gr1) and second (G2) generation Grubbs catalysts. In addition, these catalysts are capable of hydrogenating the double bonds of the resulting metathesis products.[1] However, no detailed study of the tandem synthesis of low molecular weight products based on alkyl-substituted norbornenes by metathesis oligomerization - hydrogenation has been reported. There are also no data on the effect of the structure of the corresponding metathesis and hydrogenated oligomers on their thermal, rheological and other properties. Therefore, the aim of this work was to study the possibility of obtaining oligomers of 5-ethyl-2-norbornene, 5-*n*-butyl-2-norbornene and 5-*n*-hexyl-2-norbornene using Gr1 and Gr2 in the presence of chain transfer agents (1-hexene, ethylene and dimethyl maleate), as well as to investigate the catalytic hydrogenation of obtained products over Ni and Ru catalysts. The metathesis polymerization of norbornene derivatives was carried out in THF medium at different ratios of the initial reagents according to Scheme 1. The obtained products were hydrogenated without isolation from the reaction mixtures. The initial and hydrogenated products were separated into fractions by molecular weight using preparative GPC. The product structure was confirmed by ^{1}H and ^{13}C NMR, ^{1}H-^{13}C HSQC NMR spectroscopy. The metathesis and hydrogenated products were characterized by GPC, DSC and TGA analysis, and their rheological properties were investigated. The influence of the synthesis conditions on the properties of the metathesis and hydrogenated products, as well as the relationship between their structure and thermal and rheological properties, were demonstrated.



Scheme 1. Synthesis of oligomers based on 5-ethyl-2-norbornene, 5-*n*-butyl-2-norbornene and 5-*n*-hexyl-2-norbornene in the presence of 1-hexene, ethylene and dimethyl maleate by ROMP polymerization followed by the hydrogenation.

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Acknowledgements
This work was supported by the Russian Science Foundation (project No 23-73-00126).

REDOX DIVERSITY IN TITANIUM COMPLEXES WITH ACENAPHTHENE-1,2-DIIMINE

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A combination of a noninnocent ligand of reasonable π-acceptor strength with a redox-active metal is a fundamental factor for the design of complexes with fine-tunable electronic properties. The metathesis reactions of titanium(IV) chloride with sodium salts of dpp-Bian yield well-defined compounds **1** and **2**, where dpp-bian = 1,2-bis[(2,6-^{i}Pr$_2$C$_6$H$_3$)imino]acenaphthene.1 Compound 1 exhibits temperature-dependent behavior: it is diamagnetic at temperatures below 200 K but becomes paramagnetic upon heating. In contrast, in complex **2**, the unpaired electron spin density is predominantly localized on the titanium center in a whole temperature region examined. Substitution of the electron-withdrawing chlorido ligands in **2** by electron-donor alkoxy groups (compounds **3** and **4**) results in a stepwise shift of spin density from the metal to the N-ligand supporting its reduction up to a radical anion. In this context, the reducing capability of the [Ti(OR)$_3$] moiety was sufficient for bound dpp-Bian to accept two electrons, followed by the elimination of the alkoxide moiety. Although there is evident disparity in spin distribution investigated with spectroscopic studies, titanium complexes **2–4** show no apparent differences in the geometric parameters of the dpp-Bian, regardless of the nature of the auxiliary ligands. Even so, this straightforward approach to the low-valent titanium synthons, along with the benefits of a noninnocent ligand, appears to be useful for design of homogeneous redox catalysts based on early transition metals.[2]

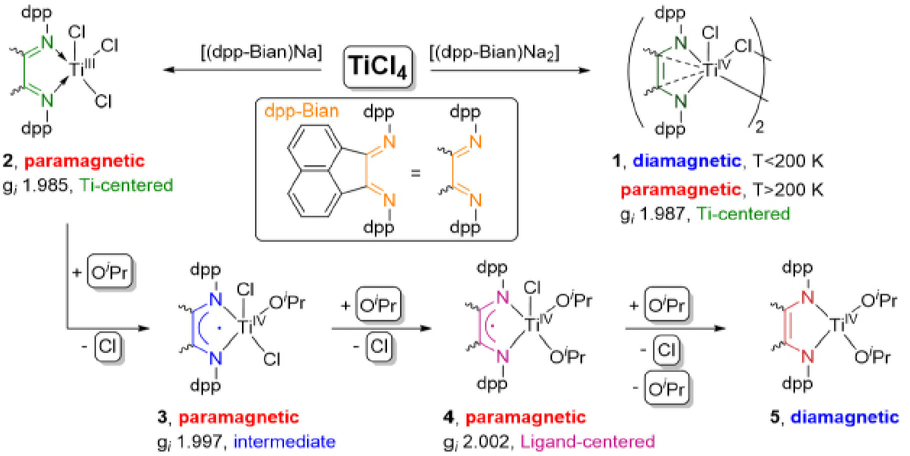

Figure 1. Titanium chlorido/alkoxychlorido/alkoxido complexes with dpp-Bian.

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DESIGN OF ANTIPROLIFERATIVE RUTHENIUM COMPOUNDS

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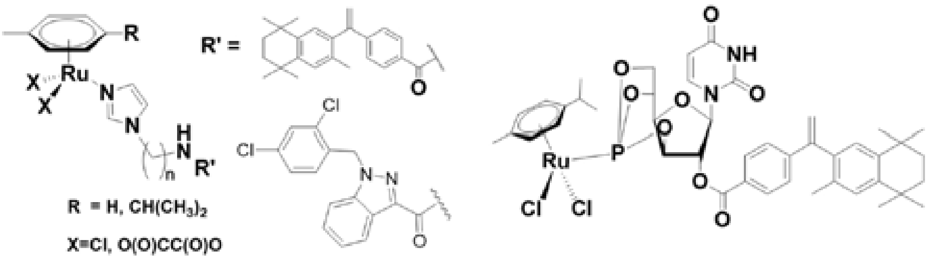
The search for new metal-based anticancer compounds has traditionally focused on platinum(II) compounds. However, in recent years, there has been a shift in interest towards the development of non-classical anticancer drugs, and Pt(IV) and ruthenium-based compounds have emerged as the most actively studied candidates. We have proposed a novel approach for the development of innovative anticancer drugs that combines two pharmacophores into one molecule.[1,2] This molecule contains Ru(III) complexes, or Ru(II) organometallic compounds, as well as a targeted ligand that can interfere with the cellular processes specific to malignant cells, or increase the protection of normal cells from the toxic effects of non-biogenic metals.

The new compounds exhibit excellent, and sometimes very specific activity against cancer cell lines in in vitro studies. The mechanism of action of these compounds has been investigated, and leading compounds with high selectivity towards malignant tumors have been identified.



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COMPLEXES OF 3d AND 3d-4f METAL CARBOXYLATES WITH N-HETEROCYCLIC CARBENES AS ANCILLARY LIGANDS

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N-heterocyclic carbenes (NHC) are very important ligands in modern coordination and organometallic chemistry. The most of publications describe catalytic activity of NHC complexes whereas other functional properties often remain in shadow. Linear NHC containing complexes of Co(II) recently were found to be single molecule magnets (SMMs) with exclusive efficiency. Despite this fact systematic use of NHC ligands for design of new magnetoactive compounds is not common. On the other hand, carboxylate ligands are uniquely suited for molecular magnetism, and they have been widely used for design of new SMMs. At the same time, carboxylate complexes with NHCs as ancillary ligands are reported in a limited number of publications.

Recently we have synthesized families of 3d and 3d-4f carboxylates supported by N-heterocyclic carbenes (Fig. 1). The features of synthetic methodology,[1–3] solid state and solution structure[4–7] as well as magnetic properties (especially in alternating current regime)[8] of selected complexes will be presented and discussed in detail.

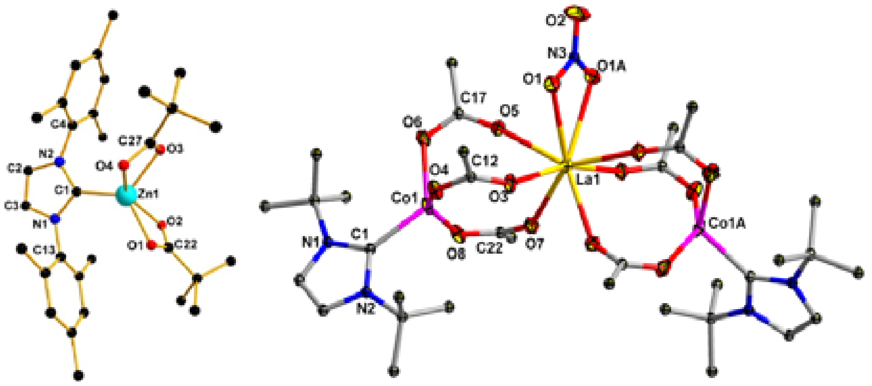

Figure 1. Examples of 3d and 3d-4f metal carboxylates supported by NHC ligands

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CATALYTIC REDUCTIVE ADDITION PROCESSES IN THE PRESENCE OF SYNGAS AS A REDUCTUNT

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Reductive addition processes are powerful instruments in organic chemistry to forge C-C and C-X bonds. One of the most widely applied catalytic hydrogenation often demonstrates low selectivity when simple and available catalysts like Pd/C are used. The traditional approach to provide higher selectivity in catalytic reductive processes involves shift to more complex albeit more expensive organometallic catalysts. However, in this work we found that application of syngas, commercially available in bulk amounts gas mixture, allows reaching high efficiency and selectivity in reductive addition reactions on commercially available catalysts.

Synthesis of amines, nitriles and esters was carried out using the developed approach. Structurally different reagents including aliphatic and aromatic aldehydes and ketones, primary and secondary amines, various carboxylic acids participated in the catalytic reductive addition reactions (Figure 1)[1]. A number of potentially reducible functional groups including OBn, CN, C(O)R, COOR, heterocycles remained intact under reaction conditions. The processes can proceed both under harsh and mild conditions. The former allowed us to decrease significantly the catalyst loading while the letter was applied for preparation of compounds with more sensitive moieties such as furan- and amino-acid derivatives[2].

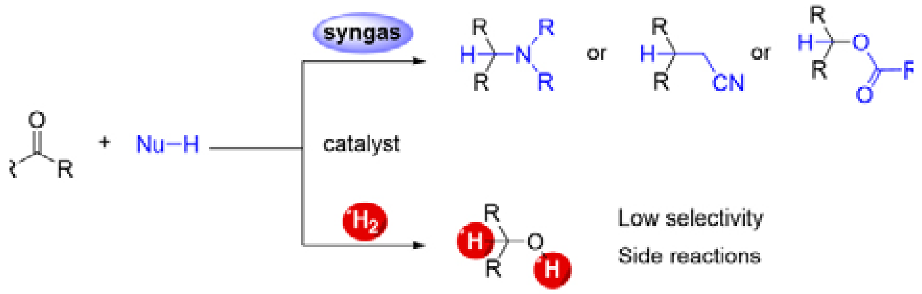

Figure 1. Reductive addition of nucleophiles to carbonyl compounds in the presence of syngas as a reductant

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THE EFFECT OF THE ADDITION OF SECONDARY POLYMER RAW MATERIALS ON THE STRUCTURE AND PROPERTIES OF THE POLYMER MIXTURE

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Today, the volume of plastic waste generation in the world exceeds 300 million tons per year. Of these, most of them are polyethylene (about 19% are LDPE, 13% are HDPE), about 18% are polypropylene, 11% are PET packaging waste, 14% are various fibers (of which most are polyester, PET).

The involvement of polymer waste in recycling is one of the important solutions to environmental safety issues and contributes to the development of a waste management culture. Special attention is paid to the creation of new materials using secondary resources.

Secondary polymers differ in their properties from the original polymers. For example, acidified polyethylene has a higher melting point and degree of crystallinity, which may be due to an improvement in the crystalline structure of the polymer. [1]

In this study, the effect of the additive of secondary polyethylene produced in industry on the change in the structure and properties of the polyethylene-polylactide mixture is considered.

With the addition of acidified polyethylene up to 30 wt.% in the PE/PLA mixture, the melting point of polyethylene decreases by an average of 3°C. The degree of crystallinity of polyethylene decreases by 5%, and the degree of crystallinity of PLA, on the contrary, increases. PLA and polyethylene are crystallizing polymers, which complicates the nature of their interaction at the macromolecule level. Apparently, the crystallization process of PLA accelerates in the presence of a more flexible PE chain when the mobility of macromolecules increases.

The analysis of the structure showed that at a content of 30 wt. % PLA phase separation is clearly manifested, the phase distribution is close to uniform and there are no obvious defects. It should be noted that there are no pronounced spherulites in the structure of pure PLA, which is typical for samples obtained from the melt. [2]

The addition of secondary raw materials affects the interfacial interactions in mixtures, which can lead to susceptibility to environmental factors. The processes of oxidation and hydrolysis in such systems are accelerated. [3]

Thus, when developing new compositions of polymer mixtures with the addition of secondary raw materials, it is important to take into account an integrated approach, taking into account the long-term operation and processing of the material.

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THE INFLUENCE OF POLYVALENT METAL PROMOTER ON THE Pt DISPERSION AND PERFORMANCE OF Pt/MFI PROPANE DEHYDROGENATION CATALYSTS

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Propylene is used as a feedstock for polymer and as an intermediate product for various chemicals. The production of propylene through propane dehydrogenation (PDH) reaches millions of tons annually and is steadily increasing. The primary challenge with Pt-based PDH catalysts is their relatively low stability due to the harsh reaction conditions.[1]

This work focused on the role of polyvalent metal M as a promoter on Pt dispersion and catalytic performance of MFI zeolite derived catalysts in PDH. The catalysts were prepared in two stages. First, the zeolites were neutralized with Na^+ cations using the ICW method[2] and then co-impregnated with a mixture of H_2PtCl_6 and a promoter salt.

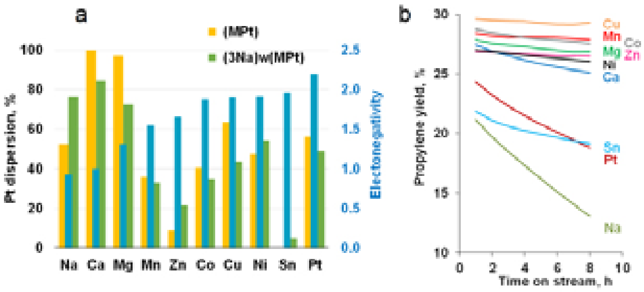

Figure 1. Effect of electronegativity of promoter on a) Pt dispersion; b) catalytic performance. PDH reaction conditions: 540°C; 0.1 MPa; WHSV 28 h^{-1}

High Pt dispersion (CO chemisorption) and lower stability of catalysts are characteristic of alkali and alkaline earth promoters. Transition metals exhibit lower dispersion values but higher activity and stability (Figure 1). Zn, Mn, and Cu were the best promoters in terms of productivity, while Zn and Sn showed the highest propylene selectivity.

The (0.5Zn0.5Pt)/MFI ICW catalyst demonstrated higher specific activity and stability compared to the best Zn-promoted Pt/MFI catalysts known in the literature. The specific activity of 1.91 s^{-1} with deactivation constant of 0.0016 h^{-1} were reached while maintaining a propylene selectivity of 98-99% in 35-h reaction run.

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CARBONYL COMPOUNDS OF FERROCENE IN THE SYNTHESIS OF BIOLOGICALLY ACTIVE HETEROCYCLES

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More than 70 years have passed since the discovery of ferrocene in 1951 by T. Kealy and P. L. Pauson. During this time, interest in this sandwich compound has not diminished, but on the contrary, we have seen an exponential growth in the number of publications. The use of ferrocene-containing compounds for medical purposes has long been considered a promising method for developing and modifying known drugs, due to the unique properties of this wonderful molecule. Ferrocene promotes the distribution of the active substance in the body and the passage of hydrophobic cell membranes. In addition, the different lipophilicity of the reduced (ferrocene) and oxidized (ferricinium salts) forms with the ability to easily and reversibly redox transition, low toxicity for humans and animals, sufficient stability of the complex in aqueous environments and the presence of a large number of simple derivatives ready for further transformation make the bioorganic chemistry of ferrocene a unique platform for solving a variety of problems.

Currently, a huge number of studies are being conducted to study the biological activity of ferrocene derivatives.[1-5] Since many heterocyclic compounds possess biological activity, it is not surprising that the synthesis of ferrocene-containing heterocycles and a comprehensive study of the properties of such conjugates remains a relevant area of research to this day. In this study, we propose approaches to the synthesis and biological activity of heterocyclic ferrocene derivatives from available carbonyl precursors.

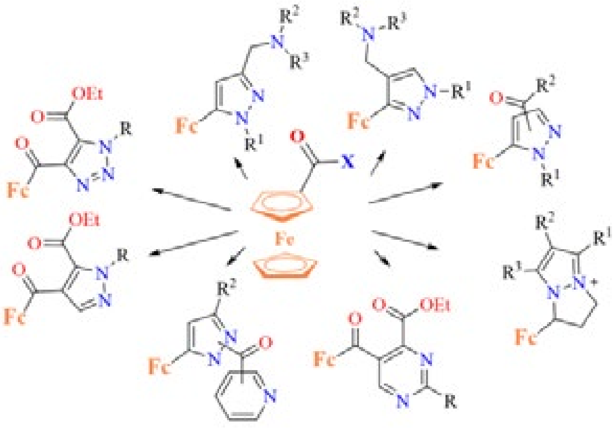

Figure 1. Biologically active heterocyclic compounds of ferrocene

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IS IT POSSIBLE TO FIND A UNIVERSAL TOOL FOR THE DESIGN OF COORDINATION COMPOUNDS OF THE LANTHANIDE SERIES?

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Of particular interest in modern 4f-element chemistry is the design of complexes and their synthetic precursors, with a certain structure and composition that provide a desired set of physicochemical properties. Meanwhile, one of the reasons holding back the development of organolanthanide chemistry is the low solubility of their precursors in organic solvents. Previously, numerous attempts have been made to obtain mononuclear lanthanide halide complexes with a well-defined $MCl_3(L)_n$ structure, where L is the electron pair donor ligand that is either O- or N- bonded to the metal ion. The use of a tridentate N-donor ligand such as the readily accessible and inexpensive 1,4,7-trimethyl-1,4,7-triazacyclohexane (Me_3tach) provided well-defined complexes $LnCl_3(Me_3tach)_2$ or $LnCl_3(Me_3tach)L$ or $Cp'LnCl_2(Me_3tach)$ that also could serve as precursors for the preparation of individual organolanthanide compounds.[1]

Lanthanides at the beginning of the series form complexes $[LnCl_3(Me_3tach)_2]$, whose structure can be described as « pseudo sandwich» or $[LnCl_2(Me_3tach)(thf)(\mu\text{-}Cl)]_2$, depending on the reaction stoichiometry. Heavier lanthanides form complexes such as $[LnCl_2(Me_3tach)_2]^+[LnCl_4L]^-$.[2] The complexes ($[LnCl_3(Me_3tach)_2]$ are perfectly soluble in organic solvents, aromatic hydrocarbons, and their core is characterised by an unusual planar-trigonal structure of the $\{LnCl_3\}$ fragment. The complexes of Pr, Sm, Eu, Tb and Dy are luminescent in the visible region.

The action of pyridine or 2,2‘-bipyridine or phenantroline on $LnCl_3(Me_3tach)_2$ leads to the formation of $[LnCl_3(Me_3tach)L]$ L = 2Py, 2,2’-bipy, 9,10-phenantroline.

The talk will discuss the synthesis, structure, and photophysical properties of different types of lanthanide coordination compounds with Me_3tach and Me_3TACN ligands.

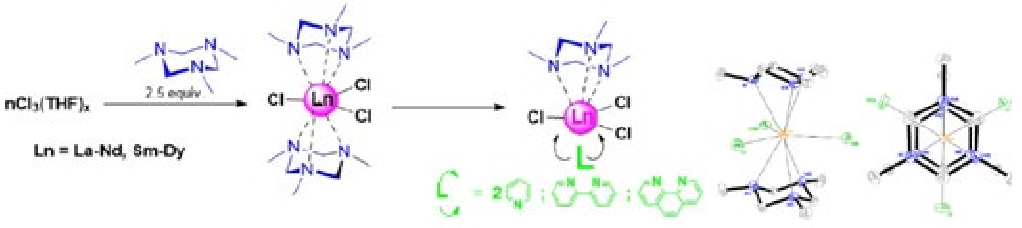

Figure 1. Synthesis and molecular structure of “pseudo sandwich” $LnCl_3(Me_3tach)_2$

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BIODEGRADABLE SELF-ASSEMBLED PLA-B-PEG NANOCARRIERS FOR ANTICANCER DRUGS: SMALL PARTICLES – BIG PERSPECTIVES

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Nanomedicine offers great opportunities for development of targeted formulations of anticancer drugs with improved efficacy and reduced side effects. Developers are generally focused on 100-200 nm particles as carriers for anticancer agents due to passive tumor targeting via enhanced permeation and retention effect. However, recently it was demonstrated that 10-20 nm nanocarriers might be a better alternative because they present an optimal trade-off between the long-term blood circulation and nonspecific background tissue uptake[1]. Micelles and nanoparticles of biodegradable amphiphilic polylactide-block-poly(ethylene glycol) (PLA-b-PEG) copolymers are perspective materials for development such carriers. Size and morphology of nanoparticles can be controlled via block lengths and their chemical composition. To design nanocarriers with pre-determined properties it is crucial to synthesize block copolymers with well-defined molecular structure. In present research we focus on synthesis and study of PLA-b-PEG copolymers with linear and star-shaped architecture. It was shown that PLA block length and its crystallization strongly affect size and morphology of self-assembled micelles and nanoparticles, as well as drug loading and kinetics of release. Nanoparticles with diameter ranging from 10 to 30 nm were prepared and studied by light scattering, X-ray scattering and electron microscopy. Anticancer drug nanoformulations of Pt-based agents were developed and studied in vitro.

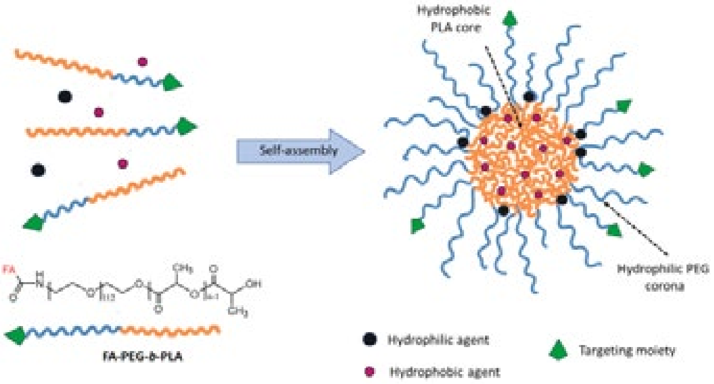

Figure 1. Design of PLA-b-PEG nanoformulations

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LOW-COORDINATION F- AND S-BLOCK METAL COMPLEXES WITH A SUPERBULKY CARBAZOLE LIGAND IN CATALYTIC DEAROMATIZATION OF N-HETEROCYCLES

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Hydride complexes of “heavy” alkaline earth metals and divalent lanthanides are unique objects of study due to their high reactivity, which is due to the presence of highly polarized M-H bonds. The carbazole platform seems promising for the synthesis of hydride complexes due to some of its properties, such as the donor character of the anion, the absence of pathways for intramolecular CH-activation, easy modulation of the steric properties of the ligand by molecular design methods, and, the possibility of creating low-coordination hydrides.

In this work, four bulky carbazoles with different steric-electronic properties were synthesized: $(tBu)_2CarbHPh_2$, $(tBu)_2CarbHAr_2$ (Ar = a 3,5-tBu_2Ph, b 1,3,5-iPr_3Ph, c 1,3,5-Cy_3Ph). Based on $(tBu)_2CarbHAr_2$ (Ar = a 3,5-tBu_2Ph), hydride complexes of Yb(II) and Ca(II) $[((tBu)_2CarbAr_2)MH]_2$ (1, 2, Fig. 1) were synthesized. This is the first example of coordinatively unsaturated hydrides of ytterbium and calcium.

In reactions of catalytic dearomatization, the interactions of heterocyclic substrates with PhSiH3 in the presence of 2 mole % of hydride complexes 1 and 2 were studied. Annelated heterocycles easily yield silane addition products at positions 1,2- of the heterocycle at room temperature for 24 hours, or at 60°C for 2 hours. When the temperature is increased to 90°C, the reverse process of restoring the aromaticity of the pyridine ring with the elimination of the initial PhSiH3 is observed.

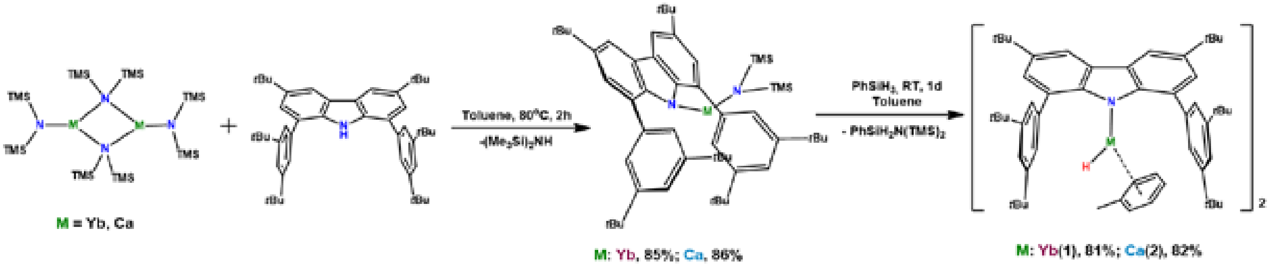

Figure 1. Synthesis of hydride complexes of Yb(II) and Ca(II).

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PREPARATION AND CHARACTERIZATION OF POLY(ACRYLONITRILE-CO-VINYL ACETATE) HOLLOW FIBER MEMBRANE FOR WASTEWATER TREATMENT

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The management of water consumption in textile dyeing and separation of dyes from textile dyeing wastewater have always been of interest to researchers and industries. The use of membranes in the separation of dyes from colored solutions can be one of the methods of interest in the treatment of colored wastewaters. In this work, the hollow fiber membrane of commercial poly(acrylonitrile-co-vinyl acetate) was fabricated by dry jet wet spinning method and it was used as a membrane to separate disperse dyes from the aqueous solution. The effect of adding dimethyl sulfoxide (DMSO) in the internal coagulant and external coagulation bath on the mechanical properties of hollow fibers and the performance of dye penetration and removal from dye solution was investigated. The morphology and structure of prepared hollow fibers were evaluated by scanning electron microscope and porosity and the diameter of the prepared hollow fibers were determined. Separation of disperse blue 165 from aqueous solution was studied by an assembled membrane module. Ultraviolet-visible (UV-vis) spectroscopy (UV-VIS) has been used to investigate and analyze the amount of dye separation by the fabricated hollow fiber membrane. The results showed that adding solvent to coagulants in the spinning process leads to a decrease in permeability. The tensile strength of the produced membrane increased by increasing the amount of solvent in the coagulant. The rate of exchange and displacement of solvent and non-solvent or the rate of enrichment of polymer solution in phase inversion from non-solvent and its effect on membrane properties were analyzed. In addition, hollow fibers spun with higher solvent content showed lower hydraulic permeability and higher dye removal efficiency.

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THE SECOND LIFE OF CYCLOBUTADIENE COMPLEXES

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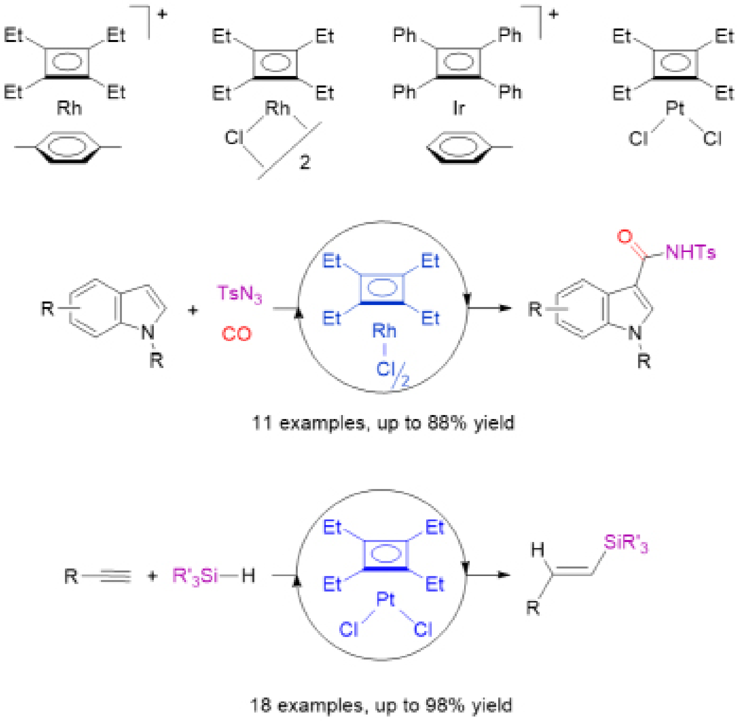
Cyclobutadiene complexes are known for many transitional metals[1] but no one has tried to use them as catalysts for organic reactions.[2] The possible explanation of this fact is the inert structure of the most synthesized cyclobutadiene compounds. We have found that cyclobutadiene complexes bearing labile ligands are active catalysts for various organic transformations such as amidation of donor arenes[3] and hydrosilylation of unsaturated substrates[4].Therefore, cyclobutadiene complexes of transitional metals represent a relatively unexplored class of organometallic catalysts which can find further successful applications in catalysis.



11 examples, up to 88% yield

18 examples, up to 98% yield

Figure 1. Catalytic activity of cyclobutadiene complexes

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POLYHETEROARYLENE-BASED POROUS ELECTROSPUN CARBON NANOFIBER MATS FOR FUEL CELL APPLICATIONS

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Polyheteroarylenes, such as the polymer of intrinsic microporosity (PIM-1) and polybenzimidazole (PBI), are used to produce porous electrospun carbon nanofiber (CNF) materials with the goal to apply them in high-temperature polymer-electrolyte membrane fuel cells (HT-PEMFC). The CNF mats are obtained from polymer solution by the Nanospider (needle-free) electrospinning followed by the stabilization procedure and pyrolysis step at different temperatures (900-1500 °C) and media (vacuum, Ar and Ar-H_2 mixture). The obtained CNF samples are characterized by N_2 and CO_2 adsorption. The methods used for the obtaining of specific surface area and volume include BET, BJH, Dubinin–Radushkevich (DR), NLDFT and GCMC methods. Raman spectroscopy, elemental analysis, electrical conductivity measurements, electron microscopy and XPS are applied also. The resulting materials are porous CNF self-supporting mats and contain micropores (< 2 nm) and mesopores. The role of the polymer precursor is found to be essential for the formation of porous structure of the resulting materials.[1] Thus, for the PBI-based CNF material pyrolyzed at 1500 °C in Ar, CO_2 uptake reaches 4.0 mmol g^{-1}, and micropore specific surface area (MSSA) is 873 m^2 g^{-1} (according to N_2 adsorption at 77 K applying the t-method) and 919 m^2 g^{-1} (according to CO_2 adsorption at 273 K). These close values confirm high accessibility of micropores. However, in the case of the PIM-based CNF (pyrolyzed at 1500 °C in Ar), the MSSA calculated from N_2 adsorption is much lower than in the case of CO_2 adsorption. It indicates partial inaccessibility of micropores to N_2 gas molecules at a low temperature of 77 K due to kinetic reasons, and the formation of a tight system of micropores. The PIM-based CNF (pyrolyzed at 1000 °C, vacuum) reaches the MSSA of 919 m^2/g and micropore volume of 0.257 cm^3/g, which is higher than the MSSA for initial PIM-1.[2] The CNF mats with deposited Pt, are successfully tested as electrodes in HT-PEMFC. However, further optimization is required. Thus, HT-PEMFC performance reaches 0.69 V at 0.2 A cm^{-2} and 0.53 W cm^{-2} at 1.4 A cm^{-2} for the PIM-based CNF anode. The obtained results show high dependence of the porometric values and HT-PEMFC performance from the CNF polymer precursor and preparation conditions. It has been suggested that the use of both N_2 and CO_2 adsorption techniques is essential for a comprehensive characterization of CNF materials of this type.

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Acknowledgements

The study was supported by Russian Science Foundation (grant # 22-13-00065). Elemental analysis was performed with support of Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for Molecular Composition Studies of INEOS RAS. The authors would like to thank O.M. Zhigalina, D.N. Khmelenin, E.N. Cherkovskiy, A.G. Buyanovskaya, R.R. Aysin, S.S. Bukalov and A.D. Modestov for their help.

RECENT ADVANCES IN BIO-ORGANOMETALLIC FERROCENE CHEMISTRY

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This report is intended to sketch out the 'ferrocene picture' in broad strokes. Ferrocene is undoubtedly one of the most studied metal-organic frameworks. Ferrocene compounds have been intensively studied for more than 70 years since their discovery.

INEOS and ferrocene have a long history together. Ferrocene, $Fe(\eta^5\text{-}C5H_5)_2$, is just over seven decades old. This unusual compound, in which an iron atom is bonded to each of the ten carbon atoms, was first reported by Kealy and Pauson in late 1951. Over the years, ferrocene has demonstrated inexhaustible synthetic and practical potential. Currently, only one drug based on ferrocene is known on the global pharmaceutical market. This is Ferrocerone, the sodium salt tetrahydrate of ortho-carboxy benzoylferrocene, that replenishes iron stores in the body and treats iron deficiency pathologies such as anemia, ozena and periodontosis. Ferrocerone was developed and introduced into clinical practice in the Soviet Union in 1970s. This iron-containing medicine was on the Russian pharmaceutical market from the 1970s to the mid-1990s. In the 2000s, there were unsuccessful attempts to resume the production of ferroceron. At present, there is no production of ferroceron in Russia and its use in clinical practice.

This review accentuates on the recent advances in the bio-organometallic ferrocene chemistry area and biology. Novel ferrocene-modified analogues of various bio-structures were synthesized, namely, betulin, artemisinin, steroids, and alkaloids. In addition, studies of the biological potential of ferrocenes have been expanded. We also tried to highlight potential benefits, challenges and future directions of ferrocene-based compounds in various industries.

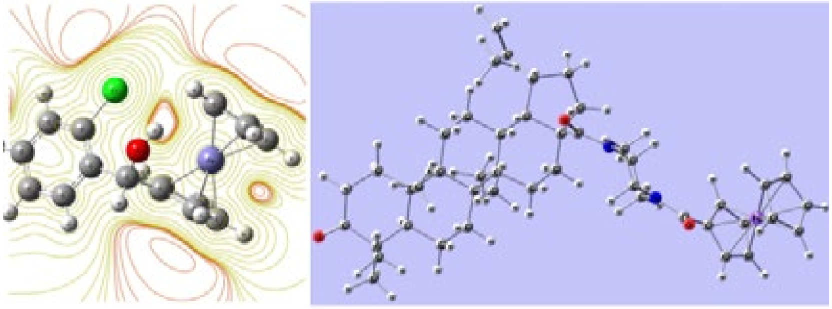

Figure 1. Ferrocene-modified compounds.

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SILVER THIOLATES: CLUSTERS ANDS COORDINATION POLYMERS

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Silver chalcogenolates AgQR (Q = S, Se, Te) are low-dimensional hybrid materials which can be used as light emitters, field-effect transistors, photoconductors, photonic reflectors, and sensors. Tuning of the optoelectronic properties and transformation of the morphology of the materials can be achieved through modification of chalcogenolate unit (QR) and incorporation of extra ligands (L).

This contribution discusses the synthetic potential of perfluorinated silver thiolates [$AgSAr^f$] (Q = S, Se, Te; Ar_f is a fluorinated arene fragment like phenyl or biphenyl) in the creation of silver thiolate clusters and coordination polymers. Reactions of [$AgSAr^f$] with pyridine, and alkyl pryridines (L = py, 2-Mepy, 3-Mepy, 4-Mepy) produce coordination polymers [$AgSAr^f(L)$] which feature extensive argentofilic interactions (Ag…Ag 3.0-3.2 Å) and luminescent behaviour (temperature sensitive emission at 450 – 550 nm). The structure of [$AgSAr^f(L)$] is based on corrugated ribbons obtained by fusion of two adjacent ..Ag-S-Ag-S… chains, with terminal N-donor ligands at each Ag atom. They are thermally robust and can be used for growth of crystalline [$AgQAr^f$] and Ag_2S films on various surfaces.

Silver thiolates also form polynuclear silver nanoclusters, which are of interest due to the diversity of their geometric and electronic structures. Using HPLC-ICP-AES and preparative methods, we studied self-assembly of silver thiolate clusters in AgS^tBu - $AgNO_3$ system. In DMF solution formation of [$Ag_{20}(S^tBu)_{10}(NO_3)_{10}(DMF)_6$] was observed. In N-methylpyrrolidone and DMSO the {$Ag_{20}(S^tBu)_{10}$} core loses Ag^+ to reach equilibrium with defect cluster species {Ag_{19}} and {Ag_{18}}.[1,2]

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NIDO-CARBORANYL AMIDINES IN THE SYNTHESIS OF METALLACARBORANES OF GROUPS VIII-X

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The functionalization of *nido*-carborane via the reactions of nucleophilic addition to its nitrilium derivatives is a convenient way to prepare a great diverse of *nido*-carborane compounds, which can also be used as ligands in the complexation with transitional metals.[1-3] This work is devoted to the study of coordination ability of *nido*-carboranyl amidines, which were synthesized by the addition of primary amines of various compositions to 10-RC≡N-7,8-$C_2B_9H_{11}$ (R=Me, Et) (Fig. 1).

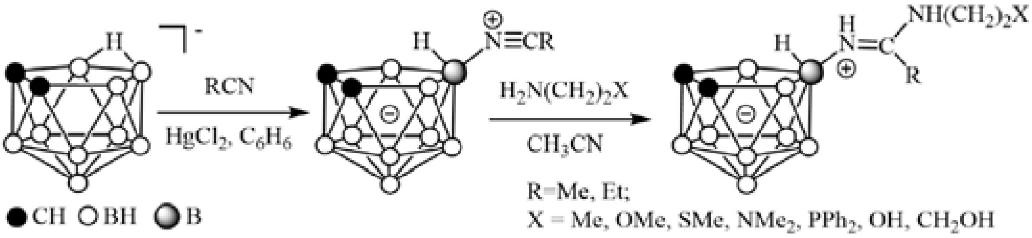

Figure 1. A synthetic pathway to the *nido*-carborane derivatives with an amidinated fragment

The prepared amidines were studied as ligands in the reactions with metals of groups VIII-X to give the metallacarboranes of various structures, including classical η^5-complexes of half-sandwich and sandwich types, as well as unusual η^5,κ^1- and η^5,κ^2-complexes, in which the metal is coordinated by *nido*-carborane open face on one side and by the substituent at *nido*-carborane from the other side (Fig. 2).

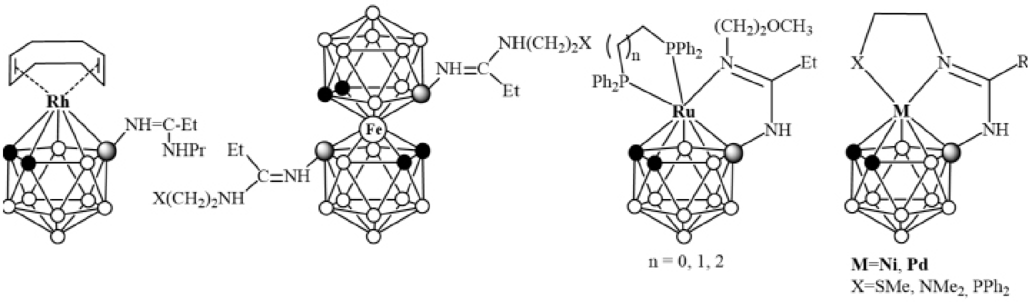

Figure 2. Some examples of the metallacarboranes obtained in this study

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ASYMMETRIC SYNTHESIS OF UNNATURAL HALOGENATED A-AMINO ACIDS

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The halogenated α-amino acids (AAs) widely distributed in the structures of natural and biologically active compounds.[1] Availability of methods for their asymmetric synthesis is limited, and the development of new efficient methods for the synthesis of halogenated α-AAs is the perspective and attractive direction.[2]

We report the method for the asymmetric synthesis of unnatural halogenated α-AA derivatives *via* radical coupling of the chiral Belokon's Ni(II) complex of the dehydroalanine Schiff's base (S)-BPB-Ni-ΔAla 1 with different fully halogenated alkanes **2** catalyzed by a dual 4-cyanopyridine/B_2Pin_2 system (Figure).[3] Diastereomeric Ni(II) complexes (*S,S*)-**3** with a ratio of up to *dr* >20:1 were isolated in 40–70% yields. Next, the obtained halogene-containing Ni(II) complexes (*S,S*)-**3** were involved in the modification reactions, giving Ni(II) complexes with cyclopropyl and protodebrominated fragments. The target unnatural α-AAs **4** were isolated with excellent enantioselectivity and yields up to 97%.[4]

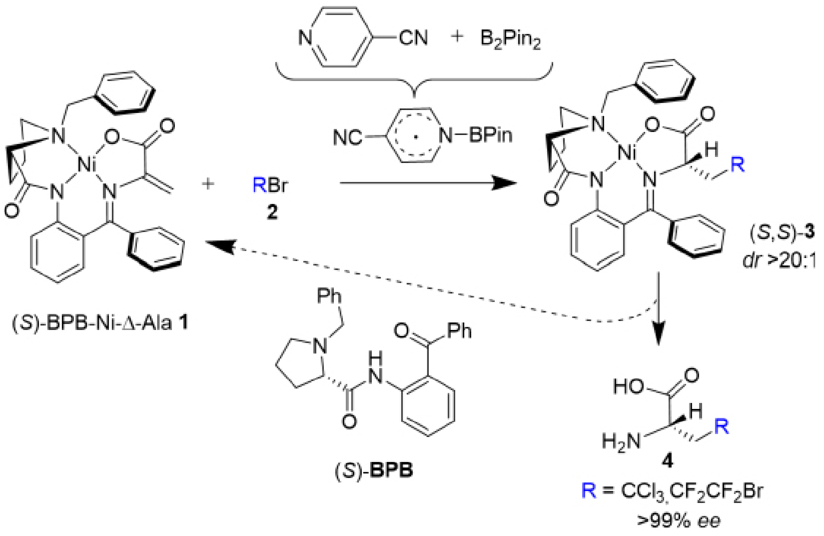

Figure. Synthetic approach to enantiopure halogenated α-amino acids.

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SYMMETRICAL RESTRICTIONS ON THE IMPLEMENTATION OF HYDROCARBON CHAINS OF PHOSPHOLIPIDS OF BIOMEMBRANES

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In the hydrocarbon chains of phospholipid of biomembranes the combination of number N of carbon atoms, number d of double C=C bonds and the chain positions ω of double bonds can theoretically produce a great number of variants. However, only 20-30 sets (N, d, ω) are being implemented.

In an approximation that can be considered physically admissible, saturated segments of hydrocarbon chains are tetracoordinated, due to the properties of the carbon atom. Its four valences are directed to the vertices of regular tetrahedron. Three-dimensional Euclidean space E^3 (of zero curvature) cannot be tessellated into centered regular tetrahedra; however, located in E^4 3-dimensional sphere S^3 (of positive curvature) can be tessellated into 600 centered regular tetrahedra.[1,2] This tessellation is the regular 4-dimensional polyhedron (polytope {720}), a 4-dimensional analog of triacontahedron.[3] Linear substructures of polytope {720} are ideal prototypes for saturated and unsaturated hydrocarbon chains, and the mappings of substructures of S^3 into the E^3 determine classification of all possible biomembrane surfaces.[4] These substructures of {720} are divided into an integer number of 14- and 11-vertex composite (CTb) and decorated (DTb) tetrablocks.[5] A tetrablock (Tb) – seven-vertex union of four face-sharing regular tetrahedra defines CTb and DTb. The tetrablock graph is defined by a finite projective geometry PG(2,2). This geometry is given by the minimal Galois field (consisting of only 0 and 1), therefore Tb (CTb, DTb) is a building block for linear structures approximated by a union of regular (centered) tetrahedra.[6, 7]

The embedding into the polytope {720} of a chain assembled from an integer number of CTb and/or DTb is possible only for a very limited number of sets (N, d, ω). This defines a very limited number of symmetrically admissible hydrocarbon chains of phospholipid of biomembranes. For example, if 3, 4, 5 CTblocks are combined sequentially through frontal vertices, then (in terms of C–H realization) chains of the $C_{12}H_{24}$, $C_{16}H_{32}$, $C_{20}H_{40}$ type are produced, respectively. When two DT blocks are combined through a frontal edge (and one of the DT blocks is the end of the chain), the region of their connection defines a double bond, and the entire union corresponds to the ω3 position of this double bond.

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PYRAZOLATE-PHOSPHINE COPPER(I) AND SILVER(I) MIXED-LIGAND COMPLEXES: STRUCTURES AND PHOTOPHYSICAL PROPERTIES

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Coinage metal pyrazolates are a promising platform for interaction with different types of bases, which allows the formation of complexes of broad type structures.[1] This is due to the main ability of pyrazolate anions to act as bridging ligand, binding with metals in different ways. The use of mono- or bidentate phosphine ligands results in the formation of mono-, di-, tri-, and tetranuclear complexes. It is known that the coordination of phosphorus-containing ligands leads to stabilization of the excited state. The formation of cage-type complexes in the case of bis(phosphine)methane derivatives allows for the production of TADF copper(I) complexes.[2] On the other hand, the substituent on phsophorus atom plays a crucial role in photoluminescence nature. The presence of aromatic substituents results in an inefficient relaxation from triplet states loacated on this fragments. But, a simple change in the substituent to aliphatic allows changing of the emission nature resulting in a significant increase of efficiency. This behaviour has also been observed for the dinuclear pyrazolate complexes containing PR_3 derivatives.[3] The structural features of the complexes obtained and their photophysical properties will be discussed.

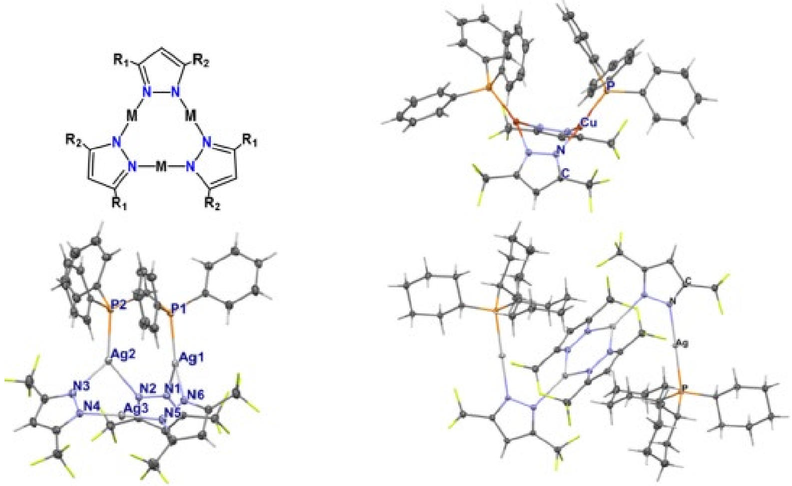

Figure 1. The chemical structure of trinuclear group 11 metal pyrazolate adducts and their complexes with P-containing ligands.

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ORGANIC ELECTRONICS AT INEOS RAS

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About 40 years ago, the idea of replacing inorganic materials with flexible and cheap organic analogs in electronic devices began to be implemented. The criterion of a band gap width of no more than 3.2 eV for maintaining semiconductor properties is easily met for many unsaturated polyconjugated derivatives of various classes of organic compounds.

The advantage of organic working bodies for devices is their great versatility. By varying the framework structure of organic molecules one can influence electronic properties of the resulting material. At the same time, it is possible to vary peripheral substituents capable of adjusting both electronic properties and the methods of laying molecules in a condensed phase. Based on organic compounds, it is possible to create ultra-thin and ultra-light integrated circuits on flexible and transparent substrates and even entire devices. The development of the methodology of laboratory and industrial organic synthesis leads to an ever-increasing gap in the cost of creating inorganic and organic materials in favor of the latter. Scientific groups of INEOS RAS, one of the leading scientific organizations in the field of organoelement and organometallic compounds, successfully develop components and materials for organic electronics devices.

This report is dedicated to the achievements of INEOS RAS researchers in organic electronics in recent years.

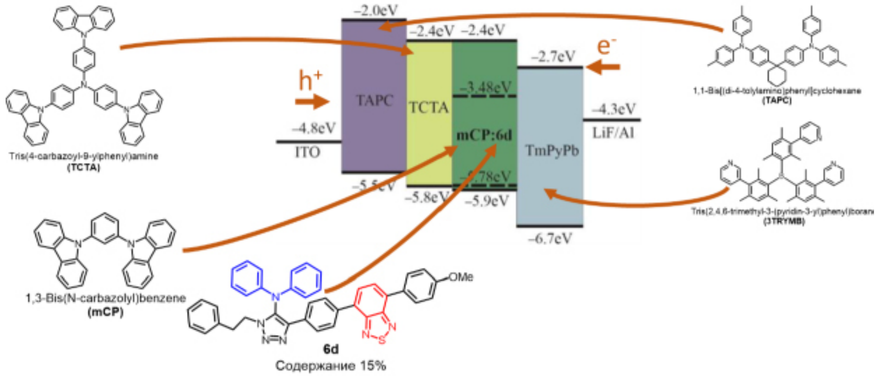

Figure 1. Schematic representation of an OLED with a peak brightness of 8000 cd·m^2 based on the 6d dye developed at INEOS RAS

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ORGANOELEMENT DERIVATIVES OF RADICALS AS BUILDING BLOCKS FOR CONSTRUCTING HIGH-SPIN SYSTEMS

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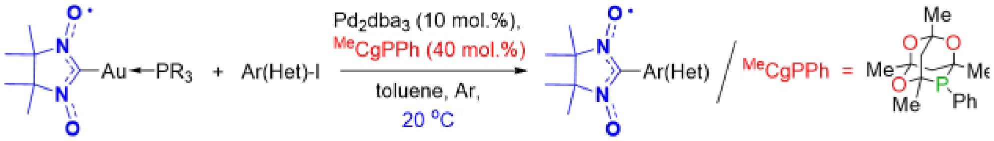
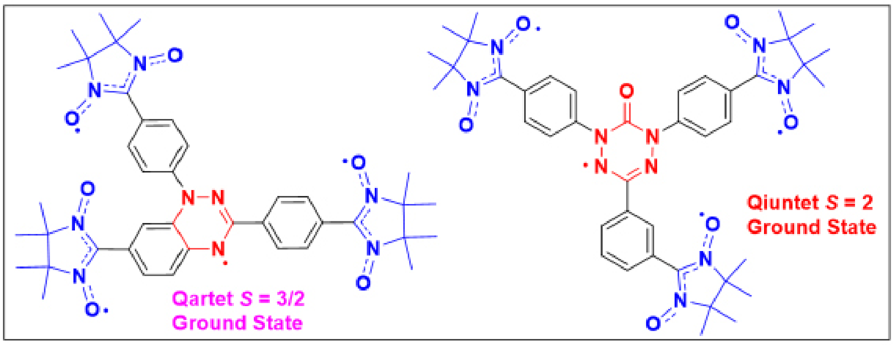
Nitronyl nitroxides (NNs) are actively used for the design of photoswitchable systems, the development of molecular magnets, and the construction of redox-active components of hybrid and organic batteries.[1] Key functional usefulness of NNs is the translation of structures optimized at the molecular level into novel technologies and nanosize devices. Despite the high relevance, effective and multipurpose synthesis protocols leading to such compounds remain out of reach. This work solved a problem of many years concerning Pd-catalyzed cross-coupling of haloarenes with NN metalloorganic derivatives. A systematic search resulted in derivatives NN-M-L (M = Au or Ag) showing excellent thermal stability and well-pronounced reactivity in terms of cross-coupling with aryl halogenides.[2] These reactions made it possible to obtain the first tetraradicals that have a high-spin ground state and a large energy gap between the ground state and the nearest excited low-spin state.[3,4]





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HYPERCROSSLINKED POLYSTYRENE: INTERRELATION BETWEEN THE TEMPERATURE AND THE SHAPE OF ADSORPTION ISOTHERMS

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Hypercrosslinked polystyrene (HP) has gained a well-deserved popularity due to its ability to take up reversibly a large amount of organic compounds from aqueous solutions and gaseous media. This property owes HP structure, which in its turn, is conditioned upon the principle of network preparation. HP has been obtained by crosslinking polystyrene chains in solution or in a swollen state with a large number of rigid bridges-struts. As the result a rigid single-phase openwork 3D polymer forms. Two main properties characterize HP polymer, the first is a large free volume comparable with the pore volume of real two-phase mesoporous polymers and the second is the presence of strong inner contraction stresses.

In this study, the adsorption behavior of three types of HP networks were investigated. These are (1) five MS samples based on microspheres (Ø 3.3 µm) of styrene-0.5% DVB prepared by dispersion polymerization, the crosslinking degree (X) ranging from 100% to 500%. (2) HP-3x200 based on gel-type styrene-3% DVB copolymer with beads of Ø 30 µm, X=200%; (3) industrial sample MN-202, beads of Ø 30 to 1200 µm, X=200%.

The adsorption isotherms for N_2 at 77K onto all the samples are identical in shape. A steep rise of adsorption branch up to the relative pressure p/po of about 0.2 could be attributed to micropore volume filling however the isotherms do not show typical plateau, on the contrary, with further increase in p/po the adsorption capacity steadily and linearly rises up to p/po=0.95 without any sign of capillary condensation. Hysteresis loop extends throughout the entire range of relative pressures. Adsorption isotherms for benzene vapors at 293 K onto MS samples look differently. The initial part of the adsorption branch is not so steep, the isotherms simply rise linearly at p/po=0.95, while the hysteresis loops have the same profile. This difference in the shape of isotherms is explained by the fact that at 77K HP network is overstressed. The N_2 uptake stimulates the partial relaxation of inner stresses thus conditioning a quick rise of isotherm even at p/po=0.005 whereas at 293 K the inner stresses in HP are smaller that is why the steep increase in benzene absorption is absent. It is important to emphasize the HP capacity for N_2 and benzene at p/po=0.95 are of the same order of magnitude, 0.40-0.46 and 0.6 ml/g respectively/ This fact together with the shape of hysteresis loops unambiguously testify to the HP swelling not only with benzene but also in liquid nitrogen. Besides, the above results suggest the type of adsorption isotherms is determined by temperature rather than the presence of micropores or mesopores or their mixture. Important conclusions is that in response to temperature, loading or diffusion of alien molecules inside network hypercrosslinked polystyrene has always adjusted its structure.

Published Isotherms for N_2 at 77 K and CO_2 at 273 K onto PIMs show same behavior.

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STUDY OF ANTIOXIDANTS IN FERGANA PLANTS AND THEIR ANTI-RADICAL ACTIVITY

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Currently, in clinical practice, for the prevention and correction of pathologies resulting from the activation of free radical oxidation processes, it is more promising to use antioxidants of plant origin.[1]

By HPLC method in the composition of the aerial parts of *Tribulus terrestris L.* (1), *Melissa officinalis L.* (2) and *Taraxacum officinale Wigg. s.L.* (3), growing in the Fergana Valley, the amount of 7 biologically active substances (antioxidants) was studied, as well as their antiradical activity towards the stable free radical DPPH (2,2-diphenyl-1-picrylhydrazyl).[2]

Table 1. Quantitative content of antioxidants in the aerial parts of medicinal plants growing in the Fergana Valley.

Biologically active substances (antioxidants)	Concentration of substances in medicinal plants (in mg/g)		
	1	2	3
Selenium	$6.9*10^{-4}$	$5.5 * 10^{-6}$	$3*10^{-5}$
Vitamin C	7.1	28.8	54.2
Rutin	39.12	54.2	11.3
Quercetin	1.51	45.50	4.65
Dihydroquercetin	1.57	35.6	25.2
Luteolin	8.01	9.74	5.64
Rosavin	21.41	4.12	1.23

Table 2. Antiradical activity of medicinal plants towards the stable free radical DPPH.

Plant extracts (alcohol infusion)	inhibition, % (at 10 min.)					
	50 µl	100 µl	200 µl	300 µl	400 µl	500 µl
1	8.9 ±1.2	12.2 ±2.1	18.1±2.4	2 6.5 ±1.8	31.5 ±2.3	32.2±2.1
2	-	-	-	-	-	-
3	-	-	-	-	-	-

Extract *Tribulus terrestris L.* (1) has high antiradical activity, accordingly actively counteracts cancer cells. Therefore, *Tribulus terrestris L.*, as a natural antioxidant, is promising for use in the treatment of cancer.

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SUPRAMOLECULAR COMPLEXES OF STYRYL DYES WITH CUCURBIT[7]URIL FOR FLUORESCENT DNA IMAGING

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The application of container molecules in studies of reversible supramolecular interactions in the field of biology and medicinal chemistry is due to their high binding constants, suitable solubility in water, low toxicity, and ability to penetrate into cells. Supramolecular DNA–CB[n] systems find successful application in numerous bio-related fields.[1] Fluorescent ligands, such as styryl dyes, are suitable compounds for visualizing changes in the structure of the supramolecular assembly.

In this work, derivatives of styryl dyes **1,2**, a molecule of cucurbit[7]uril (CB[7]), and a biomolecule of ds-DNA (double-stranded DNA) were selected as components of the supramolecular system (Figure 1). The choice of **1,2** dye molecules as a component of such a system is due to the possibility of monitoring the processes using optical spectroscopy. During the study, the physicochemical properties of the dyes in binary and ternary complexes were studied using absorption, fluorescence, CD and NMR spectroscopy. The studies allowed us to identify structural fragments in the dye that affect the formation of the architecture of the complex. The results obtained provide useful information on ligand-DNA interactions, which is valuable for the rational design of drug delivery systems and platforms for cell imaging and therapy.

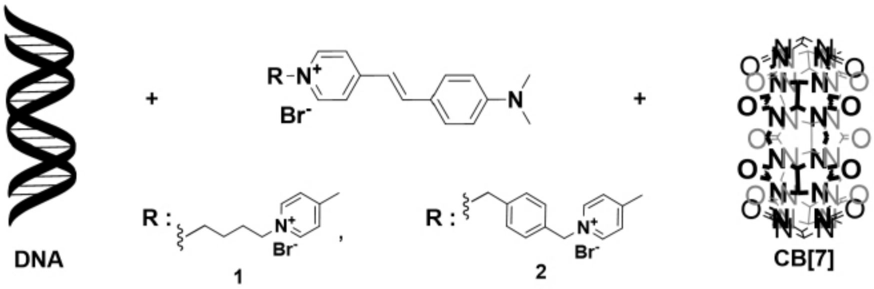

Figure 1. Structures of derivatives of styryl dyes (**1,2**), ds-DNA, CB[7].

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COMPOSITE MATERIALS BASED ON POLYETHER ETHER KETONE AND NATURAL MAGNETITE

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Composite materials are of great interest due to their ability to create innovative solutions with unique properties. Such materials include polymer composites with magnetic properties, which represent a promising field of materials science with wide possibilities for various applications. Magnetic polymer materials are widely used in medical practice due to their unique properties: controllability by a magnetic field, the possibility of functionalization, controlled magnetic properties. Of great interest is the study of composite materials based on polyether ether ketone (PEEK) and natural magnetite.

The structure of natural magnetite and its magnetic properties are investigated. Various technologies for the production of magnetite powders are considered and their sizes are analyzed. The modification of the PEEK with a powder of natural magnetite, the amount of which corresponds to 5-25 volume fractions (vol.d.), was carried out and the physico-mechanical, magnetic, thermal and thermophysical properties of composite materials were studied.

The results of the conducted studies have shown that the saturation value of the magnetization of natural magnetite differs from the empirically established value and corresponds to 83.97 emu/g. Composite materials have a residual magnetization, opening up prospects for maintaining magnetic properties even after removing the external magnetic field. By scanning electron microscopy, it was found that magnetite particles consist mainly of irregularly shaped agglomerates. A technique for producing magnetite powder with a monomodal particle distribution has been developed. The study of the physico-mechanical properties of the obtained composite materials based on PEEK and magnetite showed that the introduction of magnetite leads to a uniform increase in the elastic modulus and flexural strength and a decrease in elongation and toughness, which is natural for rigid fillers.

Thus, natural magnetite has proved to be an effective modifier for the production of polymer composite materials with magnetic properties. In addition, its non-toxicity opens up new ways of practical application, in particular, in medicine.

Acknowledgements
The work was carried out within the framework of the state assignment of the Ministry of Science and Higher Education of the Russian Federation, mnemonic code FZZR-2023-005

PET-RAFT POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF PHOTOACTIVE POLYMER COMPOSITES

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In recent decades, polymer chemistry has seen increasing interest in the use of light to initiate the polymerization process, as it becomes possible to carry out synthesis under mild conditions and to easily control the process in time and space.

One of the most promising methods for carrying out photopolymerization is photoinduced polymerization with electron/energy transfer with reversible chain transfer proceeding through the addition-fragmentation mechanism (PET-RAFT polymerization), since it allows for the controlled synthesis of functional polymers, including the modification of natural polymers with synthetic ones. The most popular photocatalysts for use in the visible region of the spectrum are complex metal compounds (in particular, iridium, ruthenium and other transition elements). However, it is quite expensive. The use of titanium dioxide, an affordable, non-toxic and stable compound, is promising. Its main disadvantage is the band gap of 3.20 eV. Photocatalytic activity occurs when exposed to UV light only. Reducing the band gap is possible by modifying titanium dioxide in various ways: using a polymer matrix to form nanoparticles, varying the size of nanoparticles, doping $TiO_2$with atoms of other elements (nitrogen, silver, zirconium, etc.).

This research dwells on the synthesis of polymer composites containing nanostructured poly(titanium oxide) and their investigation in polymerization of methyl methacrylate.

Firstly, synthesis of polymer composite was carried out based on combination of two process: hydrolytic polycondensation of titanium isopropoxide and hydroxyethylmethacrylate and radical polymerization of vinyl monomers. Obtained materials were used as photocatalyst in PET-RAFT polymerization of MMA in the presence of 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) as the chain-transfer agent. Composition of materials used: $\{TiO_n\}_m$-*co*-P(HEMA-*co*-M) (where M = acrylonitrile, styrene, octafluoropentyl acrylate or second monomer absence). Also, materials with combination $\{TiO_n\}_m$ and $\{ZrO_n\}_m$ were investigated.

Polymerization was performed in quartz glass ampoules under Ar. The mixture was irradiated with stirring for a certain time with a UV lamp at a distance of 30 cm. The conversion was determined gravimetrically. Molecular mass characteristics were determined by gel permeation chromatography.

The conversion dependence has a linear form in semi-logarithmic coordinates, indicating a controlled process mode A faster polymerization process is observed, when composite materials were used compared with anatase TiO_2.

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SPIRO-EPOXY MOIETY – A POWERFUL TOOL FOR IMPROVING CO_2-SEPARATION EFFICIENCY OF POLYMER MEMBRANES

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Carbon dioxide is one of the main pollutants responsible for the greenhouse effect. Among technologies for purifying exhaust gases from CO_2 membrane gas separation has a number of advantages, such as low cost, minimal harm to the environment, energy efficiency and ease of use.[1] Developing polymers with high CO_2 gas separation properties is a key to reducing the impact of carbon dioxide on the environment.[2,3] We found that addition polynorbornenes containing epoxy groups in spiro-centers have high permeability to CO_2 in combination with high selectivity for the separation of carbon dioxide from its mixtures with nitrogen and methane.[4]

Data on gas permeability of epoxidized polymer based on 5-ethylidene-2-norbornene (figure 1) exceed the Robeson upper bound of 2019 for CO_2/N_2 gas pair ($P(CO_2)$=1000 Barrer, $\alpha(CO_2/N_2)$=67). Experiments on the separation of gas mixtures confirmed the high gas separation efficiency of this polymer. In particular, data on CO_2/CH_4 separation were close to or above the upper bound of 2018 for gas mixtures. A similar effect of introducing an oxirane moiety into the spiro center was demonstrated for the addition polymer based on 5-isopropylidene-2-norbornene and was not observed for the isomeric polymer in which oxirane fragments were located at the end of the side chains.

The found positive effect for CO_2 separation of spiro-epoxy moiety can become a new powerful tool for the targeted design of polymers with increased CO_2 permeability and CO_2/gas selectivity. The simple synthesis of the epoxidized polymer from available 5-ethylidene-2-norbornene, combined with high carbon dioxide permeability and selectivity, could make this polymer industrially applicable for membrane gas separation.

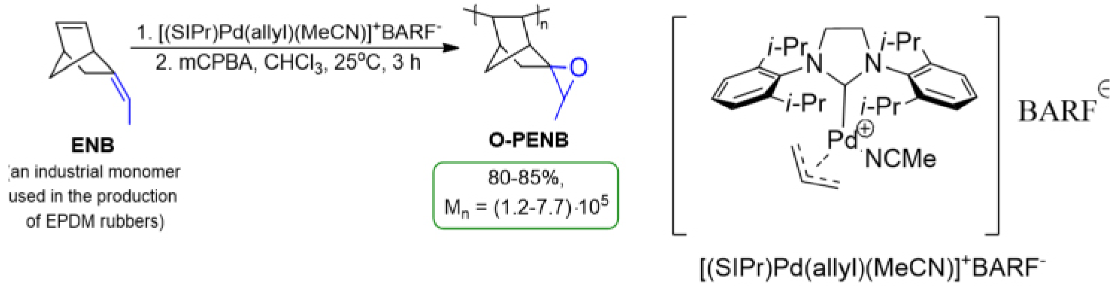

Figure 1. The scheme of O-**PENB** synthesis

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PHOSPHACYCLOPENTADIENIDE ANIONS - BUILDING BLOCKS FOR ORGANOPHOSPHORUS CHEMISTRY

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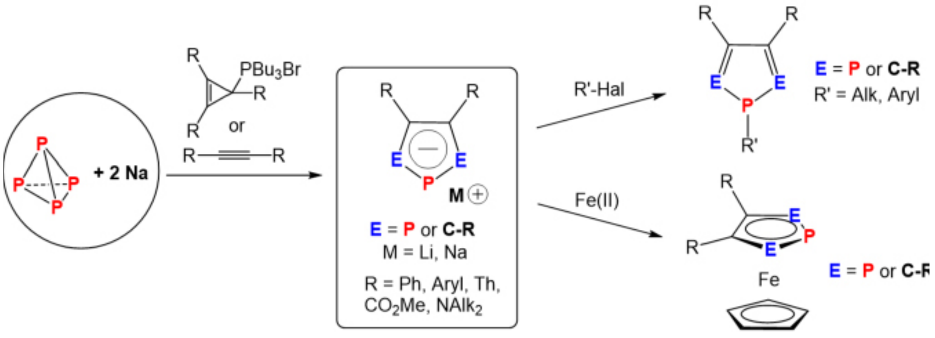
Phosphacyclopentadienide (phospholide) anions are very attractive as building blocks for the construction of versatile organophosphorus molecular materials with useful catalytic, optical, luminescent, magnetic properties.[1] Therefore, development of convenient methods for straightforward synthesis of these phosphorus heterocycles and their derivatives through functionalization of elemental phosphorus P_4 (bypassing toxic chlorine Cl_2) has a significant interest.[2] This lecture features recent advances on the synthesis of various phosphacyclopentadienide-anions and their chemical behavior toward organic substrates and transition metal complexes.



A rational and highly efficient method to access 1-mono-[3], 1,2-di-[4] and 1,2,3-triphospholide[5] anions in individual forms directly from white phosphorus P_4, alkali metals and unsaturated compounds (alkynes and cyclopropenylium salts) have been developed. Interaction with various chiral and non-chiral alkyl halides has allows for formation of novel *P*-heterocycles - 1-mono-, 1,2-di- and 1,2,3-triphospholes. Reaction with Fe(II) complexes was used as a convenient way for efficient synthesis of a number of phosphaferrocenes.[6] Results on application in material science and homogeneous catalysis of phospholide derivatives (phosphaferrocenes, phospholes and their [4+2] cycloadducts) was also presented.[7]

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1,2-BIS(TRIAZOLYL)TETRAPHENYLDIGERMANES: SYNTHESIS, STRUCTURE AND PROPERTIES

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Due to its high chemical effectiveness the reaction of click chemistry in general and [3+2] cycloaddition (azide alkyne interaction, Huisgen reaction) in particular has found wide application. Thus formed 1,2,3-triazoles represent an important class of heterocyclic compounds with wide applications. Pure organic triazoles with their biological activity are widely used in medicine. At the same time, triazoles containing organometallic groups have been less investigated. Combining an organic fragment and a Group 14 element into one molecule will be promising especially with the view to study structure–property relationships. The correlations established for model compounds can be generalized for oligomers and polymers or semiconducting materials based on Si or Ge.

In this report, by combining research into synthetic organometallic and organic chemistry, we plan to begin the application of organic synthesis methods to broaden the diversity of organogermanium compounds[1] for finding the novel properties of these unique derivatives. Based on recent results on σ-delocalized catenated oligomeric[2] and molecular oligoorganogermanes[3] (their wide application in organometallic synthesis, emissive and semiconducting properties) we intend to study the interaction of a simplest example, diethynyl digermane, in the reaction with azides. The target products were investigated by several methods (NMR, UV/vis and luminescence spectroscopy, electrochemistry, XRD analysis), indicating strong impacts of constituent functional groups.

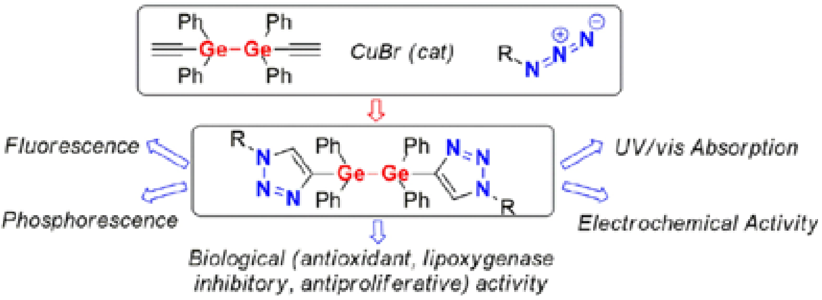

Figure 1. 1,2-Bis(triazolyl)digermanes.

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CROSSLINKING MECHANISMS FOR PMR POLYIMIDE MATRIX OF ADVANCED CARBON FIBER COMPOSITES

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Advanced fiber reinforced polyimide matrix composites are achieving acceptance as engineering materials for the design and fabrication of high performance aerospace structural components. The addition-type polyimides known as PMR (in situ polymerization of monomer reactants) polyimides has been developed as laminating resins for high temperature carbon fiber reinforced composites. The monomer reactant

mixture contains a dialkyl ester of an aromatic tetracarboxylic acid, an aromatic diamine, and a reactive capping reagent. The monomers are essentially unreactive at room temperature, but undergo sequential in situ condensation and are thermally imidized to generate well defined polyimide oligomers that are endcapped with terminated groups. The condensation reaction forming low molecular weight oligomers occurs in the temperature range of 121-232°C, and then ring-opening addition crosslinking reactions at even high temperatures form a thermo-oxidatively stable polyimide matrix resin. Polyimide oligomers can undergo diverse addition copolymerization or homopolymerization, such as reverse Diels Alder reaction and cyclotrimerization. Crosslinking of norbornene (NE) encapped PMR-15 and AFR 700B polyimide oligomer occurs at temperatures of about 280 - 320°C via a reverse Diels-Alder reaction mechanism.[1] The polyimide oligomers with 4-(Phenylethynyl)phthalic anhydride (PEPA) endcapped reagent crosslink by cyclotrimerization to form aromatic rings between 320°C to 371°C range and can be easily processed by resin transfer molding at a pressure of 1MPa [2]. The 3D crosslinked structures strongly dictate the mechanical and thermal properties of terminated polyimides. Therefore, the mechanism of the crosslink should be probed clearly. This paper discuss the crosslink mechanism of current status of PMR polyimides with different reactive capping reagents. In order to explain the capping reagents on the thermal properties, molecular dynamic (MD) simulation is carried out to investigate the glass transition temperature (Tg) of different PMR polyimides from PMR-15, AFR-700B and novel PMR polyimides. MD results indicate that the addition copolymerization or homopolymerization of oligomers occurred at elevated temperature leads to diverse 3D crosslinking structures, which tailor the Tg and thermal stability. Therefore, exploring the crosslink chemistry mechanism of oligomers with reactive capping reagents with the assistance of MD simulation is of significance in design high performance PMR polyimides.

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ARYLTRICYANOETHYLENES AS PHOTOACTIVE COMPONENTS OF THE INITIATING SYSTEM OF FREE-RADICAL POLYMERIZATION OF OLIGOESTER(METH) ACRYLATES

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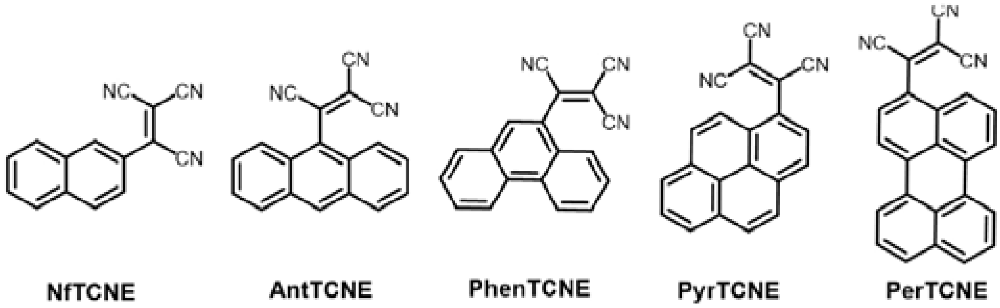
Despite the fact that the chemistry of A-π-D-type dyes is an actively developing area of organic and physical chemistry, currently there are only few examples in the scientific literature of the use of malononitrile-based dyes as photoinitiators for radical photopolymerization and, as a rule, these are dicyanethylene derivatives.[1,2] In this work, a new class of A-π-D-type dyes, aryltricyanoethylenes, comprising various bulk condensed aromatic substituents (D) in conjugation with a tricyanoethylene moiety, which is highly electron-deficient (A) due to three CN groups, has been investigated as photocomponents of initiating systems (Scheme 1).[3]



Scheme 1

The electrochemical and photoluminescent properties of the compounds presented in Scheme 1 were investigated. The kinetics of photoconversions of dyes together with tertiary amines under the action of visible radiation was investigated, and their efficiency as initiators (as part of one- and two-component initiating systems) for photopolymerization of pentaerythritol triacrylate (PETA) was evaluated by FTIR spectroscopy. For the polymers obtained on the based on aryltricyanoethylenes their thermal stability was investigated by TGA method.

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SYNTHESIS AND CATALYTIC APPLICATION OF RUTHENOCARBORANES WITH CHELATE DIPHOSPHINE LIGANDS

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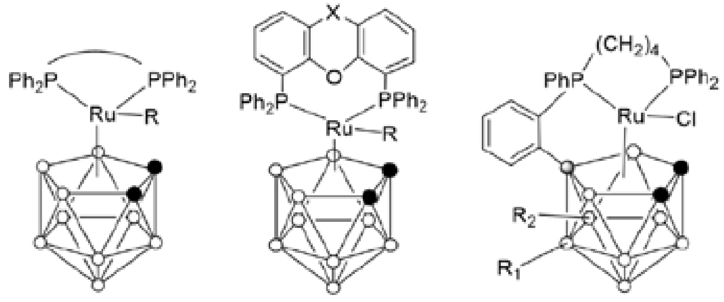
Metallacarboranes represent a wide range of compounds that have found application both in the field of catalysis of organic processes and in medicinal chemistry. In particular, carborane complexes of ruthenium (III) show good efficiency in the catalysis of polymer processes [1], and the modernization of the synthesis of these compounds is an important and promising task.

Thus, we obtained a number of ruthenium complexes containing various chelate diphosphine ligands. It was established that the redox potential of Ru (III) – Ru (II) transition measured by cyclic voltammetry correlates with the structure of ruthenacarborane [2]. The performed investigations allowed us to found the most effective synthetic approaches to complexes with various length of atom chain in the bridge of chelate ligand [3]. A method for synthesis of complexes with nitrile ligands based on *exo-nido* to *closo* rearrangement in the nitrile media with the participation of amines as reducing agents has been developed.

All compounds were isolated in individual state and characterized by IR, two-dimensional NMR and EPR spectroscopy. The structure of the most compounds was confirmed by X-ray structural analysis.

It is shown that the synthesized ruthenium complexes are capable of catalysing radical polymerization of methyl methacrylate when introduced at a concentration of 0.01 mol.%. The best control over the process is achieved using catalytic systems based on ruthenacarboranes with diphosphine ligands containing ortho-phenylenecycloborated fragments and substituents in the lower belt of the carborane cage.



$R = CH_3CN, Cl,$
PP=dppe,dppmbz,
dppbz,dppf

$R = CH_3CN, Cl$
$X = no, >C(CH_3)_2, >NH$

$R_1 = -CH_3, -Ph, -C_4H_9;$
$R_2 = -CH_3, -Ph, -H$

Figure 1. Objects of research

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TOWARDS IDEAL CHELATORS FOR LEAD AND BISMUTH FOR NUCLEAR MEDICINE APPLICATIONS

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The development of metal-based radiopharmaceuticals represents a dynamic and rapidly growing research area that requires an intimate knowledge of metal coordination chemistry and ligand design. Lead and bismuth radionuclides are particularly attractive due to their favorable emission characteristics. On the one hand, ^{203}Pb ($t_{1/2}$ = 51.9 h) and ^{213}Bi ($t_{1/2}$ = 45.61 min) are suitable for SPECT imaging as they release γ-photons during their decays. On the other hand, ^{212}Pb ($t_{1/2}$ = 10.6 h) decays by $\beta-$ emission and is an *in vivo* generator of the α-emitting daughter ^{212}Bi ($t_{1/2}$ = 60.55 min).

For the last years, significant effort has been made to find optimal chelators for radionuclides, and many different chemical scaffolds have been proposed. Our strategy is to obtain chelators whose structure combines rigid and flexible fragments, which allows us to combine their advantages in one molecule, namely, rapid complex formation and *in vivo* stability of the resulting complex. We have proposed chelators of both macrocyclic and acyclic structures, which contain a rigid aromatic fragment (Figure 1).

In a series of research,[1-4] the influence of the ligand structure, namely its size and rigidity, the type of chelating arms, on the binding behavior with Pb^{2+} and Bi^{3+} ions was assessed. Comprehensive studies of the complexing characteristics of the developed chelators, including thermodynamic stability and structure of their complexes, radiolabeling, *in vitro* and *in vivo* stability, made it possible to identify the most promising chelators for further use in nuclear medicine.

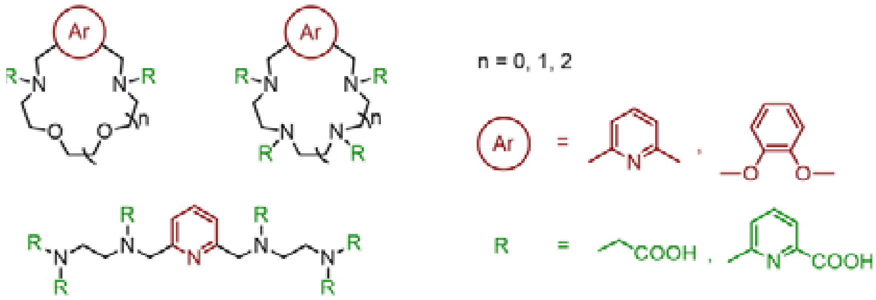

Figure 1. Structures of developed chelators.

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Acknowledgements
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ORAL PRESENTATIONS

YOUNG SCIENTISTS PRESENTATIONS

SPIROCYCLIC RU-CARBENE BASED CATALYSTS OF THE ETHENOLYSIS OF FATTY ACID METHYL ESTERS: THE EFFECTS OF LIGAND STRUCTURE AND REACTION TEMPERATURE

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Ethenolysis of methyl oleate and fatty acid methyl esters (FAMEs), obtained from renewable feedstocks, is currently viewed as one of the most promising processes in modern oleochemistry.

Spirocyclic alkyl amino carbene (SCAAC) Ru complexes, synthesized and studied in recent years, meet the industrial requirements to homogeneous catalysts of the ethenolysis of FAMEs on catalytic productivity. However, FAME conversion, selectivity of the formation of dec-1-ene and methyl dec-9-enoate as well as synthetic availability of SCAAC-Ru catalysts still need to be upgraded. In the present study we propose efficient and scalable synthetic approach to SCAAC ligand precursors, based on hydroformylation of substituted indenes, dihydronaphthalenes and their analogs. Comparative study of new Ru SCAAC complexes Ru7–Ru12 and previously obtained complexes Ru3–Ru6 in ethenolysis of FAME, prepared from technical grade oleic acid, have revealed the importance of the factor of reaction temperature, affecting both catalyst productivity and selectivity[1]. In particular, octahydroanthracene-based Ru complex Ru11 demonstrated the highest productivity (TON ~275000) whereas the complex Ru12, containing chromane spirocyclic fragment, showed temperature-independent catalytic activity (TON ~150000 at 15–50 °C) and unprecedented 99.7–99.9% selectivity.

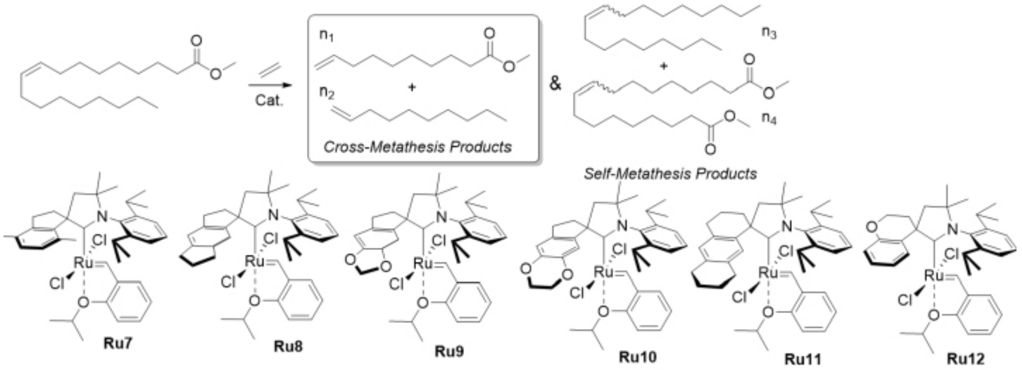

Figure 1. Ethenolysis of methyl oleate

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CATALYTIC INSERTION OF NITRENES INTO B-H BONDS

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Currently, a vast number of methods exist for the enantioselective formation of bonds between two carbon atoms. However, only a few approaches to the creation of isoelectronic boron-nitrogen bonds are known. Due to charge polarization and higher reactivity, these bonds can be even more useful for a variety of applications. Moreover, catalytic methods for the synthesis of chiral boron compounds have only emerged in the past few years.[1,2] This study proposes a new approach to such compounds based on a previously unknown reaction of nitrenes insertion into B-H bonds.

The starting boron-containing compounds were synthesized via the reaction of BBr3 with substituted 2-phenylpyridines, followed by reduction with LAH. Various sulfonamides and sulfamates were employed as nitrene precursors. The reaction was catalyzed by rhodium and ruthenium carboxylates; chiral compounds were synthesized using catalysts derived from optically pure amino acids. A representative series of insertion products was obtained, with yields ranging from 24% to 89% and enantioselectivities reaching up to 91:9 e.r.

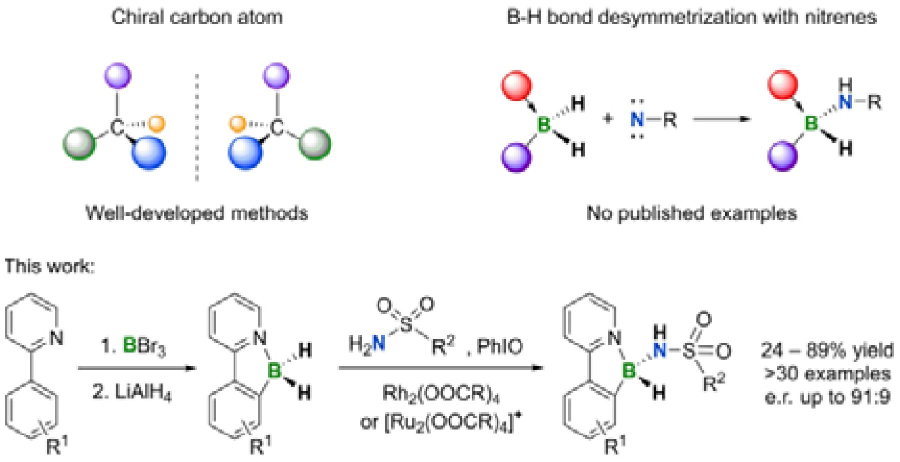

Figure 1. Synthesis of compounds with chiral boron atom.

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Acknowledgements
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HOVEYDA-GRUBBS-TYPE CATALYSTS COMPRISING A SIX-MEMBERED CHELATE RING

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Catalytic olefin metathesis in presence of Hoveyda-Grubbs-type ruthenium complexes is a highly effective method for synthesizing complex molecules with a wide range of valuable properties.

Comprehensive research was conducted to develop methods for synthesizing ruthenium catalysts containing a six-membered chelate ring with various donor heteroatoms (oxygen, sulfur[1], selenium[2], nitrogen[3-5]).

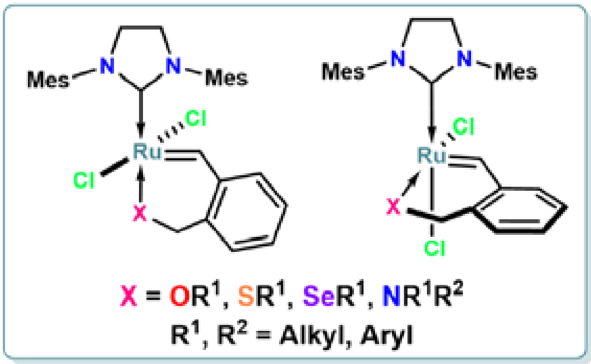

Figure 1. Hoveyda-Grubbs-type complexes with six-membered chelate ring.

It is possible to predict the impact of the arylidene ligand structure on the catalytic properties of the resulting complexes. Catalytic tests revealed key correlations between their structure and efficiency in the olefin metathesis reaction. Nitrogen-containing ruthenium chelates were successfully utilized to develop an efficient method for constructing product-like scaffolds.[6]

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The work has been supported by the RUDN University Scientific Projects Grant System, project № 021408-2-000.

CpRh(III)–CATALYZED TWO-FOLD C-H ACTIVATION/ ANNULATION REACTIONS OF TEREPHTHALIC ACID FOR THE SYNTHESIS OF UNSYMMETRICAL OCTA-SUBSTITUTED ANTHRACENES

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The rhodium(III)-catalyzed C–H activation of benzoic acids and their subsequent annulation with alkynes proved to be one of the most efficient methods for the synthesis of isocoumarins and PAHs, which are promising organic scaffolds for use in organic electronics.[1-4] This approach allows to create a polycyclic framework in one step with high atom-economy. Polycarboxylic acids are also an extremely interesting substrate for such reactions, because their annulations may open a new way to the synthesis of anthracene derivatives and polycyclic isocoumarins containing several fragments with different properties within a single molecule for further use as a components in light-emitting materials. Notably, the classical approaches to the construction of an octa-substituted anthracenes are based on the application of coupling reaction of tetraiodobenzene with zirconacyclopentadienes[5] or alkynes, catalyzed by palladium[6] or nickel complexes.[7]

Herein, we report the synthesis of unsymmetrically octa-substituted anthracenes in a few simple steps from readily available terephthalic acid based on the preliminary protection of one of the carboxyl groups, annulation with the first alkyne coupling partner, further removal of protection group and additional annulation with the second alkyne moiety (Figure 1).

This approach also proved to be suitable for the synthesis of unsymmetrical diisocoumarins, using Cp*$RhCl_2$ instead of $CpRhI_2$ as a catalyst.

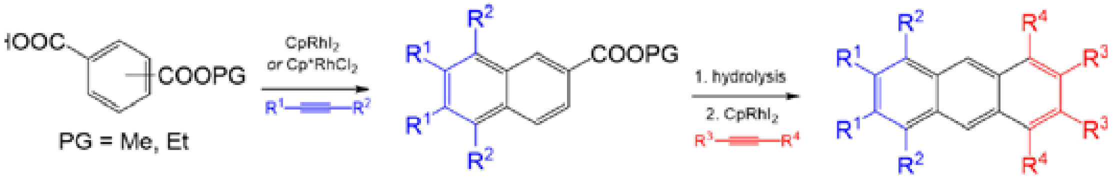

Figure 1. Synthesis of octa-substituted anthracenes based on two sequential C-H activation processes

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AMINOPHENYL PHOSPHATES AS CURING AGENTS FOR PHTHALONITRILE RESINS

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Carbon fiber reinforced polymer composites based on phthalonitrile resins are used in high temperature areas, because of high required properties at high maximum work temperatures. Resin consists of monomers and initiators of polymerization. Also, to use cost-effective molding methods such as vacuum infusion, reactive diluents are used to lower the melting point of the mixture.

Compounds containing a flexible phosphate linker and amino groups were obtained, it allows to cure monomers and exhibit flame retardant properties. The melting points of the synthesized substances [Fig. 1] are at the level of diluents which already allow to use the solvent-free prepreg technique [1].

Purity of the obtained substances was confirmed by ^{1}H, ^{13}C, ^{31}P NMR and mass spectrometry, the melting points were determined by differential scanning calorimetry (DSC). Mixtures of curing agents with phthalonitrile monomers were prepared and studied by DSC and rheological tests. Plastics were made on the basis of obtained resins, they were studied by dynamic mechanical analysis (DMA), glass transition temperatures were obtained. Carbon fiber reinforced plastics were made by solvent-free prepreg technique, mechanical and thermal properties were characterized.

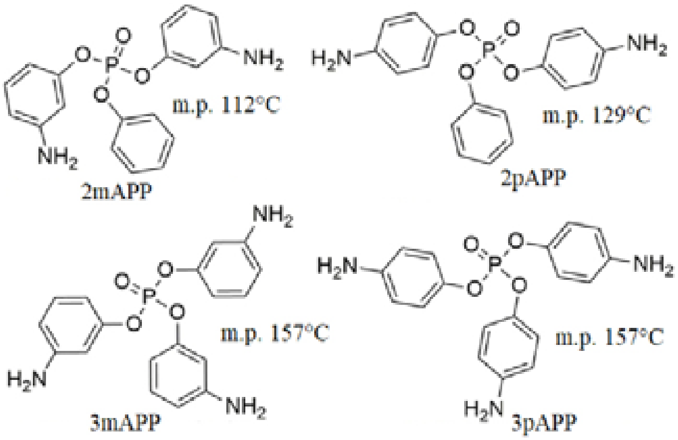

Figure 1. Research objects

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Acknowledgements
The study was carried out within the framework of the State Task no. AAAA-A21-121011590086-0.

ARE SIMPLE METAL SALTS AND HARSH REACTION CONDITIONS ALWAYS NONSELECTIVE IN CATALYTIC ORGANIC SYNTHESIS?

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As new synthetic methods are developed, researchers have common perception that milder conditions generally lead to increased process selectivity. However, the milder the reaction conditions, the more complex the catalyst structure tends to be. The multistep synthesis of ligands and target complexes can be a challenging synthetic task. The tendencies of increasing complexity of catalysts and reagents and the search for the mildest reaction conditions may lead to the erroneous conclusion that simple catalytic systems are always nonselective. Is the strategy of synthesizing a complex catalyst so effective, or can an ordinary metal salt be sufficient for the successful performance of certain reactions, despite the harsh conditions?

The use of harsh conditions – high temperatures and pressures, simple gaseous reagents – is typical of industrial chemistry and is not associated with fine organic synthesis. In this work, using the reductive aldol condensation reaction as an example (Figure 1), it was shown that converter gas (CO, CO_2, N_2, industrial steel production waste) can be used as a reducing agent in combination with harsh conditions and a simple metal salt as a catalyst to carry out the selective process. Such counter-intuitive conditions for fine organic synthesis were found to efficiently produce a wide range of substrates, including drugs and products with different functional groups.

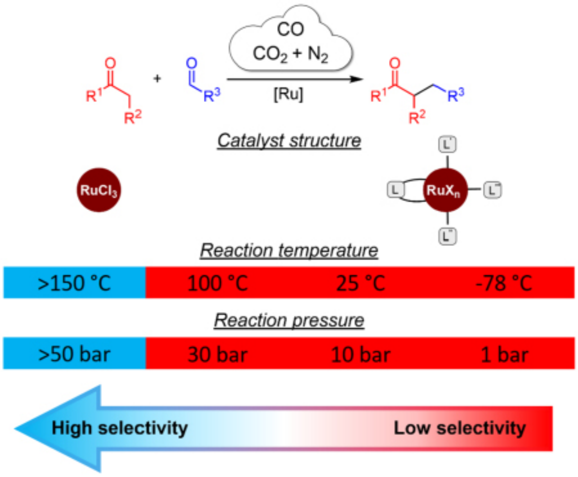

Figure 1. Perceptions of selectivity regarding temperature, pressure, catalyst structure.

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SIMPLIFIED VERSION OF THE ESCHWEILER-CLARKE REACTION

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Alkylation of amines is an important section of modern organic chemistry. Among this section, the methylation reactions of amines stand out by their diversity.

The Eshweiler-Clarke reaction is one of the simplest and most convenient reactions for methylation of amines. This reaction requires only amine, formalin and formic acid, which plays the role of reducing agent in this process. This method, however, has a few shortcomings. For example, a successful process requires the use of a nine-molar solution of formic acid, which makes this method incompatible with substances containing acidophobic groups.

At the same time, formaldehyde itself can act as a reducing agent. Therefore, this work was devoted to the study of the possibility of methylation of amines by formaldehyde without the use of an additional reducing agent.[1]

Our approach is applicable to a wide range of secondary amines. Thus, we were able to introduce compounds with a number of acidophobic groups into the reaction, whereas the classical conditions with the addition of formic acid proved to be non-tolerative to these groups (Fig.1).

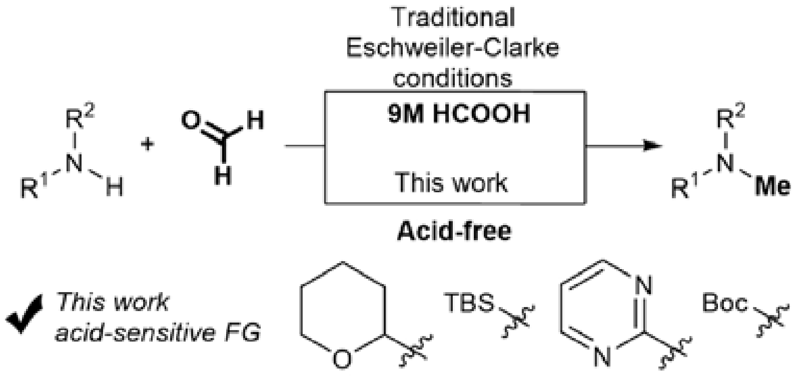

Figure 1. Comparison between traditional Eschweiler-Clarke conditions and acid-free conditions

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THERMAL AND MECHANICAL PROPERTIES OF POLYETHERSULFONES OF COPOLYMER STRUCTURE

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Polyethersulfones (PES) are a class of aromatic heterochain polymers consisting of aromatic structures linked by ether [-O-] and sulfone [-SO_2-] groups. PES are characterized by high thermal and chemical resistance, mechanical strength, biocompatibility and dielectric properties. Polyethersulfones are widely used in many areas of industry, such as aviation, automotive and medical, as well as in electronics, instrument making, 3D printing, etc.[1,2]

In the presented work we have synthesized and investigated PES of copolymer structure (Figure 1) obtained by interaction of a mixture of 2,2-bis(4-hydroxyphenyl)propane (70% mol.) and 3,3-bis-(4-hydroxyphenyl) phthalide (30% mol.) with 4,4'dichlorodiphenyl sulfone (DCDPS). The molecular weight of PES was adjusted by controlled violation of equimolarity in the ratio of the precursors using an excess or a deficiency of DCDPS up to +/- 4 % mol. This approach also allowed to obtain PES with different end groups: phenolic or chlorobenzene.

The molecular weight of the obtained thermoplastics was determined by measuring their reduced viscosity as 0.5 wt % solution in dimethylformamide (DMFA) and by gel permeation chromatography (GPC). The possibility of the processing of the obtained PES by the methods of moulding and extrusion was evaluated by studying theie Melt Flow Indexes (MFI) at 350 °C and a load of 5 kg (0.6 MPa).

The reduced viscosity of the obtained polyethersulfones at equimolar content of initial reagents was 1.23 dl/g, which, according to GPC, corresponds to a molecular weight of 350 kDa. The deviation from the equimolar ratio of the initial reagents led to a gradual decrease in the molecular weight up to 18 kDa.

The PES obtained at equimolar ratio of the initial reagents had MFI=0.1 g/10min and was unsuitable for processing by moulding or extrusion. However, when using an excess of DCDPS from 1 to 4% mol., the increase in MFI up to >50 g/10 min was observed. It is noteworthy that the observed pattern was violated in the case of using of a lack of DCDPS. When more than 2 % mol. deficit of DCDPS was used, the MFI of the obtained PES was decreased. It is suggested that the observed extreme dependence of MFI is associated with the accumulation of reactive phenolic groups at the ends of macromolecules which leads to the branching and cross-linking reactions.

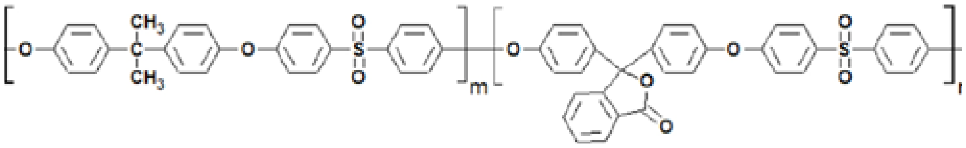

Figure 1. PES of copolymer structure

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OXO/IMIDO HETEROMETATHESIS: TOWARDS SIMPLER CATALYSTS

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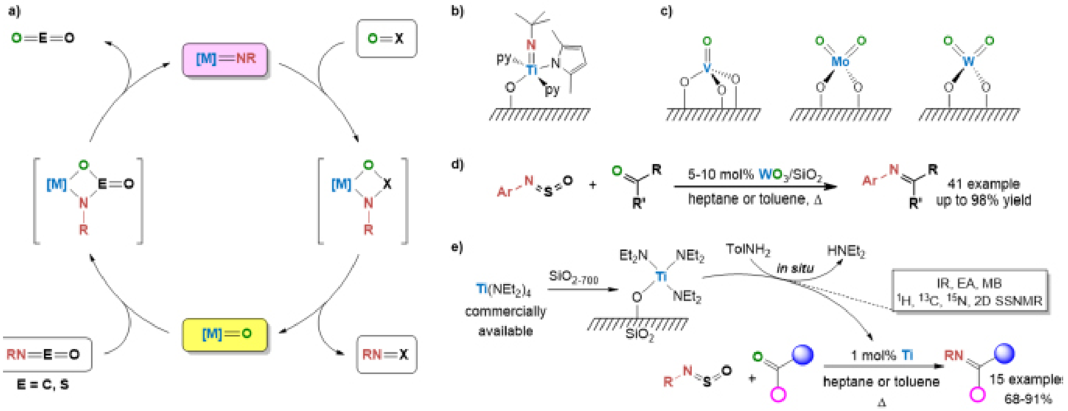
TM-catalyzed oxo/imido heterometathesis[1] (Scheme 1a) opened a new nontrivial approach to X=N (X = C, S) bond construction. Recent advances in the field of silica supported Ti imides (Scheme 1b) designed via Surface Organometallic Chemistry (SOMC) techniques allowed us to unlock noticeably the applied potential of the method. Yet, such catalysts are prepared in several steps and require strictly inert conditions, which hampers their routine application.

In search for the more available and stable catalytic systems, we turned our attention to V, Mo and W oxides dispersed on silica (Scheme 1c) as robust and cheap industrial materials. All of the supported oxides revealed activity in heterometathesis, WO_3/SiO_2 being the most efficient. W-catalyzed imidation of ketones with N-sulfinylamines (Scheme 1d) was found to produce a broad range of imines including ones hardly accessible by classical methods. Noteworthy, WO_3/SiO_2 was only slightly inferior to silica-supported W imides designed via SOMC approach[2].

Since Ti-based systems are dramatically superior to the others, we regarded *in situ* generation of supported Ti imides as another option for the design of available and efficient catalysts. Commercially available $Ti(NEt_2)_4$ grafted onto silica and activated *in situ* with aniline was found to have activity comparable to that of the best catalysts known to date, allowing facile synthesis of various imino-derivatives (Scheme 1e). Detailed physicochemical study of surface species in this system, including solid state ^{15}N NMR, was performed.



Scheme 1. a) Oxo/imido heterometathesis catalytic cycle. b) The most active catalyst reported to date. c) Surface metal-containing sites of MO_x/SiO_2. d) WO_3/SiO_2-mediated synthesis of imines. e) Application of in situ generated silica-supported Ti imido species as a catalyst in oxo/imido heterometathesis.

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Acknowledgements
This work was supported by Russian Science Foundation, Grant No. 19-73-10163

STUDY OF THE POSSIBILITY OF IN SITU SYNTHESIS OF NICKEL PHOSPHIDES FROM RED PHOSPHORUS IN THE MEDIUM OF 1,4-DICHLOROBENZENE

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In the process of polyvinyl chloride pyrolysis, a liquid product (pyrolysis oil) with a high content of chloraromatic, unsaturated cyclic and aliphatic chlorine-containing compounds of various structures is formed[1], [2]. Thus, the liquid pyrolysis product may contain 2-chloro-2-methylpropane, 2-chloro-2-methylpentane, α-chloroethylbenzene, 2-chloro-2-phenylpropane, α-chloroethylbenzene with C8 and C9 alkyl chain length, polycyclic aromatic hydrocarbons[3, 4]. The presence of even a small amount of chlorine-containing compounds in pyrolysis oil does not allow its use as fuel or petrochemical feedstock.

Hydrodechlorination of pyrolysis oil allows solving the problem of high chlorine content in it. For hydrodechlorination are proposed: transition metals in reduced form[5], catalysts based on noble metals[6], transition metal sulfides[7]. The latter are characterised by high stability and resistance to deactivation. In the last decade phosphide catalysts have been actively investigated, including in the hydrodechlorination process8.

The aim of the work: to investigate the possibilities and regularities of the formation of unsupported nickel phosphide *in situ* in the medium of 1,4-dichloribenzene; to establish the optimal conditions for the synthesis of the catalyst in the process of processing of the model mixture.

The activity of phosphide catalysts synthesised in situ in the hydrodechlorination reaction of 1,4-dichlorobenzene was compared in this work. Ni_2P catalyst shows the highest activity in the hydrodechlorination reaction. Moreover, the more active form is formed from oil-soluble precursors (e.g. triphenylphosphine and 2-ethylhexanoate of nickel).

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LITHIUM BIS(DIFLUOROPHOSPHORYL)IMIDE SYNTHESIS AND ITS FEATURES

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The vast range of applications of organic and inorganic lithium salts includes lithium-ion batteries, ceramics and glass, pharmacology, metallurgy and pyrotechnics.[1,2] Most applications require lithium-containing products to achieve high hydrolytic and thermal stability. Phosphorus-nitrogen compounds characterized by high heat resistance[3] and ease of functionalization seem to be a promising basis for new lithium salts.

Within this work, we synthesized bis(dichlorophosphoryl)imide (BDCPI) via hydroxylation of trichlorophosphazodichlorophosphonyl (TCDP) with various reagents, and studied the possibility of performing a one-stage fluorination-lithiation reaction of BDCPI with lithium fluoride (fig. 1).

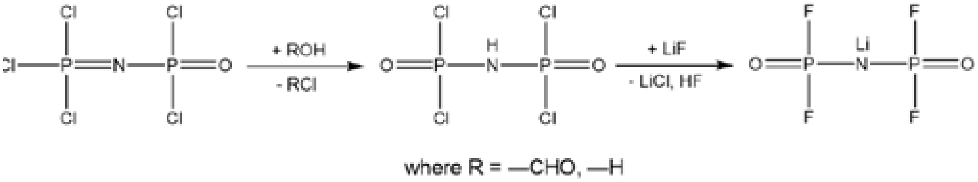

Figure 1. Scheme for obtaining lithium bis(difluorophosphoryl)imide from trichlorophosphazodichlorophosphonyl

The resulting products and intermediates were analyzed by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy, ICP-MS. Assumptions about the mechanisms of side processes were made, confirmed by carrying out model reactions of BDCPI hydrolysis and TCDP fluorination. Aspects of the coordination of lithium atoms on nitrogen and oxygen atoms in the bis(difluorophosphoryl)imide molecule are considered. It was found that at the final stage of the process, the hydroxylating agent ROH enters into a competitive interaction with the target BDCPI, which leads to the undesirable retention of 5 to 20% of the initial TCDP in the product. During further interaction of the obtained product with lithium fluoride, the presence of residual TCDP in the system leads to the formation of a hydrolytically unstable anion $[PF_6]^-$. The influence of process temperature on the occurrence of side reactions was also studied.

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Acknowledgements
The work was carried out with financial support from the Ministry of Education and Science of Russia (project FSSM-2023-0003, grant agreement No. 075-03-2024-160)

PHOTOCHEMICAL METHOD DEVELOPMENT FOR THE SYNTHESIS OF FIVE-MEMBERED METALLACYCLOCUMULENES AND STUDY OF THEIR REACTIVITY

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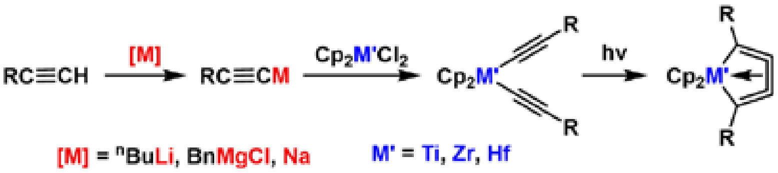
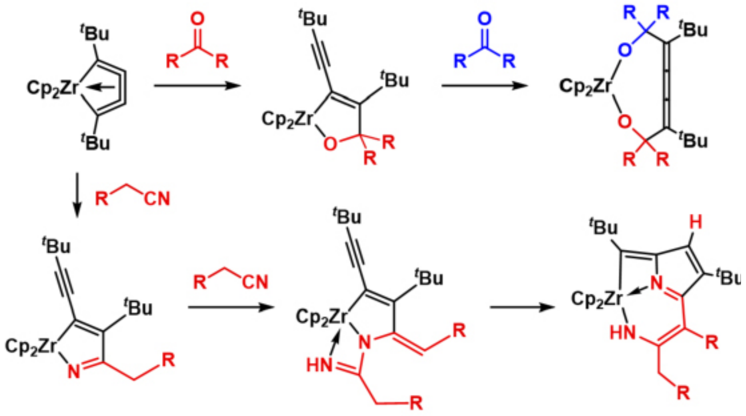
At present, a fairly large number of five-membered metallocyclocumulene complexes have been obtained. Most methods for the preparation of such compounds are based on the interaction of active forms of metallocenes with diacetylenes. The use of terminal acetylenes instead of diacetylenes may increase the synthetic availability of these complexes. We have developed a simple method for the synthesis of five-membered metallacyclocumulenes $Cp_2M(\eta^4\text{-}RC_4R)$ (M = Ti, Zr, Hf) starting from Cp_2MCl_2 and terminal acetylenes by UV-irradiation of metallocene diacetylides (Scheme 1).



Scheme 1. Preparation of metallacyclocumulenes from terminal acetylenes and Cp_2MCl_2.

We investigated some of the chemical properties of obtained metallacyclumulenes (Scheme 2). The insertion reactions of various ketones[1] and nitriles into the M-C bond upon heating or UV irradiation have been studied. The difference in the reaction direction is shown. In the case of ketones, unsymmetrical nine-membered dioxazirconacyclocumulenes were obtained.



Scheme 2. Reactions of metallacyclocumulenes with ketones and nitriles using the example of $Cp_2Zr(\eta^4\text{-}{}^tBuC_4{}^tBu)$.

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Acknowledgements
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QUANTUM DOT - APTAMER SYSTEM FOR ONCOVISUALIZATION BY BINDING EGF RECEPTORS

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Semicondutor quantum dots (QDs) have a number of advantages over existing luminophores (stability, variability of photoluminescence spectra and particle size, the ability to change QD characteristics by changing the synthesis conditions). Therefore they can be considered as a basis for the development of new biosensors potentially useful for clinical diagnostics, immunobiological studies, etc.

To create hybrid systems of the QD-aptamer type, it was necessary to obtain QD that are stable in water solutions and carry functional groups for attaching biological ligands on QD's surface. Aptamers, chosen as ligands, are oligonucleotides with a complex three-dimensional structure, which provides the ability of aptamers to structurally bind molecules, both small and large. In addition, aptamers have great advantages, such as small size, basic chemical stability, universal and rapid synthesis, as well as the ability to modify the structure and add various functional groups to the main chain of the aptamer.

The aim of this work was to create QD-Aptamer complexes that have, on the one hand, photoluminescent principles of QD, and, on the other, specificity of interaction with epidermal growth factor receptors (EGFR). The presence of EGFR in large quantities on the cell surface is a world-wide recognized cancer marker.

At the first stage, CdSe / ZnS QDs stabilized with oleic acid were synthesized. To transfer the particles into a water-sol state, a special copolymer was synthesized containing a thiol for interactions with the QD surface, as well as free carboxyl groups. Due to these carboxyl groups on the surface of the QDs, complexes with the Gol1 aptamer, containing the active NH2 group (interacting with the –COOH polymer at the surface of particles) were obtained. Aptamer Gol1 provides a specific interaction with the EGFR protein. We analyzed the resulting complex, as well as its interaction with the EGFR protein by dynamic light scattering and enzyme immunoassay.

The study was supported by a grant from the Russian Science Foundation No. 24-23-00551, https://rscf.ru/en/project/24-23-00551/

SLIPPERY COATINGS BASED ON POLYMER MATRICES WITH GRAFTED FLEXIBLE SIDECHAINS

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Slippery coatings are coatings on which the sliding angles of test liquid droplets are less than 10º. Omniphobic slippery coatings are slippery coatings that repel not only water, but also oils with low surface tension (e.g., saturated hydrocarbons). One of the promising methods for imparting omniphobic properties to a surface is to apply thin polymer films doped with a low-surface-tension lubricant (SLIPS coatings – slippery liquid-infused porous surfaces[1]). Such coatings demonstrate high resistance to external pressure, extremely low sliding angles of test liquids (<1º), and resistance to mechanical impacts. However, washing out the lubricant leads to degradation of the properties of such coatings, while the force of droplet adhesion to the coating increases with decreasing content of lubricant[2]. One of the effective ways to increase the stability of such coatings is chemical grafting of lubricant molecules to the coating matrix[3].

In this work, we study the possibility of increasing the durability of films by creating stable siloxane coatings with flexible chains of monovinyl terminated PDMS covalently grafted to the polymer matrix. Carbon dioxide under pressure is used as a solvent for applying films. The non-monotonic dependence of the slip angle of test water drops on the amount of grafted side chains of the lubricant is studied. The relationship between the elastic properties of the obtained films and their slippery properties is studied. The synthesis technique proposed in the work allows applying coatings not only to smooth substrates, but also to surfaces of complex morphology while preserving the structure of the material (in particular: fabrics, carbon aerogels). It was shown for fabrics that coatings with grafted chains are more resistant to machine washing compared to similar coatings without grafted chains. For carbon aerogels modified with the obtained films, selective properties for separating oil-water mixtures were revealed - they are able to absorb hexane, chloroform from water. The work shows that the porosity of modified carbon aerogels is preserved with their successful internal hydrophobization.

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The project was financially supported by Russian Science Foundation, grant no. 22-73-10185.

PHYSICOCHEMICAL EXPERIMENTAL METHODS AND COARSE-GRAINED MOLECULAR DYNAMICS SIMULATIONS FOR STUDY OF POLY(3-HYDROXYBUTYRATE) CRYSTALLIZATION

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Poly(3-hydroxybutyrate) (PHB) and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-HV) are storage compounds synthesized by the bacteria *Azotobacter chroococcum*. These semi-crystalline polymers are both biodegradable and biocompatible, which allows them to be used for a variety of biomedical applications. The key factor of the physicochemical properties of materials based on PHB and PHB-HV is the distribution of amorphous and crystalline phases[1]. The goal of our work was to understand how these phases arise and how they interact with each other. Five PHB and PHB-HV samples with molecular weights ranging from 3.84×10^5 to 1.095×10^6 g/mol were used for the current study. Raman spectroscopy, differential scanning calorimetry, and surface-free energy calculations were carried out for their physicochemical characteriazation. From our experiments, it was found that samples had similar values of surface free energy. Three different boxes of molecular dynamics simulations representing three different hypotheses were set up: a box according to a classical theory of nucleation, a box with shear flow, and a box with heightened hydrophobic interactions. Our simulations showed that a box according to the classical theory of nucleation demonstrate the smallest amount of self-organization while the heightened hydrophobic interactions give rise to configurations that resemble reality the most. From our results, we can conclude that for semi-crystalline biopolymers such as PHB, hydrophobic interactions play a significant role in self-organization during the crystallization process.

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HYBRID CATALYSTS IN C-N COUPLING UNDER VISIBLE-LIGHT

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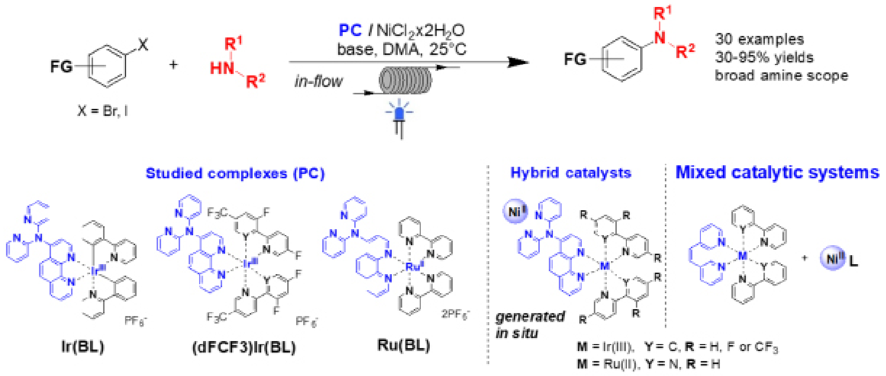
Metallaphotoredox catalysis, being a combination of visible-light photocatalysis and transition metal catalysis, is a perspective methodology for carrying out organic transformations under mild reaction conditions.[1] The C(sp^2)-N bond formation via photoredox Ni-catalysis «in-flow» is of great interests to synthesize valuable products because it allows to make synthesis rapid, easy to scale-up and cost-effective in terms of energy consumption.[2] The success of metal-photoredox-catalyzed cross-coupling reaction depends on the efficiency of electron or energy transfer process between photocatalyst and transition metal complex. Combining Ru- or Ir-based photocatalyst and Ni complex in one molecule (dinuclear complex) using bridging ligand (**BL**) may promote these processes.[3]

In this work *N,N*-di(pyridin-2-yl)-1,10-phenanthrolin-4-amine was used to prepare the Ir(III) and Ru(II) complexes **Ir(BL)**, **Ir(BL)(dfCF3)** and **Ru(BL)**, bearing additional chelating unit capable of coordinating nickel (Scheme 1). These complexes were studied as *in situ* precursors for hybrid catalysts in Ni-catalyzed amination reaction under visible-light (455 nm, 12W). The comparison of hybrid catalysts activity with mixed catalytic systems «*in-batch*» and «*in-flow*» is discussed. The advantage of binding photocatalytic and metal complex blocks using bridging ligand is demonstrated. A representative series of arylamines of various structures have been synthesized «*in-flow*» using these catalytic systems.



Scheme 1.

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PERFLUOROARYL-SUBSTITUTED PYRAZOLE BASED PLATINUM COMPLEXES

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To date, the biological activity of platinum complexes with ligands based on various heterocycles, as well as their use in medicine as antitumor agents, is being actively studied[1]. Usage of cisplatin, oxaliplatin, and carboplatin is limited by a number of side effects, prompting scientists to investigate more effective compounds. It was found that Pt(II) complexes containing pyrazole rings produced more extensive DNA fragmentation than cisplatin[2].

This paper presents a modified method for the synthesis of fluorine-containing trisubstituted pyrazoles, as well as the production of platinum complexes based on them (fig.1) and the study of the properties of new compounds. Such complexes exhibit luminescence when exposed to UV radiation.

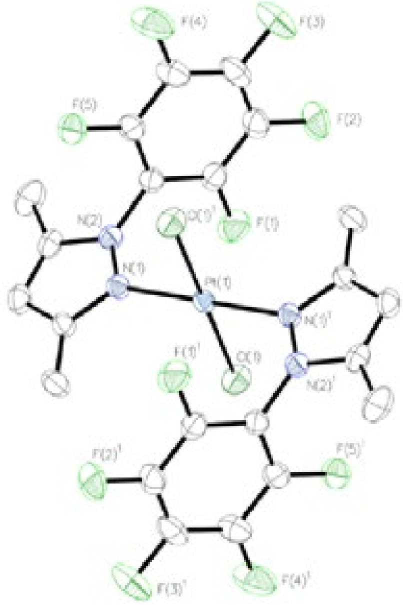

Fig.1. Structure of the platinum(II) complex with 3,5-dimethyl-1-(perfluorophenyl)-1H-pyrazole

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SYNTHESIS OF POROUS CROSS-LINKED AMINOSUBSTITUTED POLYPHOSPHAZENE MATERIALS

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Nowadays, polymeric materials are an essential part of every people's life. Most of the large-scale polymers are organic macromolecules of linear or branched spatial structure. Porous structures are of a particular significance among them, which are able to absorb and release low molecular weight compounds due to their highly enhanced surface area. These polymers can be used for gas separation, liquid chromatography, sorption of metals, extraction processes, water purification, as sensors, and as components of catalytic systems and drug delivery systems[1,2,3].

Cyclic piperazine and linear N,N'-ethylenediamine were used as amines and tetrahydrofuran and dioxane were used as solvents. Purification was carried out by extraction in a Soxhlet apparatus using chloroform or methanol. The scheme of synthesis on the example of obtaining piperazine-containing cross-linked phosphazene is presented in Figure 1.

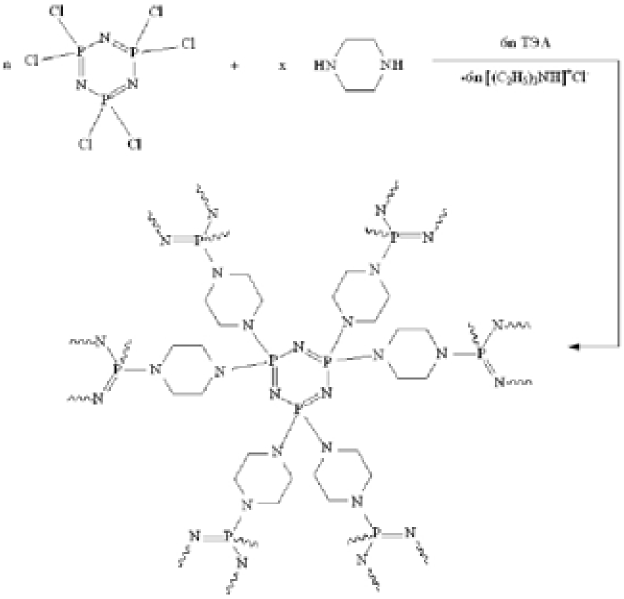

Figure 1. Scheme for obtaining piperazine-containing cross-linked phosphazene

The obtained products were analyzed by SEM, FT-IR spectroscopy and ASAP method. It was found that samples with the highest porosity were obtained using piperazine and tetrahydrofuran. The solvent used for purification did not affect the properties of the final product.

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DI- AND TRIPHENYLCYCLOPENTADIENYL RHODIUM COMPLEXES AS HIGHLY EFFECTIVE CATALYSTS FOR SP^2 C–H ACTIVATION

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Nowadays, rhodium complexes are widely used in homogeneous catalysis, in particular, for the synthesis of naturally occurring heterocyclic scaffolds via C-H activation reactions.[1] In most of these catalysts, rhodium is supported by a cyclopentadienyl ligand. Functionalization of the latter leads to changes in catalytic activity, chemo- and regioselectivity.[2] In particular, the use of electron-deficient cyclopentadienyl ligands, containing CO_2Et groups, allowed the reactions to be carried out at room temperature.[3] Herein we report the synthesis of di- and triphenylcyclopentadienyl rhodium complexes, which demonstrated the highest catalytic efficiency among known catalytic systems. We would also discuss their application for the synthesis of isocoumarins and indoles via catalytic C-H annulation reactions.[4]

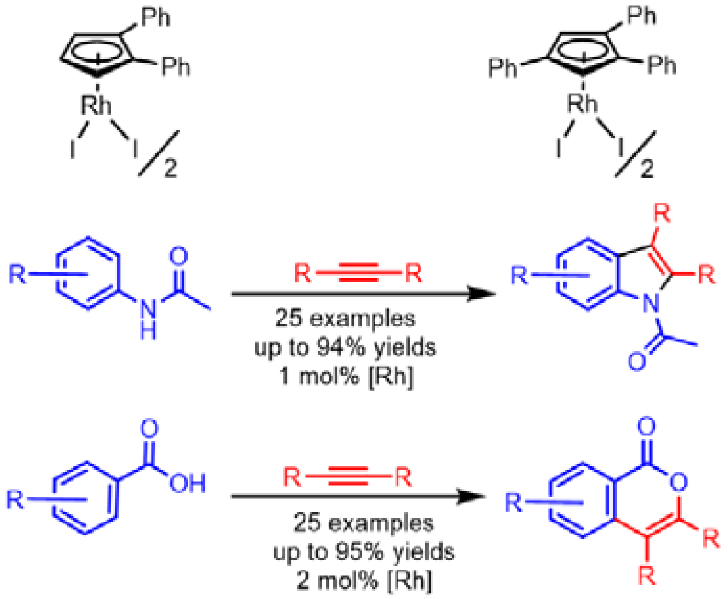

Figure 1. The rhodium catalysts and catalytic reactions studied in the present work.

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RATIONAL DESIGN OF ANSA-HETEROCENES WITH A LONG SIOSI BRIDGE AS A CATALYSTS FOR SELECTIVE DIMERIZATION OF OCT-1-ENE

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Methylenealkanes $RC(=CH_2)CH_2CH_2R$ are valuable raw materials for the synthesis of branched functionalized organic compounds with a wide variety of uses. Selective coordination dimerization of α-olefins is a simple and inexpensive way to methylenealkanes, however, currently known dimerization catalysts possess low productivity, TON ~ 10^3.

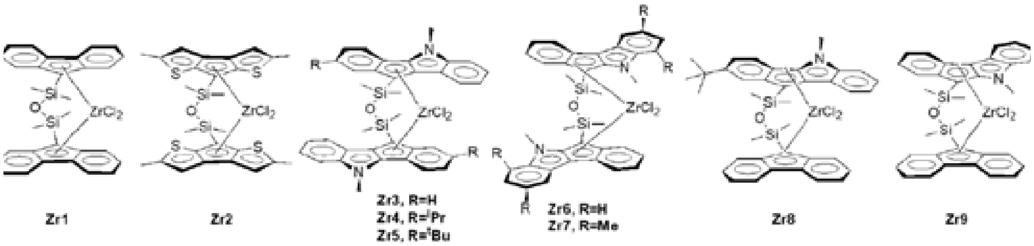

Figure 1. Promising (Zr1-Zr9) heterocenes for selective dimerisation.

Novel $-SiMe_2OSiMe_2-$ bridged Zr1-Zr9 ansa-zirconocenes derivatives of 9H-fluorene, cyclopenta[1,2-b:4,3-*b*']dithiophene, 5,10-dihydroindeno[1,2-*b*]indole and 5,6-dihydroindeno[2,1-*b*]indole have been synthesised. The complexes were characterised by NMR spectroscopy and X-ray diffraction analysis[1] and studied in the dimerization of oct-1-ene using the activators MMAO-12 and TIBA/$[PhNMe_2H][B(C_6F_5)_4]$ at [oct-1-ene]/[Zr] molar ratio of $3{\cdot}10^4$ in the absence and in the presence of H_2. In the absence of H_2, Zr6 and Zr7 complexes showed high activity and dimerization selectivity up to 94%, when $[PhNMe_2H][B(C_6F_5)_4]$ was used as an activator. In H_2 atmosphere, when the Zr9 complex was activated with TIBA/[PhNMe2H] $[B(C_6F_5)_4]$, the dimerisation selectivity reached more than 99% and no dimer hydrogenation was observed.

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NOVEL SOLUTION-PROCESSABLE [1]BENZOTHIENO[3,2-B][1]- BENZOTHIOPHENE DERIVATIVES AS PROMISING MATERIALS FOR HIGH-PERFORMANCE ORGANIC FILED-EFFECT TRANSISTORS

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Derivatives of [1]benzothieno[3,2-b][1]benzothiophene (BTBT) are one of the most popular types of compounds used in basic elements of organic electronics – organic field effect transistors (OFETs) with high mobility. Excellent chemical and thermal stability of the BTBT fragment allows both variation of conjugated substituens and solubilizing groups or groups contributing to the self-organization of semiconductor molecules in crystals. The high degree of planarity of molecular semiconductors and the ability to self-organize, along with high processability, allows the use of BTBT derivatives in devices with various configurations: high performance OFET, electrolyte gated OFET, organic light emitting transistors, phototransistors, etc[1]. In addition to these peculiarities, it is possible to vary the position of solubilizing substituents in conjugated fragments to achieve useful properties[2].

Novel dithienyl derivatives of BTBT with solubilizing groups in 3, 4 or 5 positions of thienyl rings were synthesized via Suzuki cross-coupling reactions and isolated in pure form (Figure 1). The effect of the position of the alkyl substituents on the optoelectronic, thermal and electrophysical properties of these derivatives of BTBT will be presented. In addition, difunctional monomers were obtained from the compound BTBT-T-C8-3, which showed very high solubility. Thus, the work presents a route to easy processable BTBT-containing conjugated polymers, which are promising for high performance OFETs.

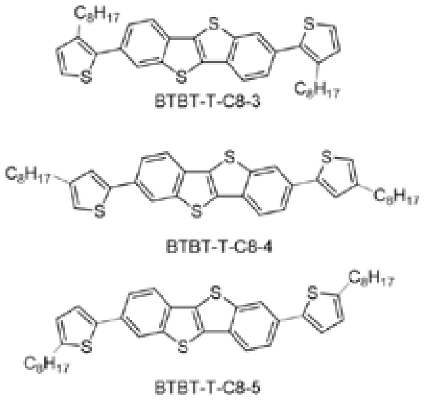

Figure 1. Novel dithienyl derivatives of BTBT

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BISSILYLATION OF NORBORNADIENE – A PATH TO THE NEW POLYMER MATERIALS

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Polynorbornenes have been drawing attention of the scientific community for a long time. The abundance of synthetic approaches for such monomers, their capability to be polymerized by various mechanisms and vast possibilities for polymer modifications provide a wide area of possible applications of such materials. In particular, silyl-substituted polynorbornenes are of interest as materials for gas-separating membranes. It is known that introducing silyl-groups into a polymer leads to the increase in its permeability, while keeping selectivity of gas separation almost the same, and increasing the number of silyl-groups per monomer unit results in strengthening of this effect.

One of the major difficulties in obtaining such polymers is the synthesis of corresponding monomers. Most of the previously proposed methods were multistage[1] and resulted in mixtures of *exo*- and *endo*- isomers[2], inactive in polymerization reactions. One-stage methods of synthesis[3] were not suitable for obtaining di-silyl-substituted norbornenes.

In order to obtain di-silyl-substituted norbornenes the bissilylation reaction of 2,5-norbornadiene with various substituted disilanes was proposed and tried out (Scheme 1). As a result, optimal conditions of this reaction leading to the formation of target di-silyl-substituted norbornenes were found. Thus, the one-step method of synthesis of such substanses was developed. This method does not require the use of hardly obtainable silyl-substituted olefins and metalloorganic compounds. Obtained monomers were involved in ring-opening metathesis polymerization with formation of high-molecular weight products.

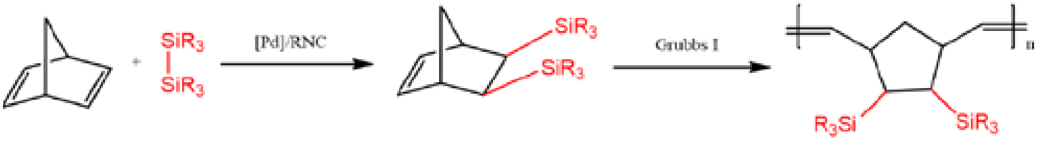

Figure 1. Synthesis of 5,6-*bis*-(trialkylsilyl)-2-norbornene and its polymerisation

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CHLORIDE-ASSISTED TRANSFER HYDROGENATION OF CARBONYL COMPOUNDS BY HALF-SANDWICH RHODIUM IMINOPHOSPHONAMIDE COMPLEXES

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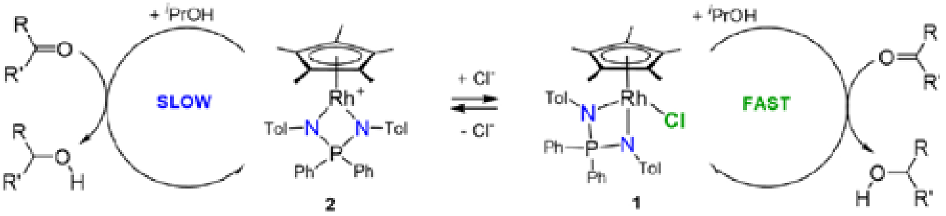
Catalytic Transfer hydrogenation reaction, in which hydrogen atom is transferred from a donor molecule to ketones, is a highly enantioselective process to produce chiral alcohols that has received great attention thanks to the groundbreaking work of Noyori and Ikariya1 discovered highly efficient half-sandwich ruthenium and rhodium complexes with amine-amide or amine-alcoholate ligands.

We have recently reported the synthesis and chemical properties of a series of half-sandwich 18ē and 16ē arene rhodium complexes with a strong σ,π-donating zwitterionic iminophosphonamide (NPN) ligand [Cp*Rh(NPN)(X)] (NPN = Ph$_2$P(NR')$_2$; X = Cl$^-$, PF$_6^-$),$_2$ which are the structural analogues of Noyori-Ikariya catalysts. Indeed, both 18ē [Cp*RhCl(NPN)] (1) and 16ē cationic [Cp*Rh(NPN)](PF6) (**2$^+$PF$_6^-$**) were found to catalyze transfer hydrogenation of carbonylic substrates. Surprisingly, complex **2$^+$PF$_6^-$** performed an order of magnitude slower. The studies on the effect of the added co-ligand (halogen-ions, OTs$^-$, n-ligands) revealed that the activity is strongly enhanced only by chloride. Kinetic studies including KIE and activation parameters measurements carried out for two model ketones (acetophenone and cyclohexanone), as well as model spectroscopic investigation accompanied by the DFT calculations, allowed us to propose unconventional chloride-assisted mechanism of transfer hydrogenation to account for different behavior of 18ē chloride complexes *vs* their less active 16ē cationic counterparts. Large substrate scope including acyclic/cyclic alkyl ketones, aromatic ketones and aldehydes has been tested in the reaction showing that the activity is greatly enhanced by the electron withdrawing substituents in substrate and by electron donating substituents at the N atom in catalyst.



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LUMINESCENT COMPLEXES CU(I) AND AG(I) WITH PYRIDINE-PHOSPHINE: SOLVATOCHROMISM

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Group 11 metal pyrazolate complexes attract the interest of researchers by their ability to form supramolecular systems with a wide range of bases and photophysical properties.[1-2]

Copper(I) and silver(I) pyrazolate adducts were prepared by the reaction of amounts of cyclic trinuclear complexes $[MPz]_3$ (Pz = 3,5-$(CF_3)_2$Pz) and the tris(2-pyridinyl)phosphine(Py_3P). The Cu(I) complexes show emission shifted to the red region. By mixing $[Ag^{I}Pz]_3$ and Py_3P complexes of different compositions are formed. Dinuclear and quadnuclear complexes show emission shifted to the blue region. Phosphorescence at room temperature is characteristic of all complexes. We observed the phenomenon of solvatochromism in the coordination of DCM to the complex.

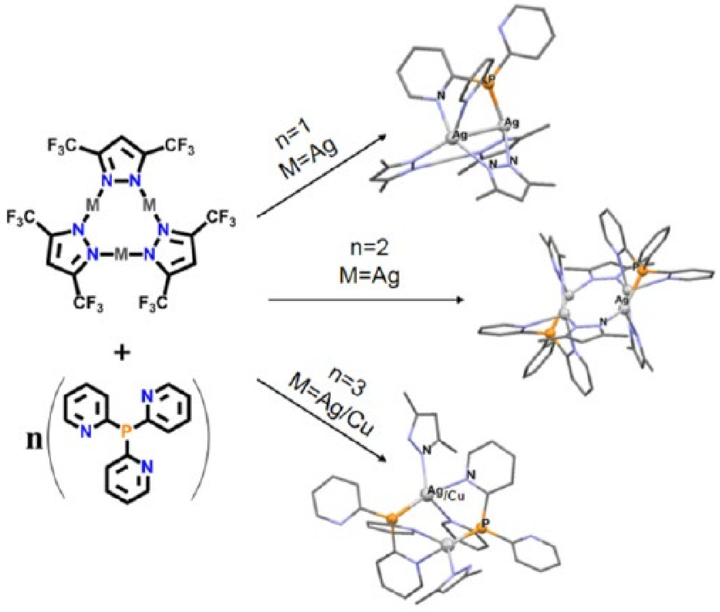

Figure 1. Reaction scheme and XRD structure of complexes

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SORPTION PROPERTIES OF POLYGLYCIDYL ETHERS BASED ON HYDROXYL-CONTAINING POLYMERS

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A pressing issue in many industries is the removal of heavy metals from wastewater involved in industrial chemical and technological processes. Sorption is considered one of the promising methods for purifying aqueous solutions due to its high efficiency, low cost, and simplicity of the equipment and technology used.[1,2].

The aim of the work was to synthesize and study the sorption capacity of polyglycidyl ethers based on glycidyl acrylates and hydroxyl-containing compounds with respect to metal ions, as well as to suggest a mechanism for their sorption.

Glycidyl acrylate was synthesized by the interaction of acrylic acid with epichlorohydrin. To obtain polysaccharide esters, glycidyl acrylate was mixed with carboxymethyl cellulose or starch and then polymerized in a dimethylformamide medium in the presence of an initiator. The final products were analyzed by IR and NMR-spectroscopy.

We studied the sorption capacity of carbohydrate-glycidyl esters with respect to metal ions such as Cu^{2+}, Mn^{2+}, Fe^{2+} and Ni^{2+}.The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were used to process the obtained data on equilibrium sorption. It was found that the experimental data on equilibrium sorption are reliably described by the Langmuir model. The sorption mechanism was studied using the Dubinin-Radushkevich model. The numerical values of the apparent energy of sorption of metal ions in all cases were less than 8 kJ/mol, which indicates that the process occurs via the ion exchange mechanism.

Thermogravimetric analysis showed that the presence of Cu(II) in the structure of the obtained esters increases their thermal stability. Thermooxidative destruction of these complexes with copper ions ends at 425-445°C, and the greatest loss of sample mass does not exceed 85%. Based on the obtained thermogravimetric analysis data, the activation energy Ea of the initial esters and the resulting complexes with Cu^{2+} was calculated.

As a result of the studies, it was established that the obtained esters based on glycidyl acrylate and hydroxyl-containing polymers can be used as effective materials for removing metal ions from aqueous solutions.

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POLYHEXAFLUOROISOPROPYLACRYLATEMETHYLSILOXANE AND POLYDECYLMETHYLSILOXANE COPOLYMER: A NEW MATERIAL WITH LOW SURFACE ENERGY

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The development of new membrane materials with low surface energy is essential for improving the efficiency of separation processes, such as the isolation of bio-alcohols from fermentation mixtures. Fluoropolymers are a class of polymers with the lowest surface energy values. Fluorinated polysiloxanes are a unique type of polymer that combines the properties of amphiphobic fluoropolymers and alcohol-selective siloxanes.

In this study, a copolymer of polyhexafluoroisopropylacrylate siloxane (F6) and polydecylmethylsiloxane (C10), with a block ratio 1:1, was synthesized for the first time. Using 1H NMR spectroscopy, the hydrosilylation reaction was confirmed, and it was shown that a conversion rate of more than 90% was achieved for the copolymer. It was found that the introduction of F6 groups into C10 resulted in a decrease in surface energy (γ) from 25.5 MJ/m^2 to 16.5 MJ/m^2, which is similar to the surface energy of Teflon (18-20 MJ/m^2). Composite membranes based on polymer C10 and the F6-C10 copolymer were developed on microfiltration substrates M1 and M2. The gas transport properties of the membranes were studied both before and after two months of exposure to solutions of pollutants, such as butanol fermentation broth, protein and lecithin. According to the change in membrane permeability, the M2 sample was found to be less prone to the formation of deposits on the membrane surface compared to the M1 sample when in contact with protein solutions. Lecithin and butanol fermentation broth treatments for M1 and M2 membranes resulted in a decrease in CO2 permeability of 29%, 44%, 32% and 83%, 89%, 45%, respectively. To determine the elemental composition of the detected sediment, energy dispersion analysis was used to examine the membrane surface. The initial membrane surfaces contained Si, O, C, and F atoms (in the case of F6-C10), whereas after contact with pollutants, N2, P atoms were observed on the surface, and an increase in C and O content was observed compared to the original membrane. Among all the studied pollutants, lecithin showed the largest deposition. The average increase in carbon atoms on the surface of the selective membrane after 2 months of contact with M1 was 11.6%, while for M2 it was about 8%. It should be noted that for M1, there was continuous deposition on the surface of the selective layer. For M2, however, "cracks" were observed in the deposits, indicating separation of contamination from the selective membrane surface.

Thus, the potential of using the M2 sample obtained as part of this work to initially separate the ABE fermentation mixture has been demonstrated.

Acknowledgements
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HETEROCENE CATALYSIS IN COPOLYMERIZATION OF ALPHA-OLEFINS WITH POLAR VINYL MONOMERS

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Despite the wide range of physical and mechanical characteristics, providing a variety of practical applications, polyolefins possess a fundamental flaw – poor compatibility with inorganic fillers and dyes. Using polar olefins, in particular, ω-alkenyl carboxylic acids, alcohols, amines and other functionalized comonomers in copolymerization with α-olefins, one can solve the compatibility issue in composites. Heterocenes, sandwich complexes of Zr(IV)[1], can be promising catalysts for the copolymerization of α-olefins with polar vinyl monomers.

We have shown that zirconocenes **Zr1**–**Zr3** containing heterocyclic fragments, in contrast to **Zr4**–**Zr5**, represent effective catalytic systems in the copolymerization of hexene-1 with various vinyl polar monomers at a low $[Al_{mmao\text{-}12}]/[Zr]$ ratio of ~ 20 (Figure 1)[2].

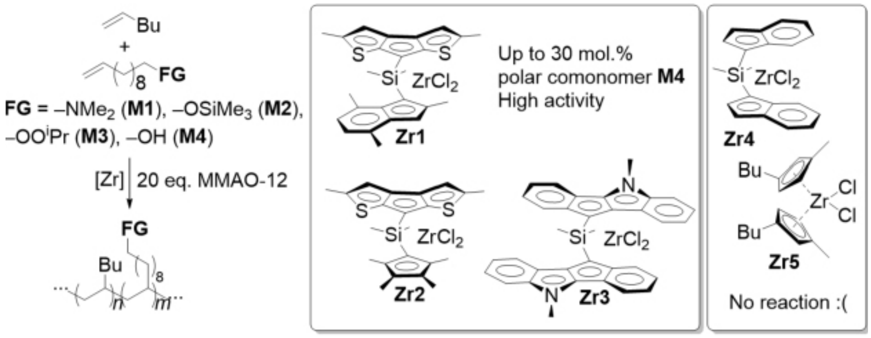

Figure 1. Preparation of the polyolefins with polar functional groups.

In this study, (co)polymers of 1-hexene with polar vinyl monomers $CH_2{=}CH(CH_2)_8{-}CH_2{-}$**FG** were obtained and characterized using NMR spectroscopy (microstructure), GPC (molecular weight characteristics) and DSC. It appears that the most active polar comonomer is TIBA-protected 10-undecen-1-ol **M4**. Via the usage of heterocene **Zr1**, an isotactic copolymer of 1-hexene with **M4** containing 32.2 mol. % of polar comonomer was obtained. The rheological and adhesive properties of the obtained (co)polymers were also studied for the first time. It was shown that with the introduction of 10-undecen-1-ol into the polymer structure, the adhesive bond failure work of the polyhexene copolymer containing 32.2 mol. % of polar comonomer increases by 32 times compared to polyhexene.

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SELF-IMMOLATIVE POLYMERIC GENE DELIVERY VEHICLES DERIVED FROM NATURAL AMINO ACIDS

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Genetic engineering using RNA has proven to be effective in the treatment of atherosclerosis, neurodegenerative diseases, cancer and HIV.[1] It has been also used for the develop of RNA vaccines, against the SARS-CoV-2 included.[2] The most promising strategy for nucleic acids introduce into cells is the development of transfectants. Such amphiphilic (usually small) molecules that trap charged NA, form micelles and enter the cells.

The new approach to the transfection, proposed in 2017, bases on self-immolative polymeric substances, CARTs.[3] These reagents are many times more effective than commercially available low-molecular-weight gene vehicles and can successfully be used in the development of RNA vaccines and cancer treatment.[4,5] Despite of their revolutionary potential, these transfectants have some drawbacks. They are not completely degradable and its structures do not allow further modification.

In this report we present the synthesis of three new classes of fully biocompatible transfectants A, B and C from natural amino acids.[6,7] The strategy of terminal monomeric unit modification has been applied.[8] The synthetic platform for targeted gene delivery, using amphiphilic glycoconjugates D, has been developed.

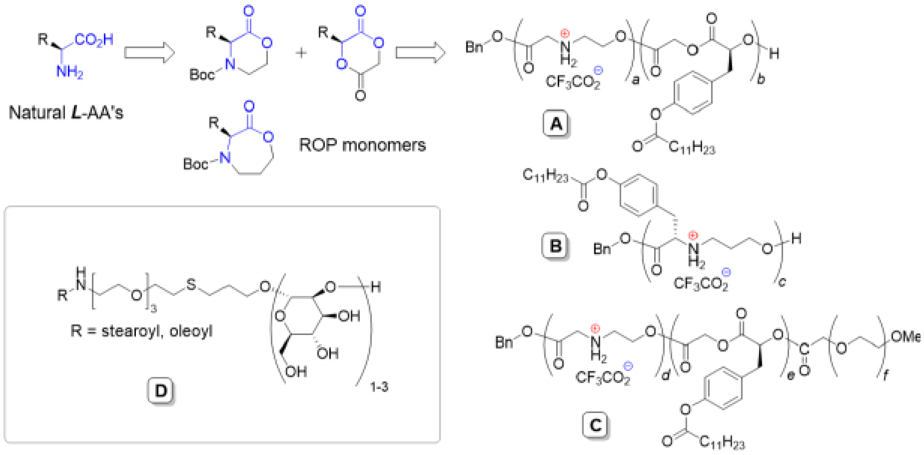

Figure 1. New classes of transfectants (A - C) and glycoconjugates (D) for targeted gene delivery.

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SYNTHESIS AND INVESTIGATION OF SURFACE ACTIVITY AND SELF-ORGANIZATION OF AMPHIPHILIC STEREOREGULAR CYCLOSILOXANES

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Amphiphilic substances of various nature and structure are used in almost every field of human activity, so the task of creating, studying and searching for new applications has always been and will always be urgent. Among other things, siloxane surfactants are widely used due to their unique surface-active properties. In the course of this work, a representative number of amphiphilic stereoregular organocyclosiloxanes with phenyl substituents at the silicon atom were synthesized on the basis of previously obtained and developed methods of template synthesis of stereoregular metallocyclosiloxanes [1-2] at INEOS RAS. The study of monolayers of these compounds using a Langmuir bath and their visualization using Brewster-angle microscopy revealed a number of dependences of the self-organization of stereoregular cyclosiloxanes on their size, the presence of a spacer between the hydrophilic group and the siloxane ring, and their stereoregularity (fully stereoregular or tris-cis/ tris-trans). The dependence of the tendency to form intermolecular bonds in the monolayer on the cycle size was revealed by the method of multiple compression of monolayers. The study of the equilibrium spreading pressure of amphiphilic stereoregular cyclosiloxanes confirmed the dependence of the thermodynamically stable state of the monolayer on the presence of a spacer between the siloxane ring and the hydrophilic group and on the stereoregularity of the cycle (fully stereoregular or tris-cis/ tris-trans). Methods of functionalization and further modification of stereoregular cyclosiloxanes were also developed.

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COMB-LIKE POLYELECTROLYTES AS CO-CATALYSTS OF SUZUKI AND HECK REACTIONS IN AQUEOUS MEDIA

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Comb-like polyelectrolytes are a multifunctional platform used for a wide range of scientific and practical applications. Such substances could be used for micellar catalysis because of their ability to self-organize in aqueous solutions.

In recent decades, micellar catalysis has been investigated in the context of constructive reactions such as Suzuki and Heck coupling and cross-metathesis reactions[1]. Surfactants in this case can play the role of co-catalysts, on the one hand, concentrating organic reagents inside micelles, and on the other hand, forming catalytically active complexes with Pd in situ with the help of functional groups. The advantages of using comb-like polyelectrolytes as co-catalysts are due to such properties as: high solubilization capacities, the possibility of purification of the reaction product from the catalyst by dialysis, the simplicity of varying the composition and arrangement of functional groups.

In this work we synthesized a new comb-like polyelectrolyte poly-11-(acryloyloxy)-undecylmethylimidazolium bromide (pAUMe-Im-Br) (Fig.1a), its copolymers with 11-(acryloyloxy)-undecyltrimethylammonium bromide (AUTA-Br) (Fig.1b) and investigated their properties and catalytic activity in coupling reactions.

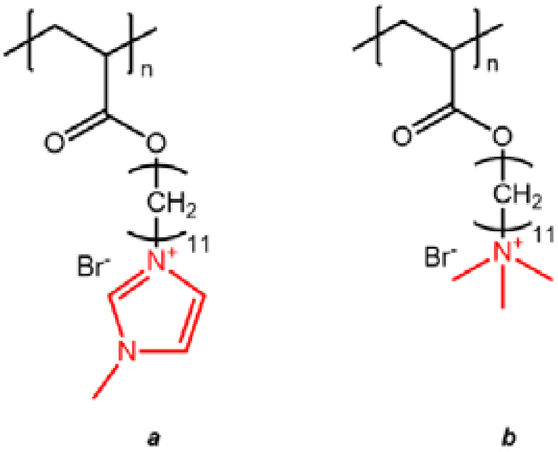

Figure 1. Comb-like polyelectrolytes

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SYNTHESIS AND CHARACTERIZATION OF SILSESQUIOXANE POLYMERS BASED ON POLYFLUORINATED TRIETHOXYSILANES

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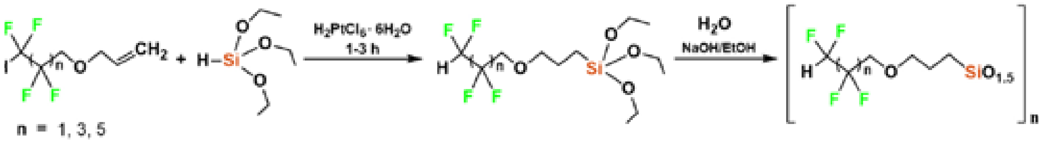
In recent years, the need for original functional polymer materials that possess a set of high performance characteristics has been continuously growing. Fluorine-containing organosilicon functional oligomers and polymers attract the interest of researchers due to the unique properties of the materials obtained on their basis. Materials based on organofluorosilicon compounds have increased thermal stability, hydrophobicity, frost, oil and gasoline resistance, high wear resistance, and also protect against biological influences. They have a wide range of potential applications in various fields of science and technology, including industrial and electronic chemistry, development of innovative polymeric materials, as coatings, membranes, adhesives, composites, etc., contributing to scientific and technological progress. Thus, the development of modern technologies is aimed at creating simple and effective approaches to the production of materials with controlled structure and is closely related to the search for new chemical compounds and materials based on them, as well as the development of methods for modifying existing ones.

Triethoxy(polyfluoroalkoxypropyl)silanes, which are the starting reagents for the synthesis of organosilicon polymer systems, were synthesized by a hydrosilylation reaction in the presence of Speier's catalyst (Scheme 1). Previously unknown soluble polysilsesquioxanes with peripheral organofluorine linear substituents with different lengths of the polyfluorinated chain were synthesized by us using an accessible classical hydrolytic polycondensation reaction (Scheme 1). The composition and structure of the compounds obtained were determined using data from elemental analysis, FTIR spectroscopy, NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, and ^{29}Si), gel permeation chromatography, and X-ray diffraction. Additionally, thermogravimetric and differential scanning calorimetric analyses were performed to obtain additional information about the compounds thermal properties.

The synthesized fluorine-containing polysilsesquioxanes are promising precursors for the creation of hydrophobic materials, composite proton-conducting membranes and materials with a wide range of applications.



Scheme 1. The synthetic route of polyfluorinated triethoxysilanes and polyfluoroalkoxypropylsilsesquioxanes

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EFFECT OF TEMPERATURE ON HYDROLYTIC DEGRADATION OF POLY(L-LACTIDE)

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Polylactide (PLA) is a biodegradable and biocompatible polymer with tailored properties, which is widely used for fabrication of medical devices, in regenerative medicine and drug delivery. The key advantage of PLA-based products is that they do not require additional surgical intervention for removal of the implant. The degradation profile of PLA materials can be adjusted by changing its stereochemical structure, i.e. L/D ratio, crystallinity and molecular weight. To develop effective medical devices, it is important to assess the degradation rate of the polymer and final implant. However, at body temperature PLA-based materials can degrade for 2-5 years and even more. So, the evaluation of the full degradation profile may be a challenge, especially in time-limited projects focused on development of new medical devices. Therefore, an urgent issue is development of the standard methods for an accelerated degradation at elevated temperatures, followed by a calculation of the degradation profile at body temperature.

To study the dependence of the rate constant of poly-L-lactide hydrolysis on incubation temperature dog-bone samples were produced. The samples were 3D-printed from REC 3D PLA filament (Mw = 170 kDa, PDI = 2.3) on a PICASO Designer PRO 250 3D printer with the following parameters: nozzle and bed temperature - 210 °C and 60 °C, respectively; layer thickness - 0.25 mm; fill density - 100%, average print time per sample - 20 min. The work length of the printed sample was 40 mm. The devices were placed in a phosphate buffer saline (pH = 7.4) at incubation temperatures of 37, 45, 55, and 75 °C. At desired time points, the samples were removed from the buffer solution, and analysis of the mass and molecular weight of the poly-L-lactide was performed. It was found that the molecular weight of poly-L-lactide decreases by 50% after 112, 49, 17, and 1 day of incubation at temperatures of 37, 45, 55, and 75 °C, respectively. A complex approach[1] was used to fit the experimental data, and the rate constants of random non-catalytic and autocatalytic hydrolysis were calculated (Figure 1). The calculated rate constants for random noncatalytic hydrolysis (k^r_n) was found to be 2.54*10^{-6}, 1.02*10^{-5}, 3.3*10^{-5} and 8.01*10^{-4} day^{-1} as the temperature increased, while the rate constants for random autocatalytic hydrolysis (k^r_a) were 7.63*10^{-6}, 2.29*10^{-5}, 7.12*10^{-5} and 1.0*10^{-3} $(mol^{-1} * m^3)^{½} * day^{-1}$. The calculated reaction rate constants were verified for matching with the Arrhenius and Vogel-Fulcher-Tamman equations. The first showed correlation coefficients of 0.995 and 0.997 for non-catalytic and autocatalytic hydrolysis, respectively, while the second showed lower correlation coefficients of 0.939 and 0.942, respectively.

Based on the experimental data, it can be concluded that an increase of the incubation temperature significantly accelerates degradation, which can be described by the Arrhenius law. Close values to those observed in the literature were obtained. The correlation coefficient close to 1 for Arrhenius equation indicates the reliability of the approximation methods and possibility for subsequent extrapolation of the results on any desired temperature. This results pave the way for development of the methods for accelerated degradation of PLA-based products.

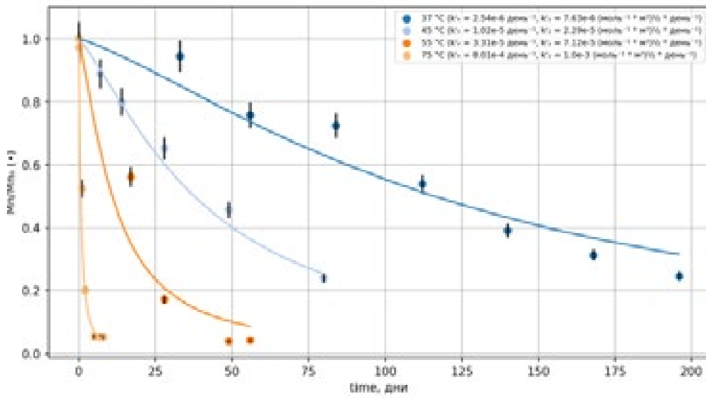

Figure 1. Normalized molecular weight of PLLA durig hydrolytic degradation at different temperatures.

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ELECTRORHEOLOGICAL RESPONSE OF A SUSPENSION BASED ON SILICON OIL AND CHITOSAN MODIFIED GRAPHENE OXIDE

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The advancement of technology has rendered the development of materials capable of altering their properties in response to electric and magnetic fields, light, or heat an increasingly pressing concern. Electrorheological (ER) fluids are a striking example of such materials, whose mechanical properties (viscosity, yield stress, loss and storage moduli) are controllable and reversibly alterable under the influence of an external electric field. ER fluids are suspensions comprise easily polarizable filler particles distributed in a liquid dielectric medium. These materials exhibit a range of potential applications, including shock absorption, smart polishing, smart lubrication, microfluidic control, robotics, and medical equipment.[1,2].

In this study, we synthesized and investigated a nanocomposite filler for ER fluids, specifically graphene oxide (GO) modified with a low molecular weight chitosan (CS). The particle morphology and their chemical structure were studied using optical and electron microscopy, and FTIR spectroscopy. TG analysis was conducted in a nitrogen atmosphere to evaluate the extent of chitosan grafting. To obtain suspensions, different amounts of filler were dispersed in silicone oil (PMS-100). The rheological and electrorheological properties of suspensions were investigated using a rheometer «Physica MSR 501» with an external DC voltage source. Additionally, the sedimentation analysis was conducted.

The results of FTIR spectroscopy data indicate that the amide linkage was successfully formed between GO and CS. TG analysis revealed that the grafting degree of the polymer was approximately 15%. Subsequent rheological and electrorheological tests demonstrated that the resulting fluid exhibited considerable electrorheological properties. Additionally, oscillation tests enabled the determination of the storage and loss moduli values. Furthermore, the samples demonstrated suitability for long-term cyclic operation and exhibited reversible and reproducible performance even at high electric fields without dielectric breakdown.

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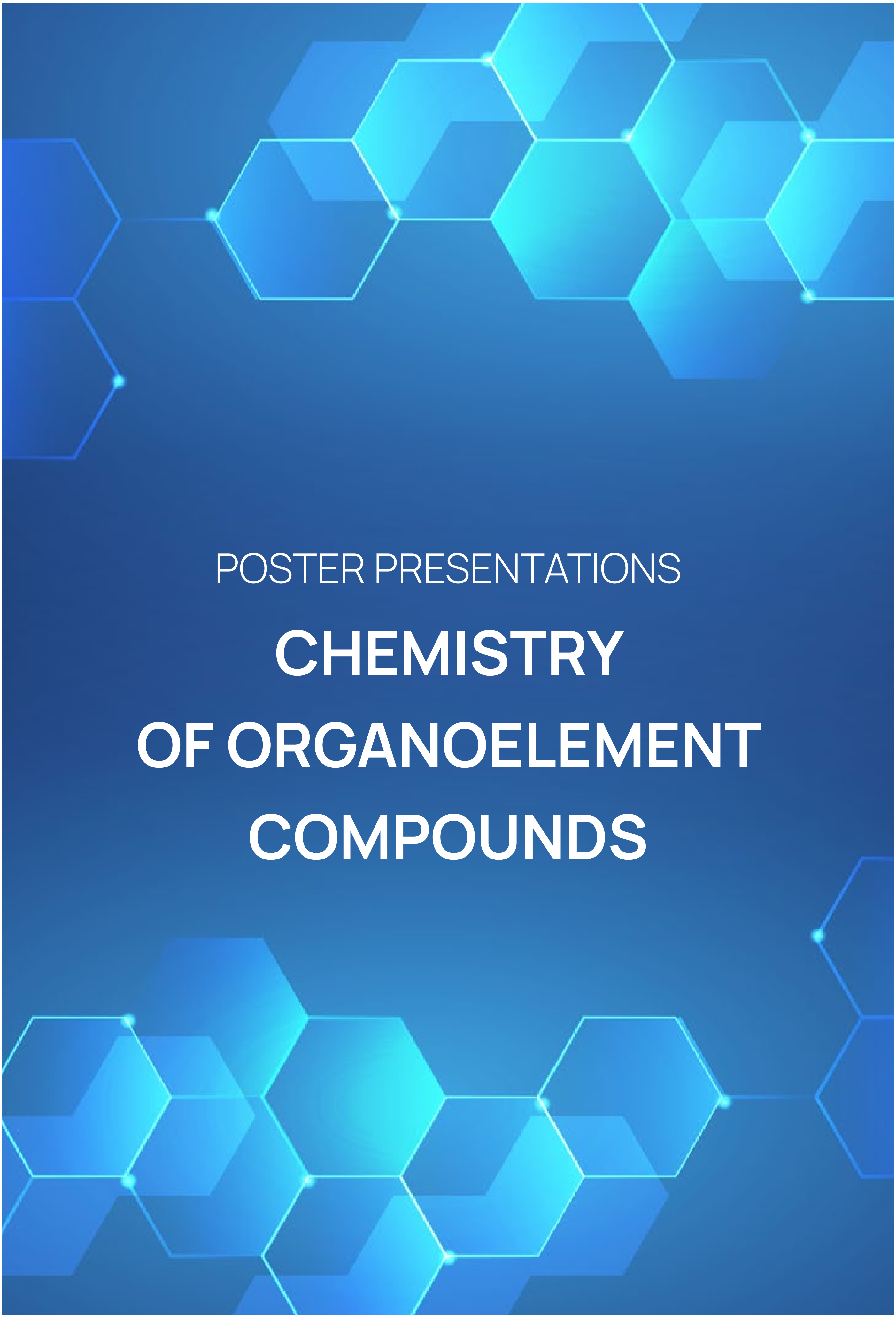

POSTER PRESENTATIONS

CHEMISTRY OF ORGANOELEMENT COMPOUNDS

REACTIONS OF ACETYLENE COMPLEXES OF ZIRCONOCENE WITH DINITRILES

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Organic amidines are an important class of compounds that have found their application in coordination chemistry, organic synthesis and catalysis. Amidines are also used in medicine to treat a wide class of diseases such as trypanosomiasis, leishmaniasis, keratitis and many others. Therefore, the synthesis of such compounds is highly relevant to modern chemistry.

Also, recent researches in the chemistry of the metallocenes 4 group have shown the possibility of synthesizing an amidinate functional group in the coordination sphere of zirconium[1]. It was found that the addition of two nitrile equivalents to zirconacyclopropene complexes leads to the formation of bicyclic amidinate metallacycles.

We have studied the interaction of precursors of acetylene complexes: metallacyclopentenes, -pentadienes and aryl metallacycles with dinitriles[2]. It was found that in the case of adiponitrile, as a result of intramolecular cyclization, afford the seven-membered tetrahydroazepine zirconaamidinates. Then organic amidines were isolated by demetallization of the obtained compounds[3].

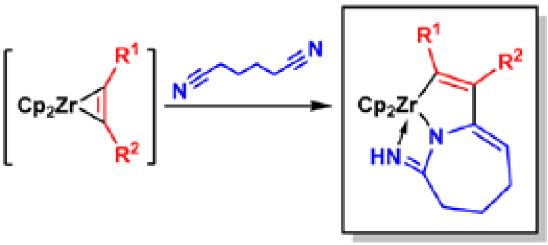

Figure 1. Interaction of precursors of acetylene complexes with adiponitrile

In summary, the interaction of precursors of acetylene complexes of metallocenes with dinitriles makes it possible to synthesize various organic amidines in the coordination sphere of the metal.

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DIARYLIODONIUM DICYANOARGENTATES(I): SYNTHESIS AND SUPRAMOLECULAR AGGREGATION

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The crystal engineering of supramolecular systems is an actively developing field at the intersection of various disciplines of the natural sciences. One of the tasks of this area is the study of noncovalent interactions to address the issue of creating functional materials with desired properties suitable for practical use.[1–4] In recent years, the nature of noncovalent interactions involving pseudohalide complex metal salts has been actively studied in order to create metal-containing systems with significant photophysical, conductive, magnetic and other properties.[5,6]

In this work crystals of $[Mes_2I][Ag(CN)_2]$ and $[PhMesI][Ag(CN)_2]$ were synthetized and studied. In both structures the C–I···N≡C interactions were discovered. The presence and nature of the contacts were confirmed by X-ray diffraction data and theoretical calculations with periodic boundary conditions.

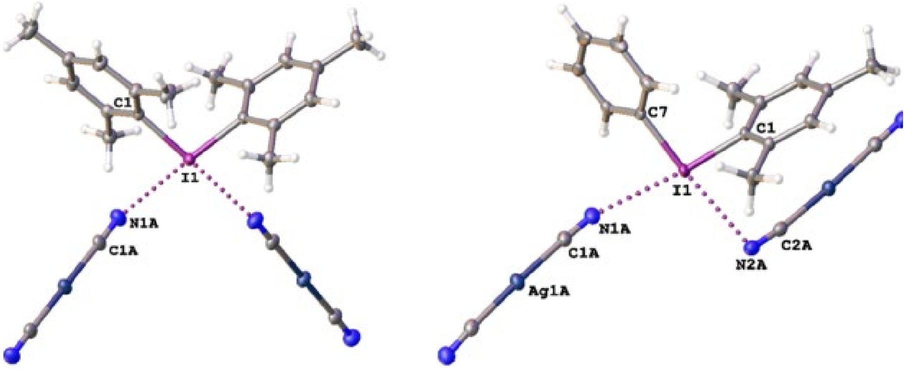

Figure 1. The C–I···N≡C contacts in the structures of $[Mes_2I][Ag(CN)_2]$ (left) and $[PhMesI][Ag(CN)_2]$ (right).

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Acknowledgements
This work was supported by the Russian Science Foundation (project 24-73-00143).

CARBORANYL-SUBSTITUTED PORPHYRINS OF A_3B TYPE WITH FUNCTIONALITIES ENHANCED THEIR BIOLOGICAL ACTIVITY

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Porphyrins exhibit outstanding biological properties such as high biocompatibility, long Stokes shift, fast clearance, low side effect, and longer residence time in tumors. These compounds are easy to modify and structural changes have been attempted to achieve more efficient conjugates for biomedical application.

A synthesis of A3B-type carboranylporphyrins as potential photo/radio- sensitizers for photodynamic therapy (PDT) and boron neutron capture therapy (BNCT) was developed based on 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**1**) and 5-(4-amino-2,3,5,6-tetrafluorophenyl)-10,15,20-tris(pentafluorophenyl) porphyrin (**2**). Using functionalization of porphyrin **1** with cyanuric chloride in which three of its reactive chlorine atoms are capable of easily being substituted in SNAr reactions three component systems based on porphyrin, cyanuric chloride and carborane clusters were prepared by a one-pot stepwise amination of cyanuric chloride with porphyrin **1**, followed by the replacement of the remaining chlorine atoms with carborane *S*-, *N*-nucleophiles or by the residues of biologically active compounds. The modification of pentafluorophenyl substituents in porphyrin **2** *via* the S_NAr substitution reaction with carborane S-nucleophiles resulted in the corresponding carboranylporphyrins containing three carborane polyhedra bound to the fluorophenylporphyrin substituents *via* the boron atom and *p*-aminotetrafluorophenyl-substituents in its structure. Acylation of amino group of porphyrin **2** made it possible to obtain conjugates containing maleimide or biotin residues.

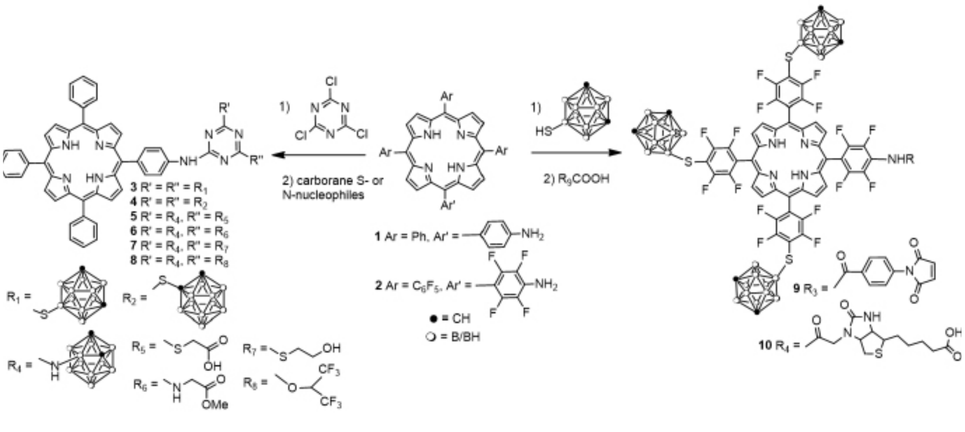

Figure 1. Structures of synthesized compounds.

The obtained compounds have low dark cytotoxicity and high phototoxicity, which makes them promising in further studies as photosensitizers for PDT and BNCT.

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PREPARATION OF A HIGHLY EFFICIENT ORGANOPHOSPHORUS EXTRACTANT OF RARE EARTH METALS

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We have developed a neutral organophosphorus extractant based on alkyl halides and phosphorus chloroxide, which has the general formula (Hex)3-oct (Oct)3-hex PO. The optimal conditions for the synthesis process of the product with adjustable molecular weight composition were found. Comparison of the samples obtained by us with the extraction reagent Cyanex 923 showed (Table 1) that with a relatively equal number of substituents at the phosphorus atom, the laboratory technology developed by us allows us to obtain a product with a significantly higher total content of phosphine oxides.

Table 1. Phosphine oxide content in products

	Hex_3 PO, %	Hex_2 OctPO,%	$HexOct_2$ PO,%	Oct_3 PO,%	Sum of all FOX %
Our sample	11.80	36.10	36.90	12.52	97,35
Cyanex 923 [1]	8.50	30.40	37.40	16.10	92,40

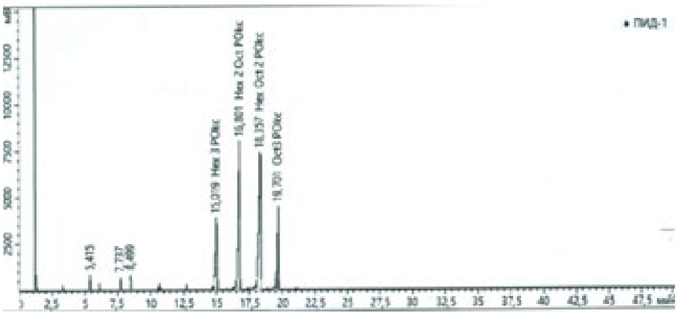

Figure 1: Results of GLC analysis

According to the results of the tests, it was found that the extractant developed by us meet the technical requirements for extraction processes of rare earth metals.

DEHYDROCOUPLING OF SILANES WITH ALCOXYARENES AND AMINES CATALYZED BY RARE-EARTH METAL ALKYL COMPLEXES WITH N,N,O-HETEROSCORPIONATE LIGANDS

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Catalytic dehydrocoupling of hydrosilanes is an efficient and atom-economical method for obtaining silicon compounds as an alternative to traditional methods based on the use of chlorinated compounds[1]. In this regard, the development of new stable catalysts based on alkyl complexes of lanthanoids for dehydrocoupling reaction of hydrosilanes with arenes and amines represents a relevant challenge.

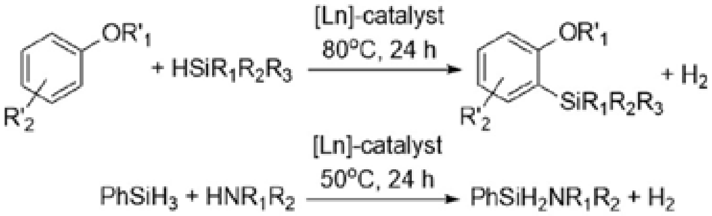

Figure 1. Dehydrocoupling reaction of hydrosilanes with arenes and amines

$PzI^{Me2}{}_2CP(=O)iPr_2$ (PzI^{Me2} – 3,5-dimethylpyrazole) was successfully used for the synthesis of bis(alkyl) complexes of yttrium, lutetium, and erbium.

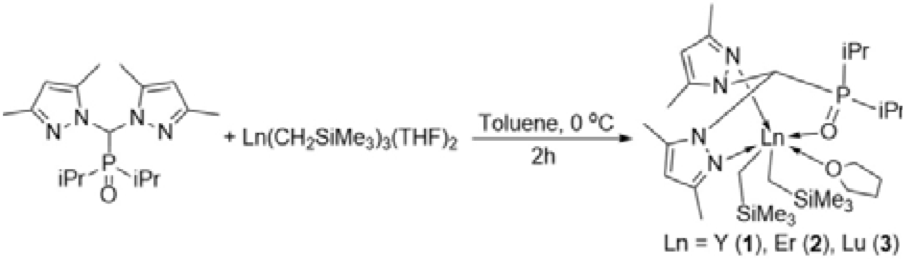

Figure 2. Synthesis of bis(alkyl) complexes of rare-earth elements

Cationic alkyl complexes, generated *in situ* by the reaction of equimolar amounts of compounds **1-3** with $[Ph_3C][B(C_6F_5)_4]$, have demonstrated significant catalytic activity in the dehydrocoupling of alkoxyarenes with various hydrosilanes ($PhSiH_3$, Ph_2SiH_2, $PhMeSiH_2$, Ph_3SiH, Et_3SiH), selectively forming silylation products in the *ortho* position of the benzene ring. Additionally, complexes **1-3** have shown efficacy in the dehydrocoupling of $PhSiH_3$ with amines ($C_4H_9NH_2$, $C_6H_{11}NH_2$, $C_6H_5NH_2$, $C_6H_5NHCH_3$, $(CH3)_2CHNH_2$), leading to the selective formation of silazanes.

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Acknowledgements
The financial support of Russian Science Foundation (Grant 23-13-00323) is highly acknowledged.

RENACARBORANE [1,1–$(CO)_2$–1,1–I_2–*isonido*–1,2,4–$ReC_2B_8H_{10}$]-. SYNTHESIS, PROPERTIES, MOLECULAR STRUCTURE

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Currently, the development of optoelectronic applications based on renacarboranes with luminescent properties is very promising. In addition, renacarborane complexes are used in medicine for binding to the estrogen receptor, for the development of targeted molecular imaging probes, and as building blocks and drug delivery vehicles. The relevance of the use of renacarboranes in many fields of science and technology makes it important to synthesize new representatives of this class of compounds, as well as study their structure, nature of the bonds and properties.

The reaction of the rhenium carborane complex [1,1,1-$(CO)_3$–*isonido*–1,2,4–$ReC_2B_8H_{10}$]-tmndH$^+$ 1 with an equimolar amount of I_2 in CH_2Cl_2 at room temperature for an hour leads to the formation of a complex [1,1 –$(CO)_2$–1,1–I_2–*isonido*–1,2,4–$ReC_2B_8H_{10}$]-tmndH$^+$ (**1**). After crystallization (CH_2Cl_2-hexane), complex **1** was isolated in quantitative yield in the form of orange crystals. The structure of complex **1**, assumed on the basis of ^1H, ^{11}B, $^{11}B\{^1H\}$, ^{13}C NMR spectra, IR spectroscopy and elemental analysis, was confirmed by X-ray diffraction. (Fig. 1)

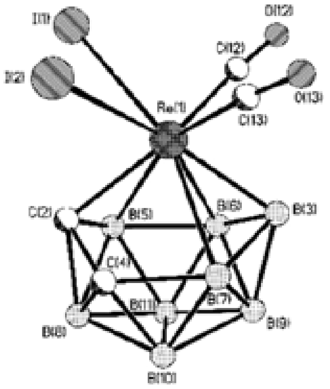

Figure 1. Molecular structure of the anionic complex **1**
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LANTHANIDE COMPLEXES WITH ARYLBOROMIC ACIDS. SYNTHESIS AND LUMINESCENT PROPERTIES

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Lanthanide complexes occupy a special place among materials for various luminescent applications due to their remarkable properties such as narrow emission bands, large Stokes shifts, long-lived excited states, and a wide emission range from visible to near infrared (NIR). The design of ligands for sensitization of lanthanide ions plays a key role. Recently, there has been a surge of interest in polycyclic ligands. In particular, lanthanide complexes with arylboronic acids are promising objects for various bioluminescent applications.

A set of heteroleptic compounds $[Cp_2Ln(ArBO_2H)(DME)]_2$ (Ln = Sm, Er, Yb; Ar = Np, Ant) were synthesized by exchange reaction of respective tris(cyclopentadienyl)lanthanide with $ArB(OH)_2$ acid in DME solution. Single-crystal X-ray analysis revealed that complexes Sm, Er and Yb are isostructural binuclear compounds which contain four Cp ligands and two bridging $Np(BO_2H)$ ore $Ant(BO_2H)$ ligands (Fig. 1 a, b). The hydrogen atom of the $Ar(BO_2H)$ ligand is directed towards the oxygen atom of the dimethoxyethane molecule. It should be noted that the intermolecular O...H distances correspond to so-called contracted contacts [6x]. Therefore, there is a specific interaction between the oxygen and hydrogen atoms, which is generally much stronger than ordinary van der Waals interactions.

The PL spectra of solid samples of the obtained complexes contain intense ligand-centered (La) and metal-centered emission bands, both in the visible (Sm) and in the NIR range (Yb).

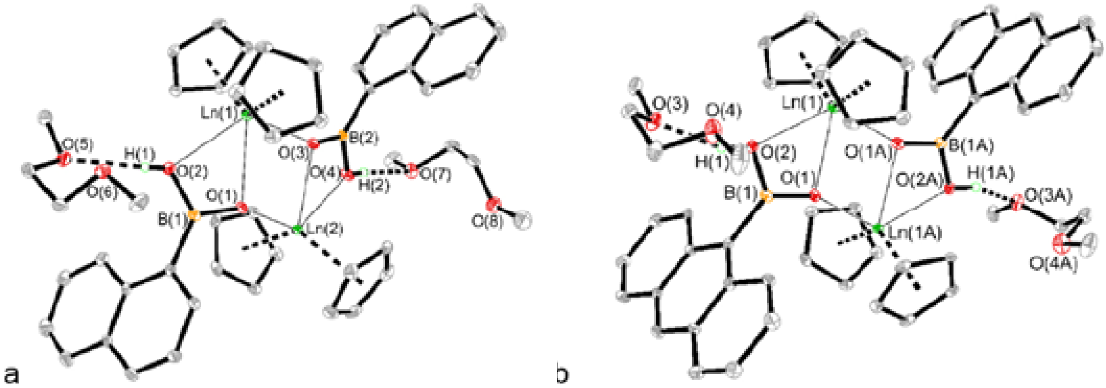

Figure 1. Molecular structure of complexes $[Cp_2Ln(NpBO_2H)(DME)]_2$ (Ln = Sm, Er and Yb) (a) and $[Cp_2Ln(AntBO_2H)(DME)]_2$ (Ln = Sm, Er) (b).

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ALUMINA-PROMOTED COPPER-CATALYZED HYDROBORATION OF ALKYNES

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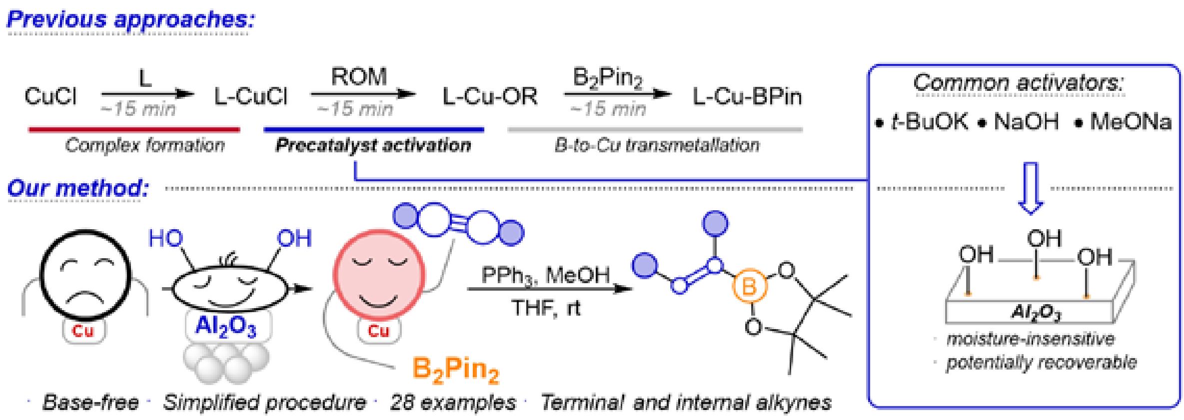
Vinylboronic esters are highly valuable intermediates in organic synthesis. Nowadays, transition metal-catalyzed hydroborations have largely replaced the non-catalytic variant. Despite the recent progress, especially in Cu-catalyzed hydroboration, the experimental procedure requires moisture-sensitive activators and stepwise preparation of “activated” catalyst.



We have demonstrated that the Cu-catalyzed hydroboration of alkynes with B_2Pin_2 can be mediated by alumina as base surrogate. The efficiency of Al_2O_3 is probably attributed to the presence of hydroxy groups on its surface. The combination of alumina with Cu precatalyst and phosphine ligand allows developing experimentally simple approaches to vinylboronates from terminal and internal alkynes. This was illustrated by the preparation of a series of styrylboronates as well as derivatization of steroid in $CuCl/PPh_3$ or $Cu(OAc)_2/PPh_3$-catalyzed hydroboration. The activation of Cu(I) by the neutral support should be considered in the development of heterogeneous catalysts for hydroboration.

Acknowledgements

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2,6-DIBENZHYDRYL-4-METHYLPHENOLATE COMPLEXES OF LANTHANIDES AND ALKALI METALS

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Bulky aryloxide ligands are extensively utilized for the synthesis of low-coordinate metal complexes. Of particular significance are commercially available 2,6-diisopropyl- and 2,6-ditertbutylphenolato ligands. However, given the relatively high ionic radii of the lanthanide ions, their complexes with the aforementioned ligands tend to oligomerize or form ate complexes.

We hypothesized that the use of the superbulky 2,6-dibenzhydryl-4-methylphenolato ligand in the synthesis of lanthanide complexes would result in the formation of compounds with low coordination numbers and short metal-ligand bonds. It was anticipated that such compounds could exhibit promising luminescent properties due to the antenna effect.

A variety of synthetic strategies were investigated for the preparation of the target complexes (Fig. 1). Deprotonation of the parent phenol with $MN(SiMe_3)_2$ (M= Li, Na, K) resulted in the clean formation of dinuclear aryloxides. Further treatment of the lanthanide chloride tetrahydrofuranates with the obtained aryloxides afforded mono- and bis(phenolates). Surprisingly, tris(phenolates) could only be obtained through protolysis reactions between lanthanide hexamethyldisilazides and the corresponding phenol. Analogous reactions with the tris(cyclopentadienyl) derivatives yielded products of incomplete reaction. The terbium compounds showed typical metal-centered luminescence with moderate to high quantum yields (25 to 60%).

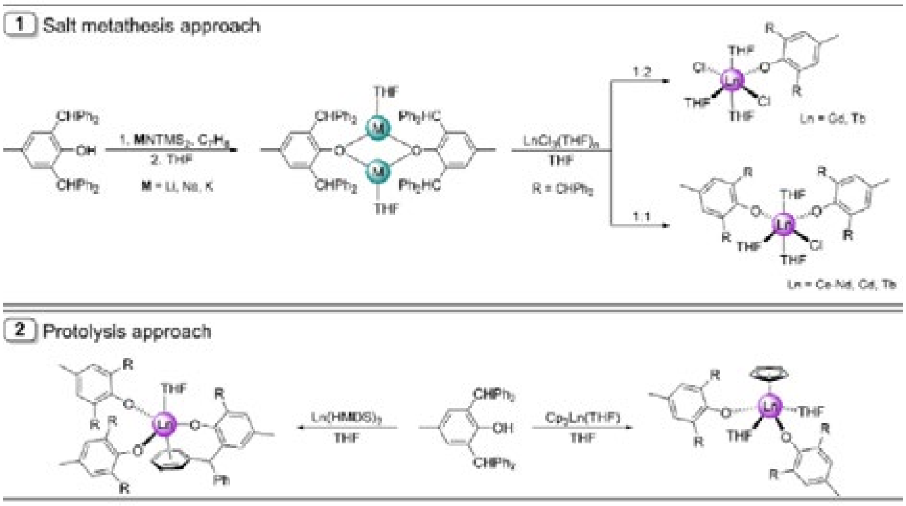

Figure 1. Synthesis of the lanthanide phenoxide complexes.

Acknowledgements
This work was supported by the Russian Science Foundation (grant no. 22-13-00312).

THE DEVELOPMENT AND INVESTIGATION OF NOVEL DERIVATIVES BASED ON BTBT FOR USE IN ORGANIC ELECTRONIC DEVICES

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The investigation of new molecules and their properties is essential for various areas of contemporary science and technology. In recent years, thienothiophenes have emerged as a promising basis for developing hole-transport materials in organic electronics[1]. However, the properties of donor-acceptor (D-A) materials featuring different nitrogen-containing groups have not been thoroughly studied. Therefore, the synthesis and investigation of structures derived from these materials and various nitrogen-containing precursors are crucial for the development of materials with optimal optoelectronic properties.

The aim of this study was to synthesize novel molecular structures based on benzothiophene [3,2-b]-[1]-benzothiophene (BTBT) analogues and to investigate their optical and thermal properties.

A dibromo-BTBT compound that had been previously prepared was subjected to Buchwald-Hartwig coupling reactions with various amines. The resulting compounds were purified using flash chromatography and recrystallization methods. Their structures were identified and confirmed using advanced analytical techniques.The results indicate that as the complexity of the amine group increases, the quantum efficiency decreases significantly, from a satisfactory value of 60% to an extremely low value of 16%. At the same time, the emission wavelength shifts towards the red region, from 20 nm to 90 nm. In terms of thermal properties, the synthesized compounds show characteristics that are either comparable to or better than those of commercially available materials[2]. This opens up possibilities for further research and development.

We believe these derivatives have the potential to surpass existing materials in TADF OLEDs, organic photovoltaics (OPVs), polymer light-emitting diodes (PLEDs due to their excellent stability and performance.

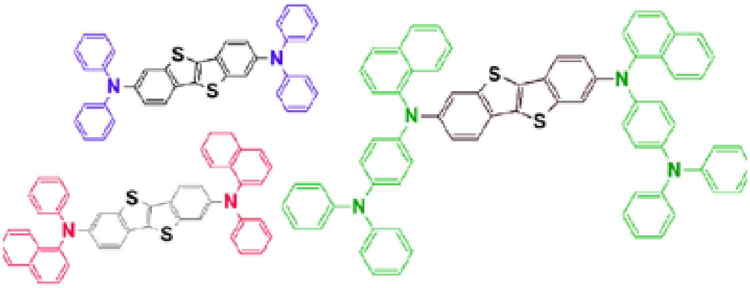

Figure 1. Structures of new BTBT derivatives

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INTRAMOLECULAR CYCLIZATION IN $[8\text{-ETC(OH)=HN-3,3`-CO}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1`,2`\text{-C}_2\text{B}_9\text{H}_{11})]$

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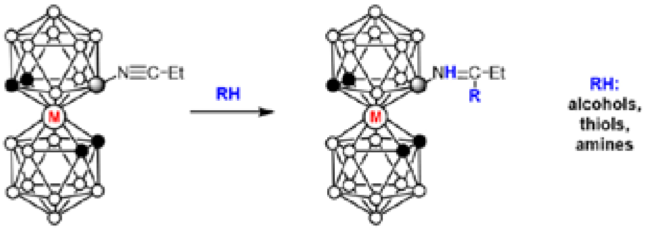
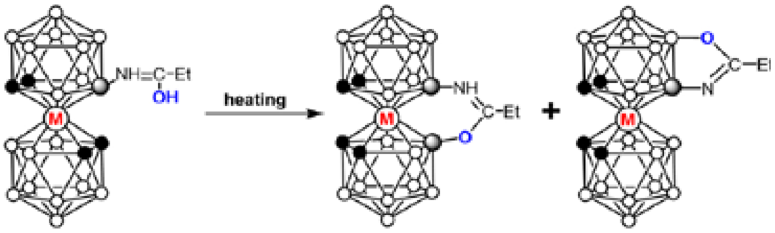
The possibility of modifying bis(dicarbollide) complexes of cobalt and iron by nucleophilic addition reactions at the triple bond $\text{B-N}^+\equiv\text{C-R}$ was demonstrated previously.[1,2]



Scheme 1. Nucleophilic addition to propionitrilium derivatives

In this work we studied the possibility of intramolecular cyclization on the example of 8-substituted iminol obtained by hydrolysis of the propionitrile derivative of cobalt bis(dicarbollide). It was shown that, depending on the temperature, heating this derivative results in different cyclization products including 6-membered oxazine-like cycle combining two dicarbollide ligands and 5-membered oxazole-like cycle in one dicarbollide ligand (scheme 1, figure 1a).



Scheme 2. Heating iminol $[8\text{-EtC(OH)=HN-3,3`-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1`,2`\text{-C}_2\text{B}_9\text{H}_{11})]$

Heating at higher temperature leads to the elimination of H_2O and produces the 5-membered cycle derivative with B-C-N-B bridge (figure 1b).

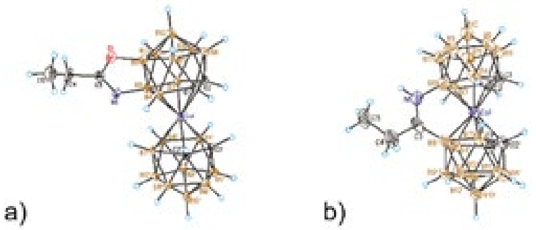


Figure 1. General view of cyclic metallacarboranes

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SYNTHESIS AND PROPERTIES OF TRIVALENT LANTHANIDE IODIDES OF COMPOSITION $Ln^{3+}(e)^{-}I_2$

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In the vast area of well-studied compounds of trivalent and divalent rare earth metals, there is a special small group of substances, all available information about which is limited only to their synthesis and the property of metallic conductivity inherent only to these compounds. These substances are binary halides of some lanthanides of composition LnX_2 (Ln = La, Ce, Pr, Gd, Tb, Ho, Er, Lu). Metallic conductivity in materials arises as a result of the sharing of valence electron that is not involved in the Ln-X valence bonds, which form the conduction band. In such compounds, the Ln cation can be written as $[(Ln^{3+})(I^{-})(e)^{-}]$. The chemical properties of such compounds were studied using very rare examples. Their luminescence and magnetic properties have hardly been studied.

The reduced lanthanide iodides of the composition LnI_2 (Ln = Sc, Y, La, Ce, Pr, Gd, Ho, Er) were previously obtained by the reaction of an excess of the appropriate metal with iodine at high temperatures.[1]

The effective magnetic moments (μ_{eff}) of the prepared compounds indicate the trivalent state of the metals in these products. In contrast to the diiodides of Sm(II), Eu(II), Yb(II), Nd(II), Dy(II), and Tm(II), the isolated solids are not soluble in THF, DME, or liquid ammonia.

It was found that the prepared compounds did not show luminescence (excitation wavelengths – 360, 390 nm).

In attempt to obtain the organic derivatives of composition $[LnR(I^{-})(e^{-})]$ the reactions of LnI_2 (Ln = Pr, Tb) with sodium phenolate were carried out. But all the reactions resulted in formation of compounds of ate-type $[Ln(OPh)I_2][NaI]\,(DME)_2$. The products were identified by elemental analysis, IR spectroscopy and magnetic measurements. Formation of the complexes is explained evidently by disproportionation of initially formed desirable products [Ln(OPh)I].

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SYNTHESIS, PHOTOPHYSICAL AND BIOLOGICAL ACTIVITY OF $R_2Sn(IV)L$, $R_2Ge(IV)L$, $Ph_3Sb(V)L$ COMPLEXES WITH O,N,O'-DONOR SCHIFF BASES

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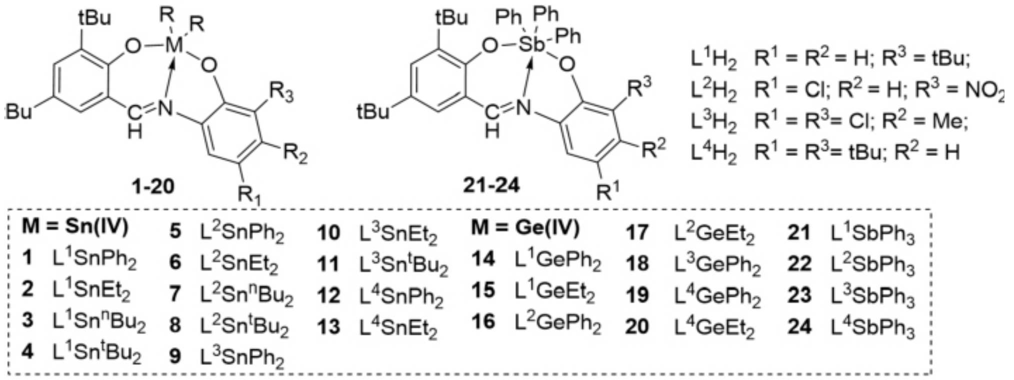
A number of novel coordination compounds of tin(IV) (**1-13**), germanium(IV) (**14-20**), antimony(V) (**21-24**) with tridentate O,N,O'-donor Schiff bases (L^1H_2-L^4H_2) containing different substituents in the imino-phenolic and organometallic fragments have been synthesized (Fig. 1).[1-4]



L^1H_2 $R^1 = R^2 = H$; $R^3 = tBu$;
L^2H_2 $R^1 = Cl$; $R^2 = H$; $R^3 = NO_2$
L^3H_2 $R^1 = R^3 = Cl$; $R^2 = Me$;
L^4H_2 $R^1 = R^3 = tBu$; $R^2 = H$

M = Sn(IV)
1 L^1SnPh_2
2 L^1SnEt_2
3 $L^1Sn^nBu_2$
4 $L^1Sn^tBu_2$
5 L^2SnPh_2
6 L^2SnEt_2
7 $L^2Sn^nBu_2$
8 $L^2Sn^tBu_2$
9 L^3SnPh_2
10 L^3SnEt_2
11 $L^3Sn^tBu_2$
12 L^4SnPh_2
13 L^4SnEt_2
M = Ge(IV)
14 L^1GePh_2
15 L^1GeEt_2
16 L^2GePh_2
17 L^2GeEt_2
18 L^3GePh_2
19 L^4GePh_2
20 L^4GeEt_2
21 L^1SbPh_3
22 L^2SbPh_3
23 L^3SbPh_3
24 L^4SbPh_3

Figure 1. Synthesized complexes **1-24**.

The luminescent activity of complexes **1-24** was studied (λ_{ex} = 340 nm, $CHCl_3$). For $R_2Sn(IV)L$, the emission bands (λ_{em}) are observed in the range 560–638 nm, the relative quantum yield (φ) takes values from 0.13 to 0.46. The emission bands of most germanium(IV) compounds are shifted to the long-wavelength region compared to $R_2Sn(IV)L$. The maximum quantum yield (0.70) was determined for L^2GeEt_2 (**19**), while for L^2SnEt_2 (**6**) φ does not exceed 0.18. In the series of $Ph_3Sb(V)L$ complexes, the emission bands are observed in the range 554–574 nm. The maximum quantum yield (1.22) was found for compound L^1SbPh_3 (**21**), which contains three *tert*-butyl groups in the aromatic rings of the ligand.

The *in vitro* antiproliferative properties for some $R_2Sn(IV)L$ complexes are studied for the HTC-116 and A-549 cancer cell lines. The cytotoxicity parameter IC_{50} takes minimal values in the case of complexes 10 (40.8±3.2 μmol/L for A-549) and **6** (12.3±0.9 μmol/L for HTC-116) containing chlorine atoms and a nitro group in Schiff bases. The general tendency towards a decrease in the cytotoxicity of the studied tin complexes is associated with the presence of electron-donating *tert*-butyl groups in the ligands.

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Acknowledgements
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COMPARISON OF METAL-INVOLVING CHALCOGEN AND HALOGEN BONDING INVOLVING SQUARE PLANAR PLATINUM(II) COMPLEXES BEARING CHELATING LIGANDS

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Hydrogen bonds and π-stacking are widely known non-covalent interactions and have been thoroughly studied for recent decades, whereas halogen and chalcogen bonds were only recently acknowledged by IUPAC. These types of weak contacts can be applied in various fields of science and industry starting from organic catalysis ending with molecular biology.[1] Metal-involving halogen and chalcogen bonds is poorly explored contacts but it is thought to provide new tool for crystal engineering.[2]

The most suitable objects in this case are square-planar transition metal complexes which d_{z^2}-orbitals are sterically available for formation of halogen and chalcogen bonds.[3] So In this work, we synthesized two new platinum(II) complexes bearing chelating ligands, $[Pt(PPy)(S_2CN(CH_2)_n)]$ (PPy – 2-phenylpyridine; n = 4, 6). These complexes were co-crystallized with various donors of non-covalent interactions, namely 1,2,4,5-tetrafluoro-3,6-diiodobenzene (1,4-FIB), octafluoro-4,4'-diiodo-1,1'-biphenyl ($C_{12}F_8I_2$), bis(perfluoropyridyl) telluride $(FPy)_2Te$ and bis(perfluorotolyl) telluride $(FTol)_2Te$, to give diverse cocrystals (Fig.1).

The cocrystals were studied by single crystal X-ray diffraction. In crystal structures of the cocrystals we identified I···Pt^{II} halogen and Te···Pt^{II} chalcogen bonds. The noncovalent nature of the revealed interactions was confirmed theoretically by DFT calculations.

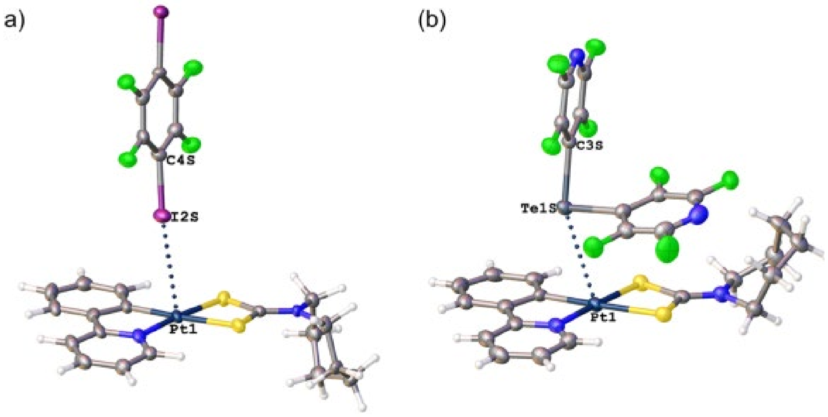

Figure 1. Examples of identified (a) halogen and (b) chalcogen bonds

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X-ray diffraction studies were performed at Saint Petersburg State University Research Centre for X-ray Diffraction Studies.

SYNTHESIS AND ANTIPROLIFERATIVE ACTIVITY OF POLYHEDRAL BORON HYDRIDE CONJUGATES WITH ACRIDINE

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Boron neutron capture therapy (BNCT) is a promising and developing method for threating oncological diseases. It is based on the selective accumulation of large number of 10B atoms in a cancer cell and their subsequent treatment with a flux of thermal neutrons. This makes possible to selectively destroy cancer cells without affecting the surrounding healthy tissue.[1]

Polyhedral boron hydride conjugates with acridine can be potential agents for BNCT. Acridine is able to intercalate DNA and selectively accumulate in cell nuclei embedding itself between two pairs of nucleic acid bases.[2] Thus, such structures may be promising compounds for boron delivery to the cancer cells.

In the presented work we synthesized a number of conjugates of polyhedral boron hydrides with 9-substituted acridine by Cu(I)-catalyzed reaction of [3+2]-dipolar cycloaddition of alkynes to azides and studied antiproliferative activity of these compounds against a series of human cell lines.

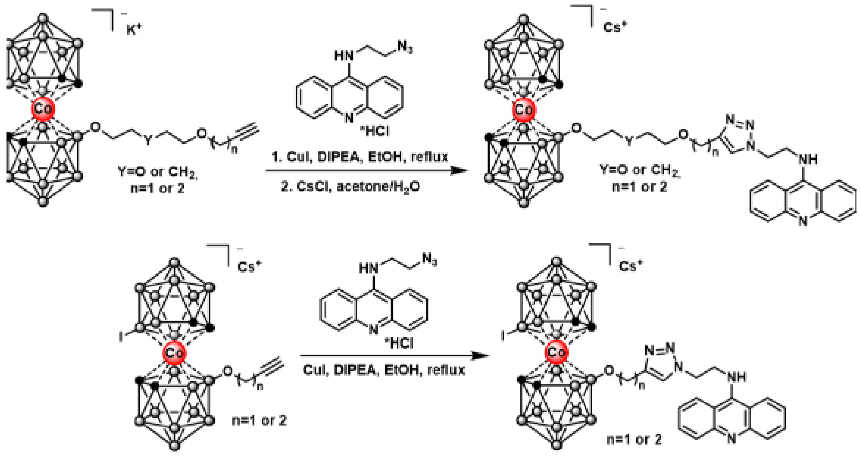

Figure 1. Synthesis of boron-containing acridines.

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PHTHALOCYANINATO-CAPPED TRIS-PYRIDINEOXIMATE 3d-METAL CLATHROCHELATES AS PROSPECTIVE HOMOGENIOUS (PHOTO)CATALYSTS

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Macrobicyclic complexes with encapsulated metal ion (clathrochelates[1]) form a separate class of coordination compounds possessing unique chemical robustness and unusual physico-chemical characteristics. The preparation of hybrid binuclear metallophthalocyaninate-capped iron, nickel(II) and cobalt(III) tris-pyridineoximates have been earlier described.[2–4] In the present work, we report the effective catalysis of an oxidation of cyclohexane into a mixture of cyclohexanone and cyclohexanol,[5] as well as the photocatalytic oxidation of thioanisole into methylphenylsulfoxide, by them as homogenious catalysts.

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INVESTIGATION OF THE INFLUENCE OF SUBSTITUENTS IN THE PHENYL FRAGMENT OF PT(II) COMPLEXES WITH NNC-PINCER LIGANDS ON THEIR PHOTOPHYSICAL PROPERTIES AND AGGREGATION-INDUCED EMISSION (AIE) FOR THE PURPOSE OF CREATING OPTIMAL AGENTS FOR BIOIMAGING

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The ability to finely tune the photophysical properties of Pt(II) complexes over a wide range opens the way for the creation of emitters to solve various tasks.[1] Several approaches can be highlighted for modifying the properties of Pt(II) complexes, one of which is the development of AIE-active molecules that are particularly attractive in the field of bioimaging due to the redshift of the emission band of aggregates.[2] Such materials can be used to create sensors capable of deep visualization of biological objects.

This work reports on four new Pt(II) complexes with NNC-pincer ligands (**Figure 1**) and investigates the influence of substituents with various electronic properties in the phenyl fragment of the NNC ligand on the photophysical properties of isolated Pt(II) complexes and their aggregates. Obtained complexes were fully characterized using ESI-MS, 1D (1H) and 2D (1H-1H-COSY) NMR spectroscopy, and **2-4-Pt-CN2** complexes were studied using X-ray diffraction.

Forced AIE was achieved by isolating the complexes in a confined volume while creating micelles with the block copolymer PCL-b-PEG. MTT testing was conducted on the CHO-K1 cell line for the obtained micelles, and their localization within the same cell line was also studied.

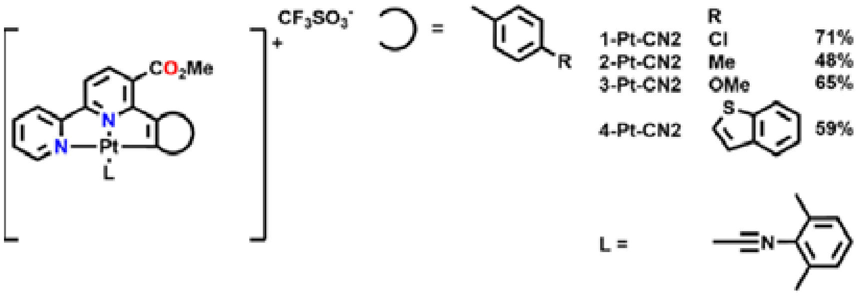

Figure 1. New complex compounds **1-Pt-CN2 – 4-Pt-CN2**

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Acknowledgements

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DIFLUOROBORON β-DIKETONATES WITH TURN-ON FLUORESCENCE RESPONSE TO METHYLBENZENES

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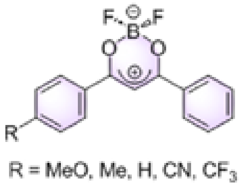
Luminescent organic supramolecular systems containing electron-donor and electron-acceptor (EDA) components have been widely studied in recent decades as active elements of new electronic, photovoltaic, light-emitting and chemosensor devices. Among the promising class of acceptor molecules are BF_2-diketonates, which form intensely fluorescent exciplexes with electron-donor methylbenzenes. A promising area for the use of such boron complexes is chemical sensing applications for the determination of vapors of BTX components (benzene, toluene, xylene).[1]

In this work, $DBMBF_2$ derivatives with electron-withdrawing (CN, CF_3) and electron-donating (Me, OMe) groups in the para-position of the phenyl ring were synthesized (Fig. 1). The optical properties of these compounds were studied in solutions of various methylbenzenes. It was found that the introduction of electron-acceptor groups into $DBMBF_2$ induces a stronger bathochromic shift in the fluorescence spectra in aromatic solvents, while electron-donating groups produce the opposite effect (Fig. 2). The fluorescence quantum yield of compounds with electron-acceptor groups is lower in dichloromethane compared to $DBMBF_2$ but increases significantly (up to 35-fold) in benzene (Fig. 1), making these compounds promising molecular indicators for methylbenzenes with turn-on fluorescence.



Compound	CH_2Cl_2		Benzene		$\Phi_{benzene}/\Phi_{CH2Cl2}$
	Φ	τ, ns	Φ	τ, ns	
$DBMBF_2$	0,24	0,47	0,61	1,8	2,5
$DBMBF_2$-CF_3	0,11	0,11	0,52	1,8	4,7
$DBMBF_2$-CN	0,01	0,10	0,35	1,95	35

Figure 1. Structural formula.of $DBMBF_2$ derivatives and summary table of optical properties of $DBMBF_2$ containing acceptor group

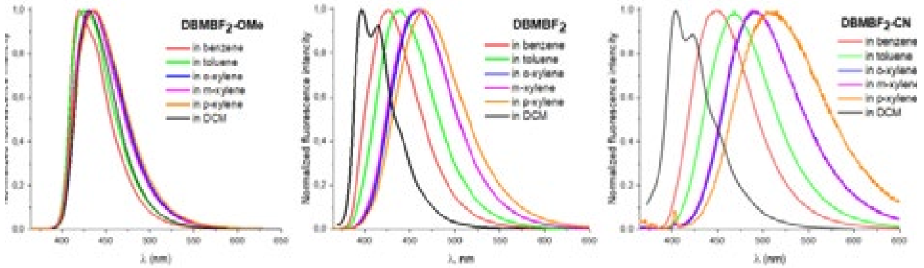


Figure 2. Fluorescence spectra of solutions of $DBMBF_2$ derivatives (left to right: MeO, H, CN) in dichloromethane and various methylbenzenes (Ex 365 nm)

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NOVEL ALKALI AND TRANSITION METAL 3,4-BIS(DIALKYLAMINO)-1,2,3-TRIPHOSPHACYCLOPENTADIENIDES

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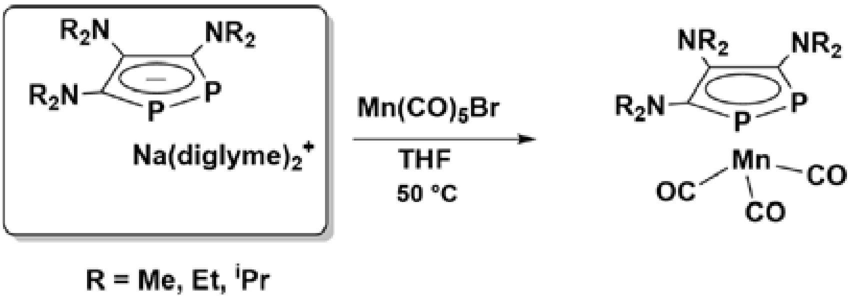
The 1,2,3-triphosphacyclopentadienide anion has received significant interest as ligand in coordination chemistry due to the possibility of realizing various coordination modes with metal atoms.[1] Unfortunately, nowadays the chemistry of the 1,2,3-diphosphacyclopentadienide anion is limited to phenyl-substituted derivatives.

Recently, we have found that the structure of the product of the reaction between sodium 1,2-diphospholide and $Mn(CO)_5Br$ is depending on the nature of the substituents at the carbon atoms. The formation of exclusively 1,2-diphosphacymanthrene was observed in the reaction of 3,4,5-tris(diethylamino)-1,2-diphospholide containing electron donating groups with $Mn(CO)_5Br$ in THF. The formation of a binuclear manganese(I) carbonyl complex with bridging coordination mode of the 1,2-diphosphacyclopentadienyl ligand as in the case of aryl-substituted 1,2-diphospholide was not observed.[2]

At the same time, the chemistry of the novel 1,2,3-diphospholide has not been studied.



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SYNTHESIS AND STRUCTURES OF LANTHANIDE (III) CATIONIC BIS(ALKOXIDE) COMPLEXES WITH STERICALLY DEMANDING PERFLUORINATED LIGAND

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In recent years, lanthanide alkoxide complexes have attracted the interest of researchers due to their potential as Single Molecule Magnets (SMM), with the best examples closely competing with the lanthanocenes in terms of energy barriers for magnetization reversal and blocking temperatures, albeit with varying degrees of Raman relaxation suppression. For a thorough investigation of magnetostructural correlations, it is important to find a suitable method for synthesis of such cationic complexes.

A series of cationic bis(alkoxide) complexes $[\{(C_6F_5)_2HCO\}_2Ln(THF)_4][BPh_4]$ (Ln = Tb, Dy, Ho) was synthesized via the protonolysis reaction of the Ln-C bond in $[Me_2NC_6H_4CH_2\text{-}o]_2Ln[(\mu\text{-}\eta^6{:}\kappa^1\text{-Ph})BPh_3]$ precursors by two molar equivalents of $(C_6F_5)_2C(H)OH$ in THF under mild conditions (Fig. 1). All the obtained compounds were characterized by X-ray diffraction and elemental analysis, as well as IR spectroscopy. All complexes are found to be isostructural and represent a separated ion pair consisting of the cation $[Ln\{OCH(C_6F_5)_2\}_2(THF)_4]^+$ and the anion $[BPh_4]^-$. The complexes possess an octahedral geometry: the metal ion is coordinated with two oxygen atoms of the bis(pentafluorophenyl)methoxide ligands in cis-configuration, and four oxygen atoms of the THF molecules occupy the remaining vertices of the octahedron.

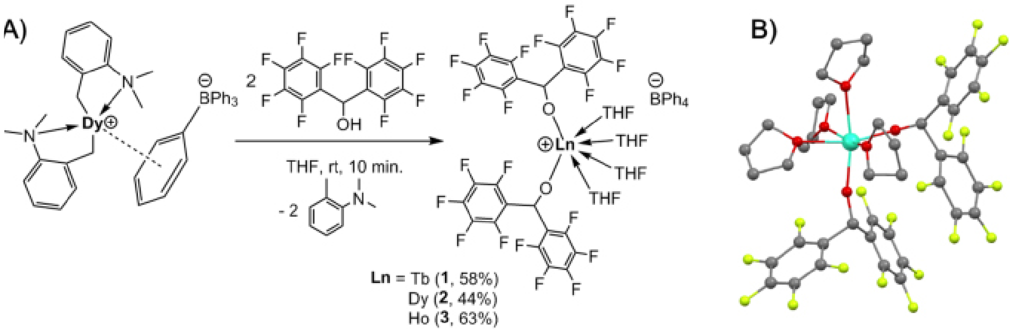

Figure 1. A) Synthesis of cationic bis(alkoxide) complexes **1-3**. B) Molecular structure of **1**, hydrogen atoms and BPh_4^- anion are omitted for clarity.

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SYNTHESIS OF PHOSPHINIC ISOSTERES OF ASPARTIC ACID

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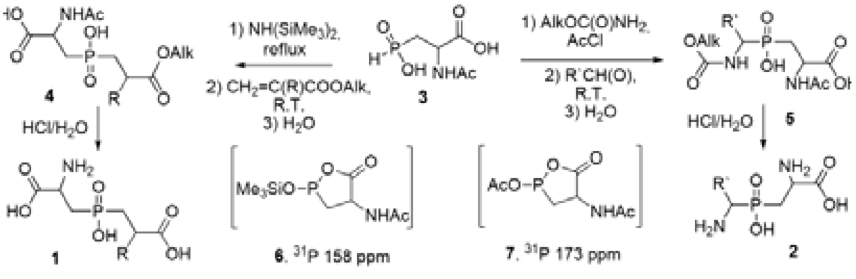
Hydrolytically and enzymatically stable structural phosphinic isosteres of peptides are formed by replacing the natural peptide NHC(O) bond with a non-hydrolyzable methylenephosphorylic $CH_2P(O)OH$ moiety.[1] The Zn-chelating phosphinic moiety combines the two amino acid components and creates very close mimic of the transition state of peptide hydrolysis with four-coordinated carbon atom. The resulting phosphinic peptides, structural isosteres of peptides, are powerful inhibitors of Zn-metalloproteinases involved in variety of biological processes.[1-3]

This work is devoted to the development of methodology for the synthesis of structural analogues of natural peptides, amino phosphinic **1** and diamino phosphinic **2** acids, based on the phosphonous isostere of aspartic acid **3** (Fig. 1).

Silyl activation of phosphonous acid **3** followed by addition to the corresponding acrylates leads to the formation of N-substituted phosphinic acids **4**, which are phosphinic isosteres of β-aspartyl-peptides. In turn, amidoalkylation of acid **3** using alkyl carbamates and the corresponding aldehydes in an acetyl chloride medium yields N,N`-disubstituted phosphinic acids **5**, which can be considered as phosphinic structural isosteres of dipeptides formed from α,β-diaminopropionic acid.

We have found that under the conditions of silyl activation of phosphonous acid **3**, a signal (δ_P~158 ppm) in the region characteristic of trivalent phosphorus compounds is observed in the ^{31}P NMR spectrum of the reaction mass. Under the conditions of amidoalkylation of phosphonous acid **3** in AcCl medium, a similar signal (δ_P~173 ppm) is observed in the ^{31}P NMR spectrum of the reaction mass. We assume that in both cases, compounds of trivalent phosphorus are formed, which are mixed phospho-carboxylic anhydrides, phospholactones **6** and **7**, which is nucleophilic component in the studied transformations.[3] Hydrolysis of phosphinic acids **4** and **5** yields a number of new phosphinic pseudopeptides **1** and **2**.



R = H, Me, $CH_2COOAlk(H)$; R' = Me, i-Pr, s-Bu, Bn; Alk = Me, Et, Bn

Figure 1. Schemes for the synthesis of amino- and diamino phosphinic acid isosteres of aspartic acid

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AZIDE-ALKYNE CYCLOADDITION IN THE SYDNONE IMINES SERIES

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An important area of organic chemistry is the synthesis of biologically active compounds with a specific pharmacological profile. Among synthetic heterocycles, sydnone imines hold a special place. These compounds exhibit a wide range of biological activities and are used in the treatment of cardiovascular diseases (Molsidomine, Linsidomine) as well as in disorders of the central nervous system (Feprosidnine, Mesocarb).[1,2]

The structural features of sydnone imines determine their pharmacological effects, making the development of methods for modifying sydnone imines, as well as introducing pharmacophoric sydnone imine fragments into drug delivery systems, a highly relevant task.

A modern method for constructing complex biological molecules is regioselective azide-alkyne cycloaddition, which allows the linkage of starting compounds via 1,2,3-triazole bridges. However, to date, only a few examples of this method have been described in the synthesis of sydnone imine derivatives. Therefore, the aim of this work is to develop methods for obtaining sydnone imines with azide **1** and terminal alkyne **2** groups, to study their reactivity in model cycloaddition reactions with benzyl azide or phenylacetylene, and to synthesize new triazole-containing bis-sydnone imine derivatives **3** (Figure 1).

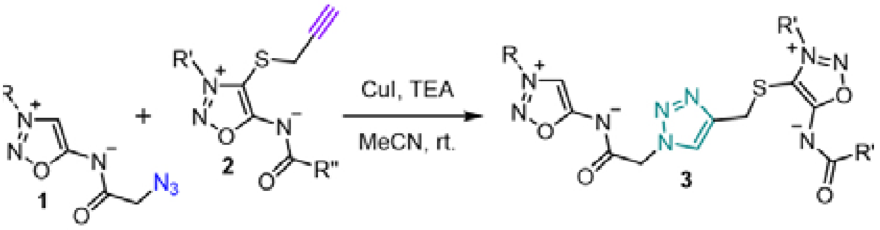

Figure 1.

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CuPt/MFI CATALYSTS FOR PROPANE DEHYDROGENATION

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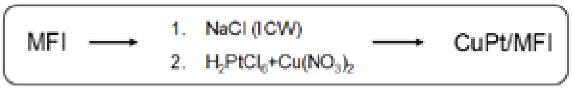
Propylene is an important product for the petrochemical and polymer industries. Although propane dehydrogenation (PDH) is a multi-tonnage industrial direct process for propylene production, the problem of catalyst stability has not yet been solved.

In this work, the influence of copper as a promoter on Pt dispersion and catalytic performance of CuPt/MFI catalysts in PDH was studied. The catalysts were prepared in two stages. First, the zeolites were neutralized with Na^+ cations using the ICW method[1], and then co-impregnated with H_2PtCl_6 and $Cu(NO_3)_2$ (Scheme 1). It was found that the platinum dispersion, activity and stability of the catalysts are most influenced by the concentration of acid centers of the zeolite, calcination temperature and Cu/Pt atomic ratio.



Scheme 1. Synthesis of CuPt/MFI catalysts

Pt dispersion (CO chemisorption) increases with the increase of acidic centers concentration. The activity and stability of the catalysts demonstrates the similar trend.

At higher calcination temperatures (500°C) excess NaCl suppresses zeolite acid centers. This leads to a weakening of the Pt-zeoite support interaction and to a decrease of the catalytic's activity and stability. Conversely, reducing the calcination temperature to 150°C generates an active and stable catalyst while increasing side reactions on residual acid centers.

The optimum Cu/Pt atomic ratios for CuPt/MFI-80 catalysts are 1-10 with Pt dispersion of 50-60%. As the Cu/Pt ratio increases, the availability of platinum centers decreases, causing the activity and stability to decrease.

The 0.3Cu0.1Pt/MFI catalyst showed 7 times higher specific activity in propane dehydrogenation (Fig. 1) compared to the best CuPt/MFI catalyst known in the literature 0.1Pt0.4CuK@S-1.[2]

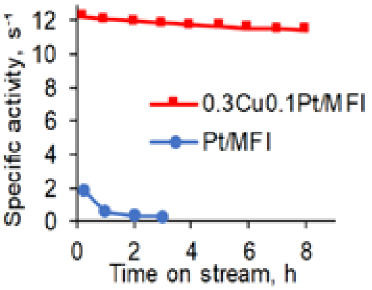


Figure 1. Activities of ICW Pt/MFI catalysts with and without Cu (570 °C, 0.1 MPa, 28 h^{-1})

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BETULIN-BASED HYBRIDS WITH A FERROCENE CORE: DESIGN, SYNTHESIS, CYTOTOXICITY AND COMPUTATIONS

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Betulin (see the formula on the birch leaf) is a natural plant-derived triterpene with a wide range of pharmacological properties. However, due to limited bioavailability and efficacy, it requires chemical modification. In this work, we used ferrocene modification to improve its pharmacological profile. The figure below shows schematically typical synthesized ferrocene-betulins [1-3].

We have developed a series of innovative approaches to ferrocene-betulin hybrids. These involve the coupling reactions between betulonic acid (at positions C-28, highlighted in green) or 3-aminobetulinic acid (at C-3, shown in red) and either readily available ferrocene carboxylic acid or ferrocenoyl piperazinide [2]. Amides and amines derived from betulonic acid bearing ferrocene were successfully prepared from ferrocene amines [3] or by click chemistry from ferrocenyl azide. Furthermore, this study presents the results of DFT calculations and bioassays.

DFT calculations were conducted to forecast the antioxidant capacity of ferrocene amides and ferrocene amines with aliphatic and aromatic components, in comparison to natural antioxidants including vitamin E, ascorbic acid and glutathione. The results for a series of ferrocene derivatives were found to be consistent with those of known antioxidants.

The MTT assay results demonstrated that the incorporation of a ferrocene moiety at C-28 of the betulin core via an amide linker exhibited selective inhibition of MCF-7 cancer cells, IC_{50} = 26 µM [2]. This synthetic approach, which involves modifying bioactive natural plant compounds with ferrocene, has the potential to become a viable strategy for the synthesis of potent anticancer agents.

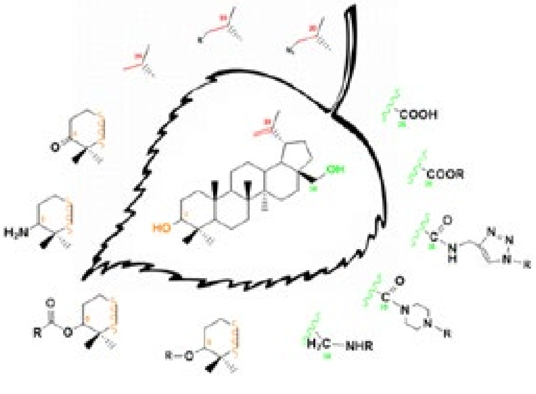

Figure 1. Ferrocene-betulin hybrids.

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SYNTHESIS OF PERFLUORO-4-VINYLOXYBENZENESULFONYL FLUORIDE — A PROMISING MONOMER FOR PRODUCING POLYMER ELECTROLYTES

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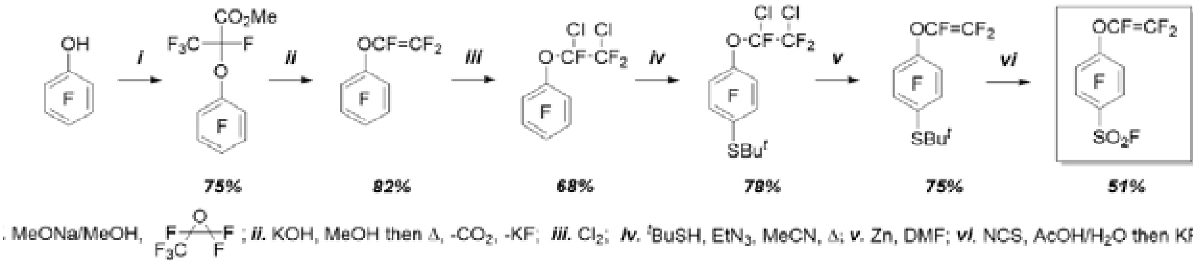
The creation of polymeric materials for various electrochemical devices, including fuel cells, is an important area of research aimed at the development of modern technologies. Fuel cells use different types of electrolytes, one of which is proton-conducting membranes mainly represented by commercially available fluorinated polymers containing sulfo groups (Nafion®, Aciplex®, Dow®). It is known that the monomers for such polymers are perfluorovinyl ethers, in which the -OCF=CF$_2$ moiety is connected by a perfluoroalkoxy linker with an acidic function.[1]

In our work we propose a synthetic route to a new monomer (Scheme 1) containing a fully fluorinated benzene ring as a linker, which is a convenient building block for creating a large number of polymeric materials. Previously, we have not encountered examples of such monomers in the literature, which is of great interest of studying their activity in polymerization and the properties of the resulting polymers.



Scheme 1. Synthesis of perfluoro-4-vinyloxybenzenesulfonyl fluoride

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FAST MOTIONS OF AN IRIDIUM DIHYDRIDE COMPLEX IN AQUEOUS MEDIUM REVEALED BY NMR RELAXOMETRY WITH HIGH-RESOLUTION

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A recently discovered method for significantly increasing the sensitivity of nuclear magnetic resonance (NMR) is based on the use of para-hydrogen with organometallic iridium complexes. This is a game-changing development in the field. This method, known as Signal Amplification by Reversible Exchange (SABRE), has rightfully attracted a lot of attention in recent years. The most commonly used precursor in SABRE is the [IrIMes(COD)Cl] complex, which forms stable dihydride species [Ir(IMes)Py_3H_2]Cl (see Figure 1). This plays a key role in transferring polarization from hydrogen to nuclei of the substrate (Py), enabled by interactions with hydrogen and an electron-pair donor substrate. IMes denotes 1,3-dimesitylimidazol-2-ylidene, COD is 1,5-cyclooctadiene, and Py is pyridine.

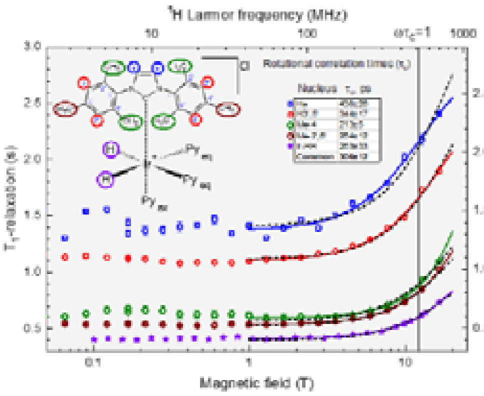

Figure 1. Magnetic field dependence of the proton T_1 relaxation time of [Ir(IMes)Py_3H_2]Cl. Symbols show experimental data, solid lines show the result of fitting by the model **$1/T_1=A*\tau_c/(1+(\omega\tau_c)^2)+B$**. The colored lines represent independent fits, while the black dashed lines show global fits with a common τ_c parameter.

Our study investigates an iridium hydride complex with pyridine in an aqueous medium, which remains stable for several days in water. We measured the magnetic field dependence of T_1-relaxation times of individual protons of this complex using high-resolution NMR and a specialized setup designed for rapid sample positioning along the axial axis of the cryomagnet. Figure 1 clearly shows that the T_1 dependence on the magnetic field has distinctive features at high magnetic fields. We determined the rotational correlation times of individual protons in the complex using a simplified model. The employed model focuses on the relaxation caused by fluctuating local fields, and it is sufficient in this case to obtain the correlation times of rotational motion. The τ_c values obtained are summarized in Table 1 of Figure 1, which clearly demonstrates statistically significant differences in the molecular mobility of various protons. Specifically, the Ha protons in the five-membered ring of the IMes ligand exhibit slower motion (τ_c = 440 ps) compared to protons in the more flexible six-membered rings of mesitylene (τ_c = 240 ps).

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NEW ERBIUM COMPLEXES WITH ALKOXIDE ORTHO-CARBORANE LIGANDS AS MAGNITO-LUMINESCENCE MATERIALS

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With the development of digital technologies, the need to store and accelerate information processing is increasing.[1] And the key way to solve the problem is the investigation of SMM (single molecular magnets). SMMs are such molecular systems, which as a result of the presence of a high anisotropic barrier are able to exhibit slow relaxation of magnetization in a zero magnetic field, which leads to the appearance of magnetic hysteresis.[2]

And lanthanide-based coordination compounds are among the most promising candidates for SMMs.[2] In addition, rare-earth metal derivatives exhibit characteristic lanthanide-centered luminescence, which opens the possibility of developing bifunctional systems combining both magnetic and luminescent properties.

A fundamentally important point in the development of SMMs based on lanthanide complexes is played by the coordination environment of the central metal ion, which influences its electron density geometry.[2] To this goal, for synthesis lanthanide complexes with magnetic and luminescence properties new carbinols based on bulk ortho-carboranes $L_{1\text{-}3}OH$ with different substituents at the carbon atom have been developed.

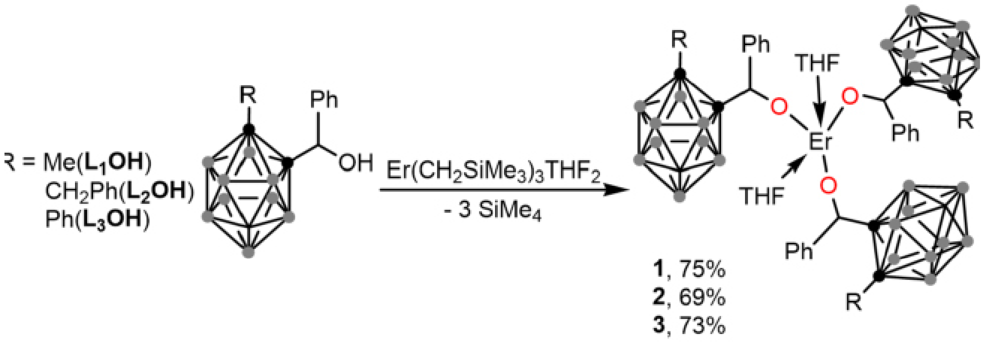

Figure 1. Synthesis of tris(alkoxide) erbium complexes (**1-3**)

The reaction of $Er(CH_2SiMe_3)_3(THF)_2$ with three equivalents of $L_{1\text{-}3}OH$ at 20°C leads to the formation of erbium tris(alkoxide) complexes **1-3** with high yields. According to X-Ray analysis the complexes have trigonal bipyramidal geometry with coordination number 5. The erbium ion is bonded to three oxygen atoms of the ligands as well as two THF molecules.

Erbium complexes showed photoluminescence in the IR range with maxima at 1540 (**1**), 1573 (**2**), 1553 (**3**) nm. The luminescence lifetimes for complexes **1-3** were 29.7, 25.4 and 31.7 µs, respectively.

Acknowledgements
The authors thank Russian Science Foundation (grant № 24–13–00275) for financial support.

NOVEL BENZIMIDAZOLE AND BENZOXAZOLE DERIVATIVES OF 3,5-DI-TERT-BUTYL-O-AMINOPHENOL AS A LIGANDS FOR HEAVY CARBENE ANALOGUES

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In recent decades, carbenes have acquired the status of important synthetic intermediates in various organic processes, which has given rise to a large number of studies on stable carbene particles and their analogs [1]. The formation of complexes with pincer, bi- and polydentate chelating ligand systems [2] due to the introduction of additional functional groups in the side chains of their organic fragments becomes a new branch of development of metallene chemistry.

The introduction of bulk substituents allows reducing the association and synthesizing tetrylenes in the monomeric dicoordinated state. Recently, a new trend has emerged to stabilize them in the monomeric state - the use of functionalized organic ligands with the possibility of additional, one or more, donor-acceptor interactions.

In this work we present synthesis of O,N-heterocyclic germylenes and stannylenes bearing new o-aminophenols functionalized with benzimidazole and benzoxazole moieties. Problems in the synthesis of monoliganded as well as peculiarities of the structure of bisliganded derivatives are discussed.

It was found that benzimidazole, benzoxazole have high basicity: this is due to the spatial interaction of the basic centers, which are in close proximity.

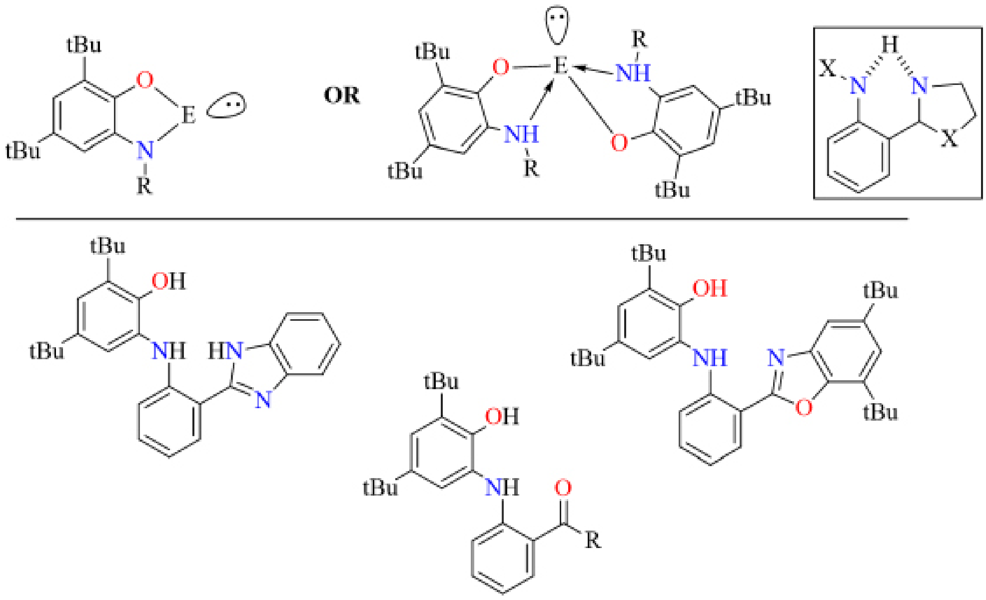

Figure 1. Ligands used to stabilize low-valent *E*: centers (Ge and Sn) and options of chelation.

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INTERACTION OF BIS-ISOCYANIDE PLATINUM(II) COMPLEXES WITH MOLECULAR IODINE

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The study of the transition of platinum oxidation states between +2 and +4, and vice versa, represents a significant area of research, as these transformations play a crucial role in understanding catalytic activity, electrochemical properties, reactivity, and the stability of these compounds. Gaining insights into the mechanisms underlying these processes is essential for deepening our knowledge of the chemical nature of platinum group metals and for developing innovative technologies based on their properties.

Platinum(II) complexes can undergo reversible oxidation by molecular iodine. The thermodynamics of this process are influenced by the nature of the ligand environment surrounding the metal center. Several instances of such oxidation have been documented in the literature. For example, the complexes $[Pt(bpy)I_2]$ and *trans*-$[PtI_2Py_2]$ were reacted with I_2, resulting in the oxidative addition of iodine to form $[Pt(bpy)I_4]$ and *trans*-$[Pt_4Py_2]$.

Previous studies have shown that the addition of molecular iodine to aryl isocyanide complexes of the form *trans*-$[PtI_2(CNAr)_2]$ does not result in oxidation, leading instead to the formation of co-crystals of *trans*-$[PtI_2(CNAr)_2]\cdot I_2$[1]. In the current investigation, we demonstrate that the structure of the isocyanide ligand influences the outcome of the reaction, resulting in the formation of either Pt(IV) complexes *trans*-[PtI4(CNR)2] or Pt(II) adducts trans-$[PtI_2(CNR)_2]\cdot nI_2$. This presentation will provide an overview of the results obtained from the interaction between bis-isocyanide complexes *trans*-$[PtI_2(CNR)_2]$ and molecular iodine.

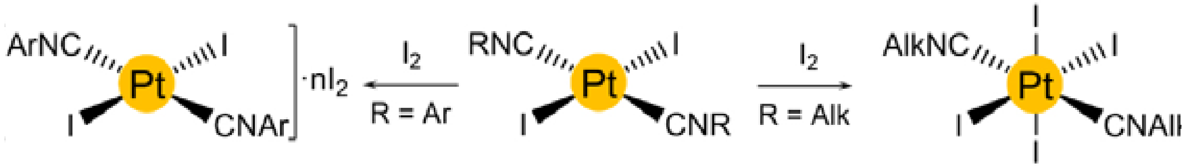

Figure 1. The interaction pathways of trans-$[PtI_2(CNR)_2]$ with I_2

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Acknowledgements
This work was supported by a grant from the Ministry of Science and Higher Education of the Russian Federation for large-scale research projects in high priority areas of scientific and technological development (grant number 075-15-2024-553).

PHOSPHINOKETENE COMPLEXES OF MANGANESE AND RHENIUM

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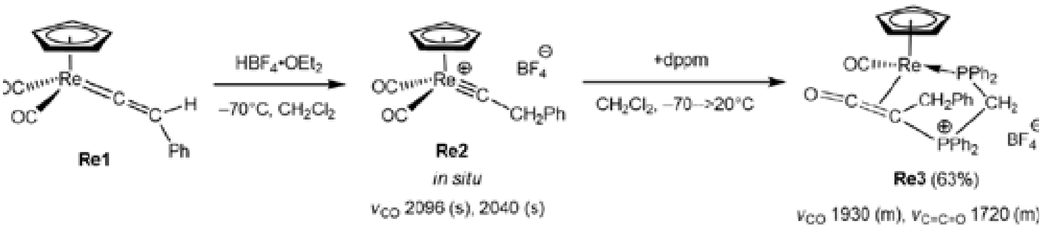
We have shown earlier that the outcome in the reaction between cationic manganese carbynes $[Cp(CO)_2Mn{\equiv}C\text{-}R]X$ and dppm is governed by the nature of R substituent at the carbyne carbon atom.[1] When R is Me or CH_2Ph, phosphinoketene complexes $[Cp(CO)Mn\{\eta^3\text{-}(\boldsymbol{P,C,C})\text{-}Ph_2\boldsymbol{P}CH_2\text{–}^{+}PPh_2\text{–}\boldsymbol{C}(R){=}\boldsymbol{C}{=}O\}]X$ result from nucleophilic addition of the phosphorus atom to the carbyne carbon followed by coupling of the phosphoniocarbene and carbonyl ligands. At the same time, the relative arylcarbyne complexes $[Cp(CO)_2Mn{\equiv}C\text{–}Ar]X$ (Ar = Ph, Tol) react with dppm to form λ^5-1,3-diphosphetium semi-ylides.

We studied the reaction of dppm with benzylcarbyne complexes of manganese $[Cp^*(CO)_2Mn{\equiv}C\text{-}CH_2Ph]BF_4$ (**Mn2**) and rhenium $[Cp(CO)_2Re{\equiv}C\text{-}CH_2Ph]BF_4$ (**Re2**) obtained by protonation of the corresponding vinylidene precursors $Cp^*(CO)_2Mn{=}C{=}C(H)Ph$ (**Mn1**) and $Cp(CO)_2Re{=}C{=}C(H)Ph$ (**Re1**) and found this reaction to afford phosphinoketene complexes $[Cp^*(CO)Mn\{\eta^3\text{-}(\boldsymbol{P,C,C})\text{-}Ph_2\boldsymbol{P}CH_2\text{–}^{+}PPh_2\text{–}\boldsymbol{C}(CH2Ph){=}\boldsymbol{C}{=}O\}]BF_4$ and $[Cp(CO)Re\{\eta^3\text{-}(\boldsymbol{P,C,C})\text{-}Ph_2\boldsymbol{P}CH_2\text{–}^{+}PPh_2\text{–}\boldsymbol{C}(CH_2Ph){=}\boldsymbol{C}{=}O\}]BF_4$.



Scheme 1. Reaction of the rhenium carbyne complex **Re2** with dppm.
The structure of the rhenium complex **Re3** was confirmed by X-ray diffraction.

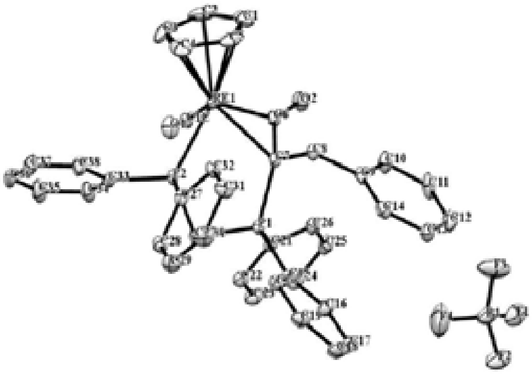


Figure 1. Molecular structure of the phosphinoketene complex **Re3**.

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HEAVIER ISONITRILES, $[ARNE:]_2$, LUMINESCENCE, OXIDATIVE ADDITION, HALOGENATION, ISOMERIZATION

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This report is dedicated to new stable heavy isonitriles $[ArNE]_2$ E = Ge, Sn, Pb, stabilized by exceptional steric protection with $^{R1,R2}Ar$ (Ar = 2,6-((4-$R^1C_6H_4)_2CH$)-4-R^2-C_6H_2; R^1 = H, Me, tBu; R^2 = Me, Cl, CF_3). These compounds exhibit a rare phenomenon – intense tetrylene-centered phosphorescence. Additionally, the report discusses their structural and electronic features as well as their reactivity in oxidative addition, halogenation, isomerization, and other reactions.

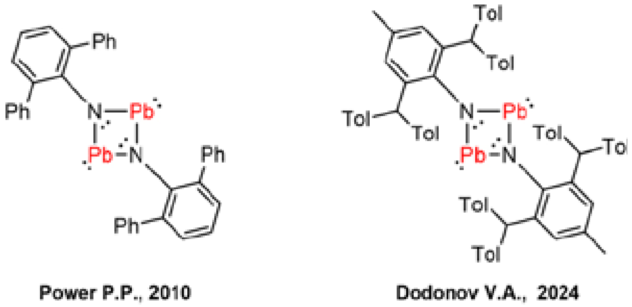

Figure 1. Smallest plumbaisonitriles known to date

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Acknowledgements

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SYNTHESIS OF CHROMOCENE $^{54}Cr(C_5H_5)_2$ FOR PRODUCTION OF ACCELERATED ION BEAMS BY THE MIVOC METHOD

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Obtaining highly charged ion beams from solids is an urgent task for modern science. It is used in such areas as radiation physics, solid state physics, nanotechnology, and in the synthesis of superheavy elements (SHE).

One of the main methods of obtaining charged ion beams for the electron cyclotron resonance (ECR) is method MIVOC (Metal Ions from Volatile. Compounds), based on the evaporation of organometallic compounds with a relatively high vapor pressure (10^{-3} Torr) at room temperature [1].

To ensure a sufficient ion flux, a high and stable vapor pressure in the ionization chamber is required. At the same time, the initial compound should not contain heteroatoms (N, O, S, P, Si, Hal). In this case, the use of highly volatile organometallic compounds, such as chromocene ($^{54}Cr(C_5H_5)_2$), to obtain beams of ^{54}Cr ions is promising. To increase the intensity of the ^{54}Cr ion beam at the STE plant, the JINR Laboratory of Nuclear Reactions needs to develop a method for regenerating substances at all stages of obtaining and synthesizing the target product $^{54}Cr(C_5H_5)_2$.The synthesis of chromocene included the following stages:

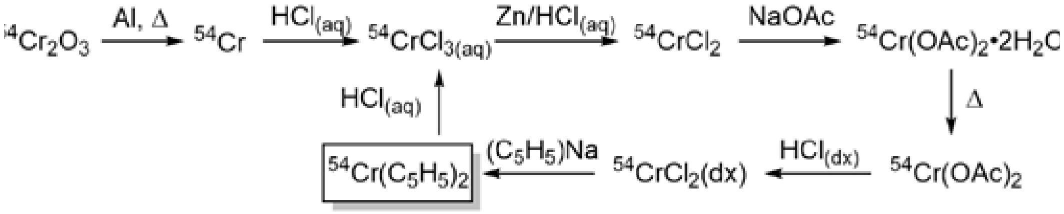

Figure 1. Synthesis of $^{54}Cr(C_5H_5)_2$

In the course of this work, $^{54}Cr(C_5H_5)_2$ was synthesized and used in the experiment on the fusion of ^{54}Cr and ^{238}U with the formation of a previously unknown isotope ^{288}Lv. A method for regenerating ^{54}Cr isotope waste has also been developed and successfully applied, which significantly reduces the consumption of the target ^{54}Cr isotope.

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FLUORESCENT RET-SENSORS FOR METAL CATIONS

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Resonance energy transfer (RET) sensors are common in biological research, since high contrast in optical signal switching in RET-chemosensors is combined with the possibility of using receptor groups that reversibly bind the metal cation being determined.[1,2] Monitoring the content of metal ions in the cell allows to study the processes of the body, as well as diagnose some diseases.

Sensor molecules **1** and **2** consist of two chromophore fragments: naphthalimide alkoxy derivatives act as energy donors (CD), and ICT-chromophores containing receptor picolylamine fragments act as acceptors (CA). The components of the RET pairs were selected in such a way that the fluorescence spectrum of CD overlapped with the absorption spectrum of CA – with such a combination of photoactive components, an effective resonant energy transfer is realized in the system (figure 1).

The coordination of the receptor with the metal cation is accompanied by a hypsochromic shift in the absorption spectrum of CA, which leads to a decrease in the integral overlap of the spectra and causes a decrease in the efficiency of the RET-process, accompanied by a donor chromophore fluorescence enhancement. The crosslinking of the photoactive components was carried out using the click reaction of the 1,3-dipolar cycloaddition azide-alkyne, leading to the formation of a triazole cycle. The complexing properties of **1** and **2** with respect to divalent metal cations were studied by optical and NMR spectroscopy, as well as mass spectrometry.

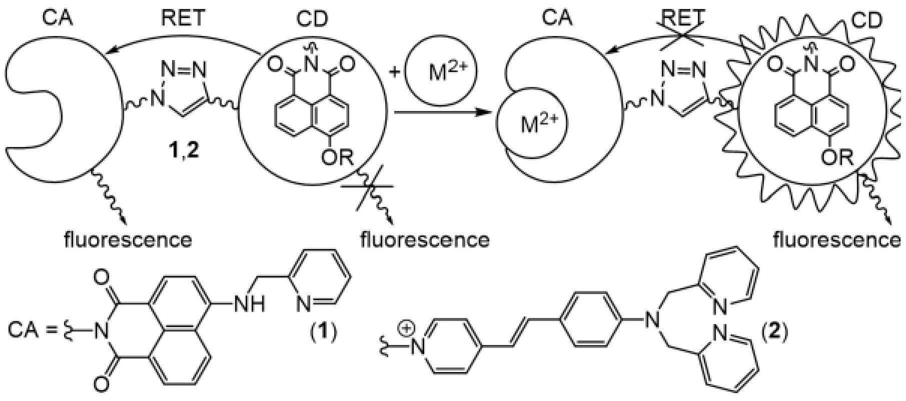

Figure 1. The working principle of sensors **1** and **2**

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CHARGE CHARACTERISTICS OF TITANOCENE DICARBORANYL BY NBO METHOD

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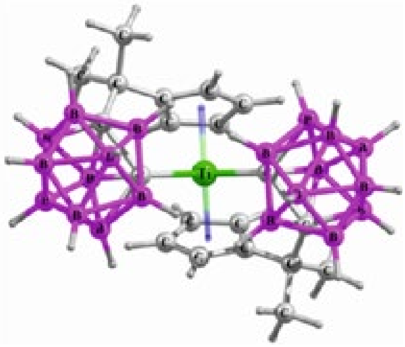
Group IVB metallocenes possess rarest and least studied ligand-to-metal charge transfer (LMCT) excited states, including unique phosphorescent ones.[1,2] Evaluation of the orbital populations and charge characteristics of metal ion(s) and ligands in coordination compounds is a key problem in coordination chemistry and, in particular, photonics of charge-transfer states that cannot be solved experimentally.



The natural bond orbital (NBO) analysis[3] program is one particular example that is made available in a number of leading quantum chemistry program suites. In this communication, for the first time in the NBO approximation, using ca. 100 methods, the orbital populations and atomic charges are systematically estimated using the example of titanocene dicarboranyl Ti(η^5:η^1-CpCMe$_2$CB$_{10}$H$_{10}$C)$_2$, possessing unique radiative LMCT states.

The vast majority of the hundred popular methods of different levels of theory used provided realistic data: charge on the metal: +1.1...+1.8, charges on the ligands: −0.05...−0.35 (cyclopentadienyls) and −0.50...−0.80 (carboranyls). In contrast to the Mulliken approach, where the charge values of the target titanocene change unpredictably to the point of absurdity4, NBO approximation describes the atomic charges much more reliably and is largely independent of the basis set.

Charge distribution on atoms determines pairs of donors and acceptors, including charge transfer. For the same molecular system, the charge value on atoms can vary significantly depending on the approach used (Mulliken, NBO, etc.), computing method ((Hartree-Fock, density functional theory, etc.) and the basis set. Based on preliminary results of our long-going systematic study, carried out for a polar species − titanocene dicarboranyl, it is reasonble to assume that NBO is a more advanced approach, which apparently solves most of the problems of the traditional Mulliken scheme, in particular, it demonstrates numerical stability with respect to changes in the basis set.

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CHARGE CHARACTERISTICS OF TITANOCENE DICARBORANYL BY MULLIKEN METHOD

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Group IV B metallocenes are promising precursors for organic synthesis catalysts, photochemical sensors, phosphorescent and polyfunctional materials, etc. This class of organometallics has rarest and least studied ligand-to-metal charge transfer (LMCT) excited states, including unique phosphorescent ones.[1-4] Evaluation of the populations of molecular orbitals and charge characteristics of metal ion(s) and ligands in coordination compounds is a key problem in coordination chemistry and, in particular, photonics of charge-transfer states that cannot be solved experimentally.

In the present work, the charge characteristics of an organometallic complex having radiative LMCT states are systematically evaluated (considering sterically hindered titanocene(IV) dicarboranyl $Ti(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ as the instructive instance) by means of ca. 200 popular quantum-chemical methods at different levels of theory and a conclusion is made on reliability of computing in the Mulliken approximation. We compared various (Hartree-Fock (HF) and density functional theory (DFT)) methods for the broadest possible description of the electronic distribution in a organometallic complex and assessed the sensitivity of the calculated charges to changes in (i) the choice of the analysis method (in this case, Mulliken approach is considered as the historically most important method), (ii) choosing a basis set, (iii) the choice of the quantum-mechanical Hamiltonian, and (iv) molecular structure (in the case of a different species, the other calculation methods can be operative). Notably, the systematic Mulliken population analysis gives very contradictory results for target $Ti(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$. In a series of ca. 200 popular methods (HF, DFT), calculations using high QZVP basis set and the Pople basis sets: 6-311G** and 3-21G (3-21G*) provided an acceptable charge analysis within the traditional Mulliken approach (the simulated charge on Ti(IV) varies from +1.1 to +2.2 and the negative charges on the ligands are >-1). The target titanocene dicarboranyl in the S_0-state has a large electric dipole moment (10−11 Debye)[5], being extremely rare for organometallic species.

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TETRAPHENYLPORPHYRINATE-PENTHAMETHYLCYCLOPENTADIENIDE SANDWICH COMPLEXES – THE FIRST AIR-STABLE Ln(III) ORGANOMETALLICS

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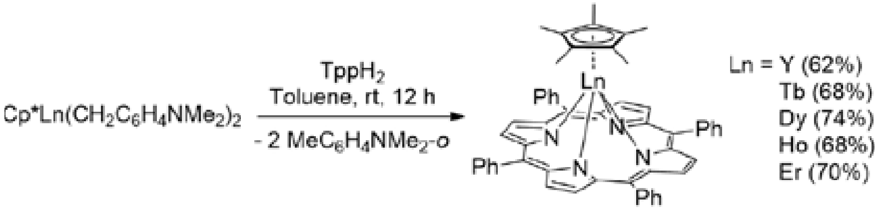
An efficient synthetic approach to the first air-stable Ln(III) organometallics supported by 5,10,15,20-tetraphenylporhpyrin ligand (Tpp) was elaborated. Sandwich tetraphenylporphyrinate-penthamethylcyclopentadienide complexes TppLnCp* (Ln = Y, Tb, Dy, Ho, Er) were synthesized by the reaction of half-sandwich bis(dimethylaminobenzyl) precursors $Cp^*Ln(CH_2C_6H_4NMe_2)_2$ with equimolar amounts of 5,10,15,20-tetraphenylporhpyrin (TppH2) in toluene at ambient temperature and isolated in 62–74% yields. X-ray analysis revealed the strictly linear structure of base-free complexes featuring Cp^*_{Centr}–Ln–TppCentr bond angles close to180° and Cp^*_{Centr}–Ln and Tpp_{Centr}–Ln bond distances of 2.325–2.365 and 1.012–1.063 Å. TppLnCp* proved to be stable under aerobic conditions and can be sublimed in vacuum (>290 °C, ~5·10^{-2} Torr).



Scheme 1. Synthesis of sandwich complexes TppLnCp*.

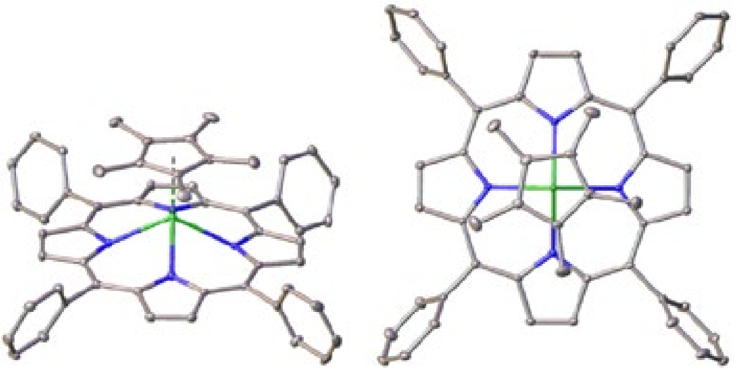


Figure 1. General view of **TppLnCp*** (a, side; b, top); C = gray, N = blue, Ln = green.

Acknowledgements
The financial support of the Russian Science Foundation is highly acknowledged (Project № 24-13-00275)

EFFICIENT IN-MAGNET ^{15}N HYPERPOLARIZATION OF ANTIMICROBIAL DRUGS INDUCED BY REVERSIBLE EXCHANGE OF PARAHYDROGEN WITH IR-BASED CATALYST

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Signal Amplification By Reversible Exchange (SABRE) utilizes non-equilibrium spin order of parahydrogen as a source of strong NMR signal enhancement aimed to increase NMR sensitivity. In SABRE, parahydrogen and to-be-polarized substrate form a transient polarization transfer complex. Performed inside high magnetic field of an NMR-spectrometer, SABRE allows to hyperpolarize nuclear spins without additional polarizers, however, requires thorough pulse sequence design. The high-field polarization transfer strategy strongly depends on the type of the spin system formed by the parahydrogen-nascent protons in the SABRE-complex: chemically equivalent or non-equivalent. SABRE hyperpolarization in chemically equivalent spin systems has drawn much attention, while targeting on a limited pool of substrates. Efficient hyperpolarization in chemically non-equivalent complexes remained a missing piece of the puzzle for completeness of high-field SABRE and possibility to polarize an arbitrary SABRE substrate. Thus, this work reports multinuclear ^{1}H-^{15}N pulse sequences for efficient ^{15}N hyperpolarization in chemically non-equivalent SABRE-complexes. The first pulse sequence relies on simultaneous ^{1}H and ^{15}N radiofrequency (RF) excitation of complex-bound nuclei with weak continuous wave (CW) magnetic fields. The proposed pulse-sequence allowed us not only to hyperpolarize ^{15}N nuclei in a mixture of antimicrobial drugs containing a 5-nitroimidazol moiety at their natural ^{15}N isotopic abundance (0.76 % of ^{15}N polarization), but also to precisely assign from which SABRE-complexes this polarization emanates. The second approach is based on INEPT pulse sequence and leads to ^{15}N hyperpolarization (0.4-0.7 % of ^{15}N polarization) in a robust manner with the minimal experimental optimization.

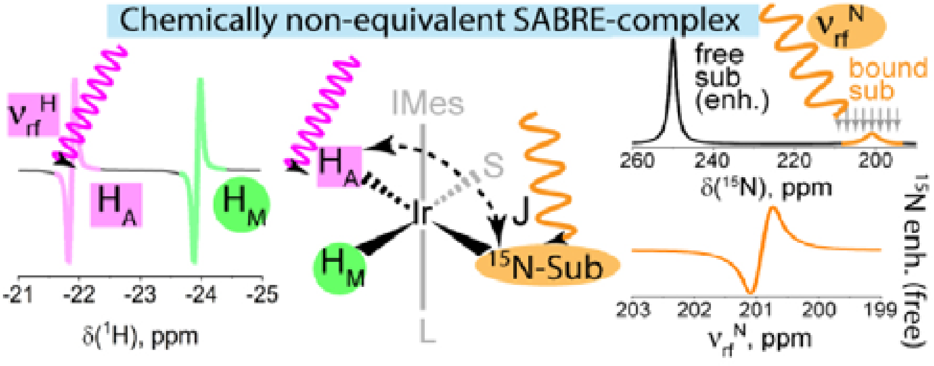

Figure 1. Schematic representation of CW-irradiation used for the high-field SABRE polarization transfer. Weak CW fields selectively excite HA hydride proton (on-resonant field) and ^{15}N nuclei (with slightly off-resonant field) in the SABRE-complex.

Acknowledgements
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CERIA NANOPARTICLES CONJUGATES WITH AZA-CROWN ETHERS AS A PROMISING NANOPLATFORM FOR RADIOPHARMACEUTICAL USE

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Nanoparticles exhibit enhanced accumulation within tumor tissues, a property that is leveraged in targeted therapies, particularly in nuclear medicine. Cerium dioxide nanoparticles are characterized by their low toxicity, high biocompatibility, efficient excretion from the body, and substantial accumulation in target organs. These attributes help to reduce systemic dose burden, rendering cerium dioxide nanoparticles promising candidates for anticancer research. Cerium dioxide possesses dual functionalities: it can enhance the viability of healthy cells by mitigating oxidative stress through its antioxidant properties and simultaneously exert cytotoxic effects on tumor cells.

In this study, we synthesized cerium dioxide conjugates with bifunctional chelators to securely bind radioactive metals. Specifically, we employed bifunctional derivatives of the recently developed in our group ligand **L** and the widely utilized in nuclear medicine ligand **DOTA**. The resulting conjugates were thoroughly characterized using transmission electron microscopy, infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis and isoelectric point shift measurements.

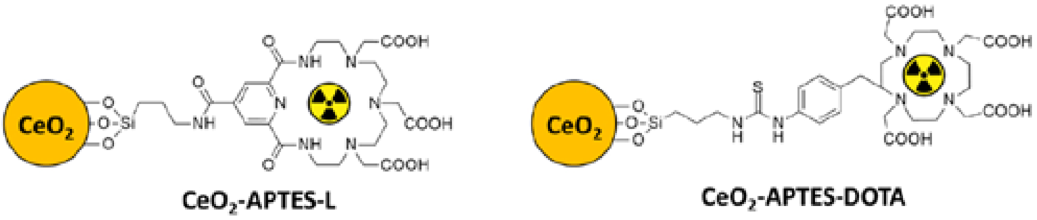

Figure 1. The structures of the conjugates discussed in this study

We investigated the optimal labeling conditions for conjugate complexes with $[^{65}Zn]Zn^{2+}$ and $[^{44}Sc]Sc^{3+}$ and assessed their stability in saline, phosphate-buffered saline, and fetal bovine serum. Our findings revealed that the **CeO_2-APTES-L-$[^{44}Sc]Sc^{3+}$** complex demonstrated stability under these conditions for more than 8 hours. Furthermore, nanoceria and its derivatives exhibited no significant toxicity towards human endothelial cells EA.hy926. The *in vivo* stability of the scandium complex **CeO_2-APTES-L-$[^{44}Sc]Sc^{3+}$** was also confirmed. These results suggest that cerium dioxide nanoparticles hold potential as nanocarriers for targeted drug delivery, particularly within the realm of nuclear medicine.

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Acknowledgements
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A NEW DIRECTION IN THE REACTION OF CHLOROPHOSPHITES WITH SODIUM BENZYLIDENE GLYCINATE: THE FORMATION OF IMIDAZOLIDINE-4-ONE DERIVATIVES

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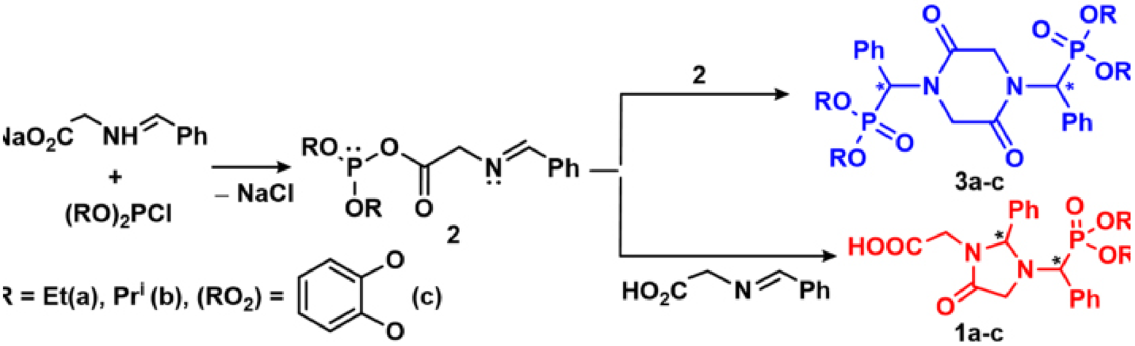
The interaction of sodium benzylidenglycinate with dialkyl chlorophosphites, as shown earlier [1], leads to the formation of 1,4-bis[1-(dialkoxyphosphoryl)benzyl] piperazine-2,5-diones – derivatives of the well-known in chemistry α-amino acids 2,5-diketopiperazines. At the same time, stereoisomeric bis[1-(dialkoxyphosphoryl) alkyl] amines were isolated as products in the similar reaction of chiral α-amino acids [2].

We have found a new direction of the reaction of chlorophosphites with sodium benzylidenglicinate [3]. During chromatography of reaction mixture on SiO_2, imidazolidine-4-one derivatives **1a-c** were isolated as well.



Iminophosphites **2a-c**, formed at the first stage of the reaction of sodium benzylidenglycinate with chlorophosphites, are converted into phosphorylated 2,5-diketopiperazine derivatives **3a-c** by dimerization. Hydrolysis of chlorophosphites with water from the sodium benzylidenglycinate crystal lattice precedes the formation of derivatives **1a-c**. In this case, during the reaction, the amino acid salt is converted into benzylidenglycine, which further reacts with iminophosphites **2a-c** and turns into imidazolidine-4-one derivatives **1a-c**.

It should be noted that the ratio of reaction products **1** and **3** significantly depends on the rate of addition of chlorophosphites to sodium benzylidenglicinate. With rapid addition, a contribution of derivatives of 2,5-diketopiperazine **3** exceeds a contribution of imidazolidine-4-one derivative **1**. With a decrease in the rate of addition, the portion of compound **1** gradually increases, and it becomes the main product of the reaction.

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SUPPORTED MONONUCLEAR METAL CARBONYLATES OF IRON, RUTHENIUM, RHENIUM AND MANGANESE AS HYDROGEN TRANSFER CATALYSTS

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Currently, one of the important problems of chemistry is the replacement of hydrogen gas with small protic solvents with a high hydrogen content in the molecule. However, due to the lack of highly effective and easily accessible catalysts, this problem remains unsolved.[1-2]

A very illustrative example of such processes, where hydrogen gas serves as a reagent in an exothermic process in the presence of catalysts (often pyrophoric), is the reduction of aromatic nitro compounds. The aim of this work is to replace hydrogen with low-boiling solvents such as CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$ or HCOOH. As catalysts for this process, we studied systems developed at INEOS RAS based on supported transition metal carbonylates, such as $K_2[Ru(CO)_4]$, $K_2[Fe(CO)_4]$, $K[Re(CO)_5]$ and $K[Mn(CO)_5]_3$ on carbon and mineral supports, which have proven themselves well in the reaction of low-temperature ammonia synthesis. It turned out that all these catalysts based on the above metal carbonylates are capable of conducting the reaction of nitrobenzene hydrogenation with alcohols (CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$) and HCOOH at boiling point, and in some cases at room temperature, with varying degrees of efficiency. The most effective source of hydrogen and simultaneously the solvent in this process is HCOOH.

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We gratefully acknowledge Ministry of Science and Higher Education of the Russian Federation for financial support (project No. 075-00277-24-00).

NOVEL DOUBLE-ARMED BENZOAZACROWN ETHERS AS POTENTIAL CHELATORS FOR LEAD AND BISMUTH RADIONUCLIDES

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With increasing clinical applications and interest in targeted alpha therapy, there is growing interest in developing alternative chelating agents for ^{212}Pb and $^{212/213}$Bi that exhibit rapid radiolabeling kinetics and kinetic inertness. The currently used DOTA and DTPA chelators have a number of disadvantages, such as slow complexation kinetics or instability of the complexes. In our work we synthesized a series of 18- and 21-membered macrocyclic chelators BADA-18, BADA-21, BADPA-18, and BADPA-21, which are benzodiazacrown compounds containing carboxylate or picolinate pendant arms. We hypothesized that the decreased conformational flexibility due to the introduction of a rigid benzyl unit into macrocyclic framework, the large cavity size, and two pendant arms would efficiently saturate the coordination sphere of large metal ions and could provide high stability of the resulting complexes.

It was shown how the stability of the complex is influenced by an increase in the size of the macrocycle, the replacement of acetate arms with picolinate ones, the rigidity of the ligand, as well as the type of conformation (syn- or anti-) of the metal complex. Labeling experiments with lead and bismuth radionuclides for the new ligands, as well as analysis of the serum stability of the resulting complexes, were carried out to evaluate their suitability for radiopharmaceutical applications. Rapid complex formation in 1-2 minutes at room temperature, as well as the high kinetic inertness of the Pb(BADPA-18), Pb(BADPA-21) and Bi(BADPA-18) complexes in biological media demonstrate the promise of new ligands for use in targeted alpha therapy.

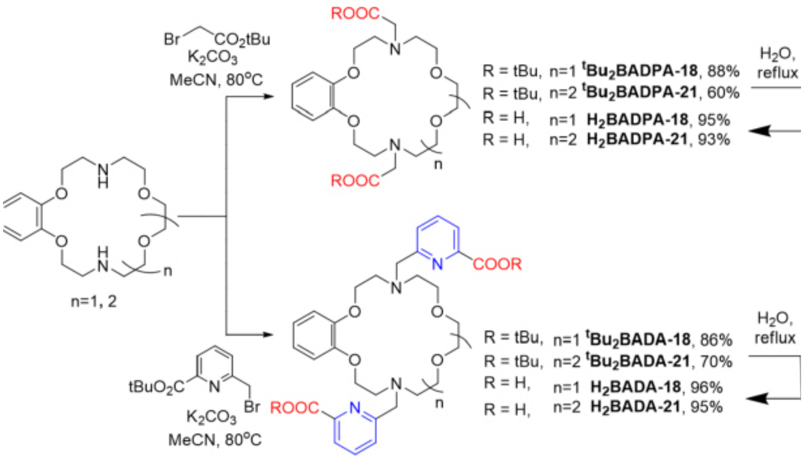

Figure 1. Synthesis of benzodiazacrown derivatives

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SYNTHESIS, SPECTRAL AND STRUCTURAL STUDIES AND IN VITRO ANTI-CANCER ACTIVITY OF NEW ORGANOTIN COMPLEXES

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Previously, we synthesized a number of complexes based on bis(trimethylsilylmethyl)dichlorostannane (I) and the six-membered heterocycle 1, 1-dichloro-1-stanna-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane (II). 1,1'-Bipyridyl (Bipy), 1,10-phenanthroline (Phen) and 1-substituted imidazoles: 1-methyl- (Me-Im), 1-vinyl- (Vin-Im) were used as ligands and their anticancer activity in vitro on various cancer cell lines: prostate cancer (PC3), breast cancer (MCF-7), colorectal cancer (HCT116), as well as on pseudonormal human embryonic kidney cells (HEK293).

In continuation of our research, we have obtained a number of new organotin complexes based on the eight-membered heterocycle 1,1-dichloro-1-stanna-3,3,5,5,7,7-hexamethyl-3,5,7-trisyl-4,6-dioxacyclooctane (III) using the same ligands.

A comparative assessment of complexes with six-membered (II) and eight-membered heterocycles (III) indicates the absence of a significant correlation between the size of the complex and cytotoxicity (Table 1).

Table 1. IC_{50} inhibitory concentration values (μMol)

Compound	Values IC_{50} (μMol)			
	PC3	MCF-7	HCT116	HEK293
II.Bipy	3.6±1.4	4.6±1.4	2.8±1.4	3.3±0.8
II.Phen	2.8±0.3	4.0±1.5	3.2±0.05	4.0±1.3
II.Me-Im	3.2±1.2	4.4±1.2	2.7±0.1	3.3±0.6
II.Vin-Im	3.7±1.7	4.0±0.5	4.0±0.6	3.5±0.8
III.Bipy	4.2±0.2	3.5±1.5	2.8±1.0	4.6±0.8
III.Phen	3.5±0.5	3.5±0.8	2.6±0.2	2.0±0.3
III.Me-Im	5.2±2.5	6.4±0.6	4.8±1.2	5.5±2.0
III.Vin-Im	6.0±0.2	4.3±0.5	6.6±1.4	4.2±1.8

Acknowledgments

We express our gratitude to the teams of INEOS RAS and the Federal State Budgetary Institution "National Medical Research Center of Oncology named after. N.N. Blokhin" of the Russian Ministry of Health for his invaluable contribution to the development of this research.

NOVEL TETRASUBSTITUTED BENZOAZACROWN COMPOUNDS AS CHELATORS FOR COPPER(II)

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Nowadays many studies in radiopharmacy are devoted to copper radioisotopes 64Cu and 67Cu, which can be used for theranostics [1]. These radionuclides bind to biological vectors using bifunctional chelators. The cyclen, cyclam and sarcofagine ligands are widely used as such chelators suffer from some disadvantages that restrict their wide application.

In order to evaluate this type of ligand for copper chelation, a series of 18-azacrown-6 ethers functionalized with acetate (BATA), pyridine (BATPy), and picolinate (BATPic) pendant groups were synthesized (Fig. 1), and their complexation ability towards Cu^{2+} was studied [2]. All considered ligands were capable of forming mono- and dinuclear complexes due to their large size and large number of donor sites. The stabilities of labeled acetate complexes and picolinate were compared; while the former turned out to be unstable to transchelation, the latter was stable throughout the experiment. Additional studies in biologically relevant media were performed for the picolinate complex and demonstrated its stability in vitro. The biodistribution of this complex in mice demonstrates a slow excretion from the body; however, the accumulation is noticeably lower than that of free copper cations.

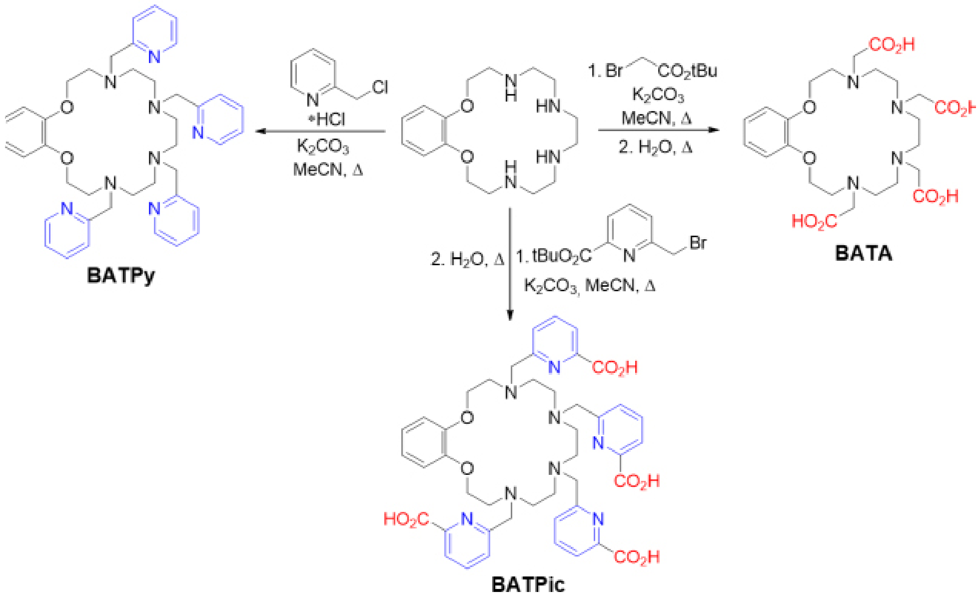

Figure 1. Synthesis of ligands BATA, BATPy and BATPic

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Acknowledgements
This work was supported by the Russian Science Foundation (project No 23-13-00424).

INVESTIGATION OF RELATIVE STABILITY OF DIENE RHODIUM COMPLEXES

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Information about bond strength between metal and ligand in complexes of transition metals is essential for homogenous catalysis. Activity of the catalyst and selectivity of the reaction depend on it. Diene rhodium complexes is one of the most widely used in different catalytic transformations class of organometallic compounds.[1] However diene ligands bind metal weaker than phosphine ligands, for example. For this reason, it is important to know how bond strength depends on structure of the diene ligand for pointed catalyst design. So, our main purpose was to suggest a method of quantitative evaluation of metal-ligand bond strength in diene complexes of rhodium.

To reach our goal, we investigated the equilibrium in reactions of diene ligand exchange in complexes [(diene)Rh(acac)] with NMR spectroscopy. Equilibrium constants of corresponding reactions were chosen as a measure of their relative stability. We investigated broad range of different dienes to have a possibility to make a conclusion about dependence of bond strength on their structure. So, we obtained an experimental row of relative stability of diene rhodium complexes (Fig. 1). Also we tested wide spectrum of different functionals and adjusted quantum calculation method in accordance with experimental data, which allows us to predict stability of complexes with newly invented diene ligands.

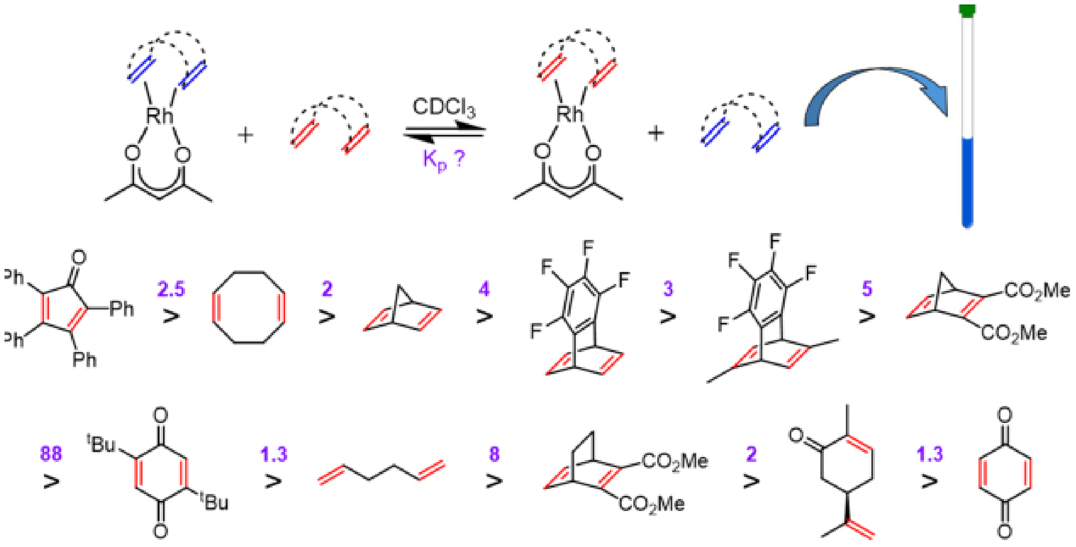

Figure 1. Row of relative stability of diene rhodium complexes.

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Acknowledgements
This work was supported by the Russian Science Foundation (grant #23-13-00345).

THE SYNTHESIS OF PALLADIUM COMPLEXE WITH TERPENYLBENZIMIDAZOLE LIGANDS

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The literature 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]. 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. So, we decided to synthesize bis[N-(2,7-dimethyl-octadienyl-2,7-)benzimidazolyl]palladium dichloride by reaction of K_2PdCl_4 with N-(2,7-dimethyl-octadienyl-2,7-)benzimidazole[2] in MeOH - H_2O medium. Structure of complexe by X-ray analyses presents on Figure 1.

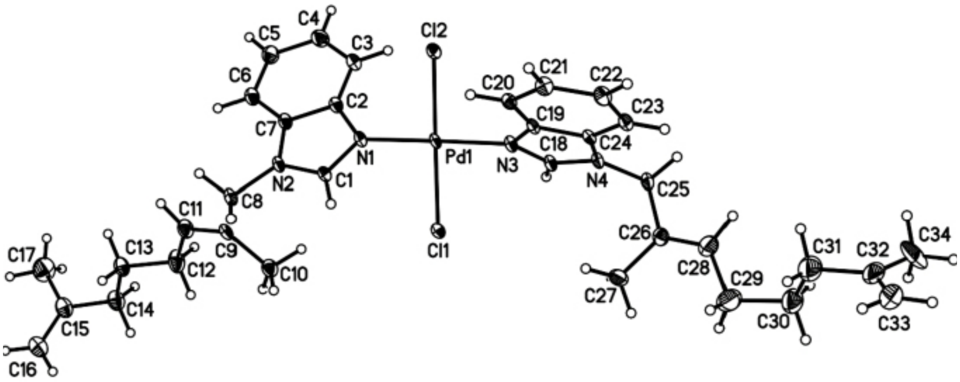

Figure 1. Structure of bis[N-(2,7-dimethyl-octadienyl-2,7-)benzimidazolyl]palladium dichloride.

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This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Contract No. 075-00277-24-00) and was performed employing the equipment of Center for molecular composition studies of INEOS RAS.

NEW PHOSPHORUS-CONTAINING AMINO ACIDS AND THEIR ANALOGUES AS PROMISING BIOACTIVE SUBSTANCES

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Phosphorus-containing amino acids, including P-C bonds resistant to hydrolysis, have antibacterial, antiviral, herbicidal and antitumor properties, and are also effective extractants and polydentate ligands. Among them are the well-known plant growth regulators glyphosate, glufosinate and phosphinothricin - environmentally friendly substances that are easily broken down by soil bacteria to form only biogenic products - phosphoric acid and amino acids[1]. New types of phosphorus-containing amino acids and their analogues, capable of exhibiting inhibitory properties against a number of bacteria and viruses, were obtained by us on the basis of easily accessible synthons - trimethylsilyl esters of trivalent phosphorus acids under mild conditions[2-4] (Fig. 1).

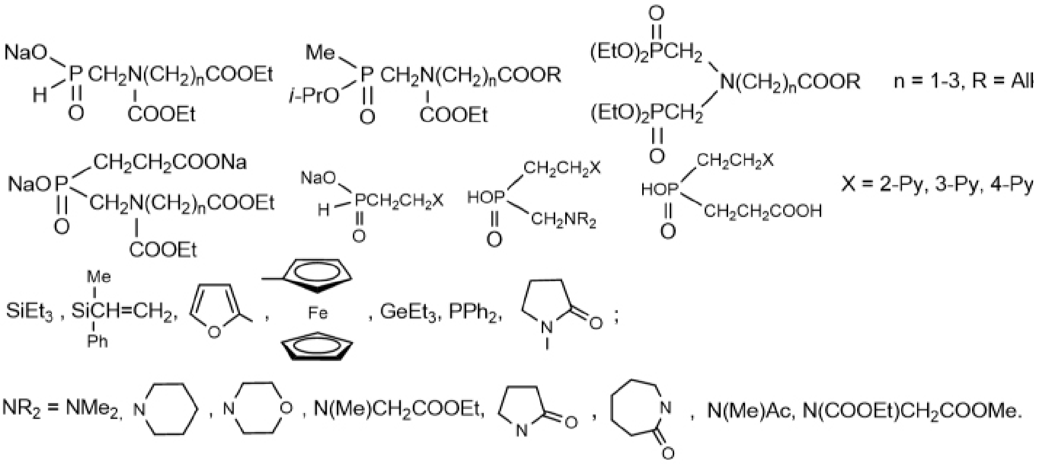

Figure 1. Functionalized phosphorus-containing amino acids and their analogues

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DYNAMIC KINETIC RESOLUTION OF AN AZLACTONE CATALYZED BY CHIRAL-AT-METAL COBALT(III) COMPLEXES UNDER PHASE-TRANSFER ALCOHOLYSIS

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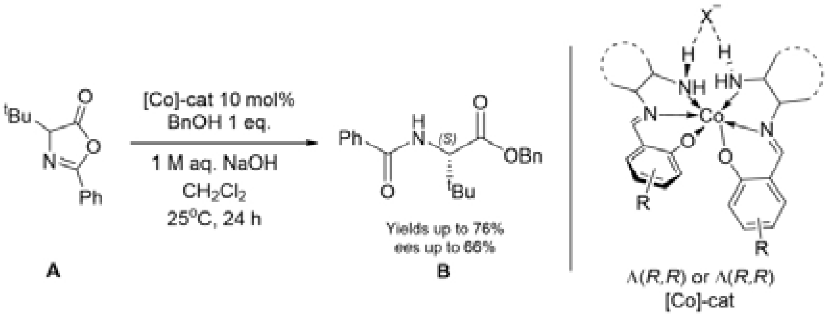
Chiral α-amino acids (α-AAs) play a significant role in various fields of chemistry, including biochemistry, catalysis, drug design, and the pharmaceutical industry.[1] One of the most effective methods for the synthesis of enantioenriched α-amino acids is the use of glycine derivatives and alkyl halides in conjunction with chiral catalysts. However, there is still a challenge in accessing enantioenriched α-AAs with branched or bulky groups at the α-carbon. One potential solution is the dynamic kinetic resolution of azlactones under phase-transfer alcoholysis. Since the scaffold of azlactones (**A** in Figure 1) mainly consists of 'masked' amino acids that can be used in the synthesis of natural or synthetic bioactive molecules, this approach to obtain chiral α-AAs appears to be an attractive alternative.

In this work, a series of well-defined octahedral cationic chiral cobalt(III) catalysts, based on (*R,R*)-1,2-cyclohexanediamine and (*R,R*)-1,2-diphenylethylenediamine, has been investigated for the dynamic kinetic resolution of an azlactone derived from *N*-benzoyl-*tert*-leucine. The reactions, conducted with a 10 mol% of Co(III) complexes in a 1M aqueous solution of NaOH via phase-transfer alcoholysis, yielded the corresponding benzyl ester of *tert*-leucine with yields reaching up to 76% and enantioselectivity of up to 66% *ee* (Scheme).[2]



Scheme

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NOVEL METALLOCENE-BASED NICKEL PINCER COMPLEXES

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The nickel PCP pincer complexes exhibit high catalytic activity in important organic reactions. The reactivity of pincer complexes relies greatly on changes in their ligand environment. The sandwich nature of metallocene offers multifold opportunities for the fine control of the steric and electronic effects at the chelated metal atom in the pincer complex. The first ferrocene- and ruthenocene-based nickel pincer complexes, $NiX[\{2,5-(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**3** (X=Cl), **4** (X=Br)) and $NiX[\{2,5-(Bu^t_2PCH_2)_2C_5H_2\}Ru-(C_5H_5)]$ (**5** (X=Cl), **6** (X=Br)) were synthesized by cyclometallation of 1,3-disubstituted metallocene phosphines (fig.1).[1] The complexes **3-6** were fully characterized by ^1H, $^{31}P\{1H\}$, $^{13}C\{^1H\}$ NMR and X-ray diffraction.

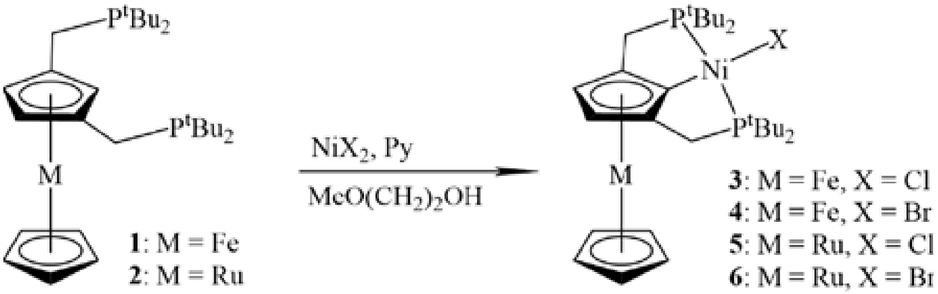

Figure 1. Novel metallocene-based nickel pincer complexes.

The reaction of complexes **3-6** with an excess of $NaBH_4$ in refluxing mixture ethanol-benzene leads to the formation of the corresponding tetrahydroborate complexes $Ni(BH_4)[\{2,5-(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**7**) and $Ni(BH_4)[\{2,5-(Bu^t_2PCH_2)_2C_5H_2\}Ru-(C_5H_5)]$ (**8**) (fig. 2). The structure of complex **8** was established by single-crystal X-ray diffraction. The compounds **7, 8** were characterized by NMR and FTIR techniques.

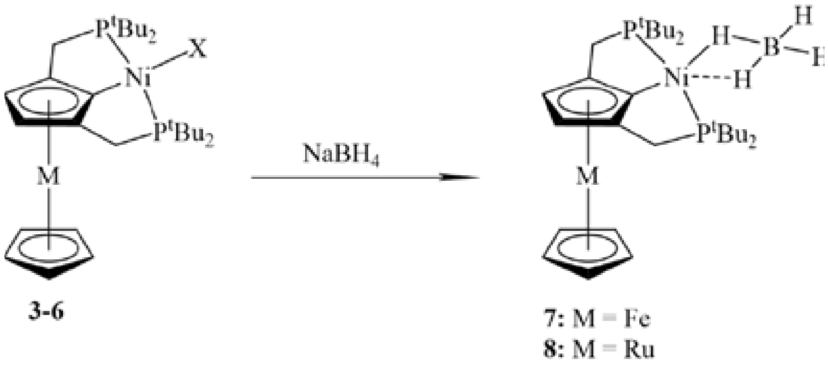

Figure 2. Synthesis of nickel tetrahydroborates

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Acknowledgements

The study was financially supported by the Russian Science Foundation (Project No. 23-23-00523). NMR studies, spectral characterization, and elemental analyses were performed using the equipment of the Center for molecular composition studies of INEOS RAS with financial support from the Ministry of Science and Higher Education of the Russian Federation (Contract No. 075-00277-24-00).

N,O - CONTAINING 18-MEMBERED CROWN ETHERS AND THEIR COMPLEXING PROPERTIES

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Macrocyclic ligands based on azacrown compounds have found wide application in many areas, since the selective complexation of metal ions represents a problem of importance [1,2]. An attractive idea is the development of crown compounds combining N, O - heteroatoms in their composition. In such crown ethers, one can expect resistance to radiation, a low dependence of complexation on the acidity of the medium, as well as the possibility of introducing additional chelating groups which allows the use of these compounds as part of radiopharmaceuticals, extractants for radioactive cations, etc.

In this work, we synthesized a series of ligands based on N,O - containing 18-membered crown ethers with acetate, acetamide, phosphonate, picolinate, and pyridyl chelating groups – chelators **PADA**, **PADAm**, **PADP**, **PADPA** and **PADPy** (Fig. 1). The resulting compounds combine hard oxygen donor atoms and soft nitrogen atoms as well as chelating groups of various nature for binding a wide range of metal cations.

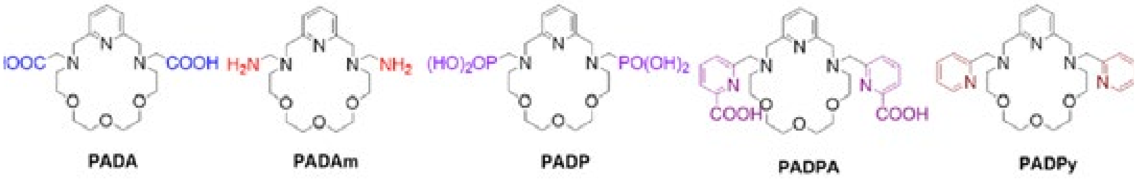

Figure 1. Synthesized ligands.

Complex formation of the obtained chelators was studied with a cations such as Ba^{2+}, Y^{3+}, Pb^{2+}, Bi^{3+} using a number of physicochemical methods. Mass spectrometry showed that all the synthesized diazacrown compounds are capable of forming mononuclear complexes with the studied cations in aqueous solutions. The structure of the formed complexes in solution was studied by NMR spectroscopy, and the stability constants of the complexes were obtained using potentiometric titration.

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HYBRID NANOSTRUCTURES BASED ON MONOAMINO ACIDS DERIVATIVES OF FULLERENE C60 AND VITAMIN B_{12}

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Approaches of preparing of biologically active substances based on transition metal complexes with biological substrates participation in closed to physiological conditions were developed for a number of years in INEOS RAS. Under academician M.E.Vol'pin's idea, catalytic sources of active oxygen species (AOS) which are capable selectively accumulate in tumor, can be active in suppressing of tumor tissue grows. The results of our studies confirmed that the catalytic systems generating AFO based on cobalt complexes with corrin ligands and *L*-ascorbic acid can be very effective as antitumor and related agents.[1]

A significant place among modern nanomaterials is occupied by nanocarbon structures, including fullerenes and their derivatives. It is shown that water-soluble monoaminoacids C60 show antioxidant, membrane, neuroprotective, antiviral, antibacterial and antitumor properties, play the role of effective compounds for the delivery of drugs to targets of various diseases.[2]

We assumed that the introduction of a pharmacophoric fullerene derivative of the active form of vitamin B_{12} into the molecule will significantly improve the efficiency of the antitumor action of the complexes. Earlier we show the fundamental possibility of the synthesis of such compounds.

Based on this, methods of the synthesis of new hybrid nanostructures were developed (fig. 1).[3] The results obtained in *L*-ascorbic acid oxidation in the presence of synthesized hybrid nanostructures are comparable to data for the compounds not modified by derivatives of vitamin B_{12}. This fact confirmed the prospects of further study of the obtained hybrid nanostructures as biologically active substances.

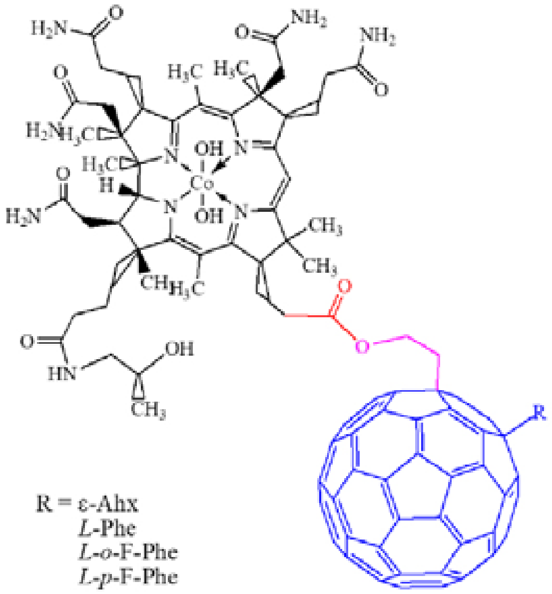

Figure 1. Obtained hybride nanostructures

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CATIONIC BIS(*O*-N,N-DIMETHYLAMINOBENZYL) RARE-EARTH COMPLEXES: SYNTHESIS, STRUCTURE AND CATALITIC ACTIVITY IN OLEFIN HYDROPHOSPHINATION AND DEHYDROCOUPLING OF HYDROSILANES WITH AMINES

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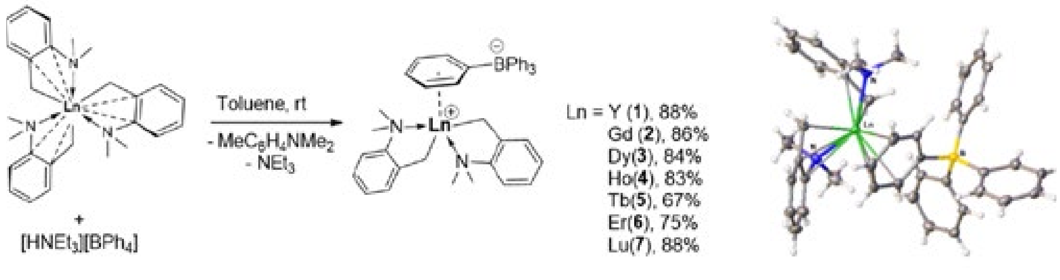
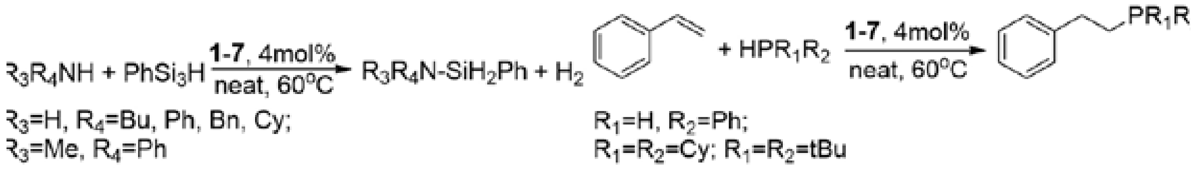
Cationic alkyl rare-earth complexes perform high catalytic activity in a variety of organic reactions, however, low thermal stability significantly limits their applications. Therefore, the synthesis of new cationic alkyl species combining enhanced stability with high reactivity characteristic of M-C bond is highly important for the development of new atom-economic synthetic approaches to valuable compounds.

A series of cationic bis(*o*-N,N-dimethylaminobenzyl) rare-earth complexes $[Me_2NC_6H_4CH_2\text{-}o]_2Ln[(\mu\text{-}\eta^6{:}\kappa^1\text{-Ph})BPh_3]$ (Ln = Y(**1**), Gd(**2**), Dy(**3**), Ho(**4**), Tb(**5**), Er(**6**), Lu(**7**)) were synthesized by the reactions of equimolar amounts of $[Me_2NC_6H_4CH_2\text{-}o]_2Ln$ with $[HNEt_3][BPh_4]$ in toluene (Scheme 1) in 67-88% yields. X-ray analysis revealed that complexes **1-7** are isostructural and adopt a structure of contact ionic pair, featuring η^6-coordination of Ph-ring to Ln^{3+} ion.

Complexes **1-7** were evaluated as catalysts for intermolecular olefin hydrophosphination (neat, 60°C). Within 24 h quantitative subtrates conversions were reached. In all cases the exeptional formation of an anti-Markovnikov addition products was detected. Complexes **1-7** also proved to be efficient catalysts for dehydrocoupling of amines and hydrosilanes. The formation of silazanes in quantitative yields was demonstrated.



Scheme 1. Synthesis of bis(N,N-dimethyl-o-toluidine) complexes of REE **1-7**.



Scheme 2. Dehydrocoupling and hydrophosphination reactions.

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ARENE MANGANESE COMPLEXES AS A NEW TYPE OF CATALYSTS

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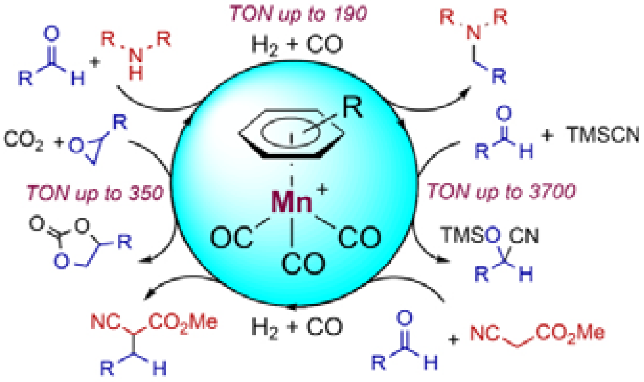
Nowadays, in catalysis one can observe a trend away from the study of noble metals towards the search for and modification of systems based on 3d metals. In particular, manganese, which is non-toxic and abundant metal, is well suited for the study of compounds based on it. Despite this, there are not many examples of catalysis on manganese. In reductive processes, the main type of catalysts used are pincer complexes of manganese (I), which have proven to be active and selective catalysts allowing, for example, the hydrogenation of carbonyl groups[1]. Despite the decent activity of such catalysts, their high cost, difficulty of modification and tendency to degrade in air leads to significant limitations in the use of complexes of this type.

Meanwhile, well-known organometallic compounds such as manganese (I) arene complexes have practically no application in catalysis. These complexes are synthesized in one step from cheap and common reagents, which opens a simple way to modify the complex for specific application. These catalysts are air-stable which allows working with them without the need for an inert atmosphere.

In this work, the synthesis and investigation of catalytic activity of arene manganese complexes in various reductive and redox-neutral catalytic processes were carried out. The complexes exhibited good activity in such reactions as: reductive amination and reductive Knoevenagel condensation using syngas as a reducing agent, the cycloaddition reaction of CO_2 with epoxide and the reaction of cyanosilylation of carbonyl compounds (Scheme 1)[2,3]



Scheme 1. Catalytic activity of arene manganese (I) complexes

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SYNTHESIS AND CRYSTAL STRUCTURE OF NEW RHOMBOID $\{Mn^{II}_2Mn^{III}_2\}$ CLUSTER BASED ON CALIX[4] ARENE AND BATHOPHENANTHROLINE LIGANDS

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Single molecule magnets (or SMMs) have attracted a growing interest due to their fascinating ability to exhibit slow magnetic relaxation behavior during long time in absence of the external magnetic field, which can find application in development of quantum spintronics for data storage or operating. The calix[4] arenes are especially suitable molecular platform for design of SMMs. When combined with Mn-ions, they are able to form polynuclear $\{Mn^{II}n^{III}m\}$-clusters of mixed valency, which nuclearity, self-assembly in the crystalline phase and magnetic properties (including SMM behavior) can be controlled via either upper rim functionalization or the nature of the used coligands[1-3].

A cooperative coordination of calix[4]arene and bathophenanthroline, acting as bidentate N,N-donor coligand, with manganese(II) ions led to formation of the tetranuclear $\{Mn^{II}_2Mn^{III}_2\}$ cluster in the crystalline phase. The X-ray diffraction revealed the generation of symmetrical metal cluster core, displaying rhomboid geometry of Mn-ions disposition, resulted in extremely shortest distances between metal ions, compared to previously reported calix[4]arene supported mixed valency tetranuclear manganese clusters.

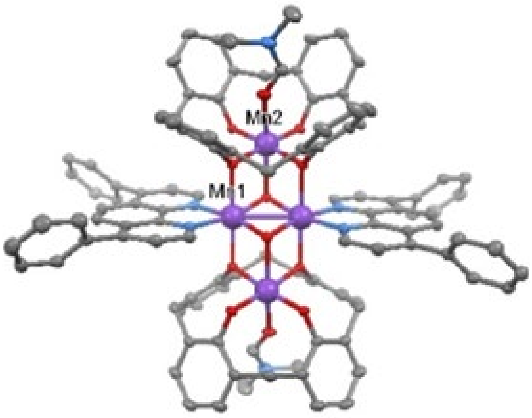

Figure 1. X-ray diffraction image of the tetranuclear manganese cluster calix[4]arene

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Acknowledgements
This work was supported by Russian Science Foundation (grant 19-73-20035)

SPIN-CROSSOVER FERRIC COMPLEX BASED ON PYRUVIC ACID THIOSEMICARBAZONE LIGAND $Li[Fe^{III}(THPY)_2]\cdot 3H_2O$: SYNTHESIS, CRYSTAL STRUCTURE AND THEORETICAL ANALYSIS

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The iron(III) anionic complex based on pyruvic acid thiosemicarbazone ligand with lithium cation $Li[Fe^{III}(thpy)2]\cdot 3H_2O$ (**1**) has been synthesized and characterized by FTIR-spectroscopy, powder and single crystal X-ray diffraction.

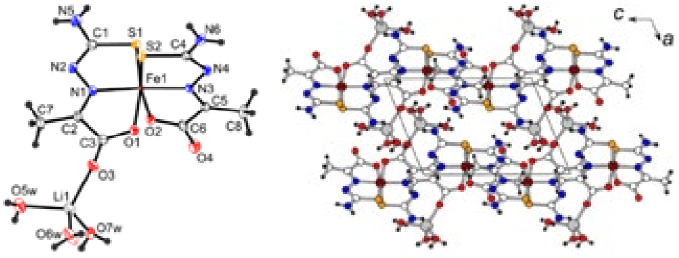

Figure 1. *Left:* The asymmetric unit in **1** with the atom numbering scheme (ORTEP drawing, thermal ellipsoids at a 50% probability level). *Right:* Projection of the structure **1** along b.

The $[Fe(thpy)_2]^-$ units in the triclinic P lattice of 1 are assembled into layers parallel to the *bc* plane. The Li^+ cations and water molecules are located between the layers and the structure is stabilized by hydrogen bonding. The $[Fe(thpy)_2]$- anions form interconnected dimer pairs through hydrogen bonds and short contacts with Fe…Fe separation of 6.7861(4) Å. According to dc magnetic measurements, the compound **1** demonstrates an incipient spin-crossover transition from LS (S=1/2) to HS (S=5/2) state above 250 K.[1]

BS-DFT calculations for optimized structure of two isolated $[Fe(thpy)_2]$- anions also correctly predict weak exchange $J_1(calc)=-0.92$K. DFT calculations revealed the OPBE (GGA-type) functional that correctly predict the spin-crossover transition for the iron(III) thpy-compounds. Besides, the effect of the N_2O_4, $N_2S_2O_2$, and $N_2Se_2O_2$ coordination environments on the energy stabilization of the LS state of Fe(III) anionic thpy-complexes was noted as well.

The results shed light on the anionic spin-crossover complex iron(III) with pyruvic acid thiosemicarbazone ligand, which can be applied for the creation of new hybrid molecular systems, as well as materials for spintronics.

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Acknowledgements
This work was supported by the Ministry of Science and Higher Education of the Russian Federation (State task, state registration No. 124013100858-3).

μ-NITRIDO- AND μ-CARBIDODIMER HETEROMETALLIC HETEROLEPTIC MACROHETEROCYCLIC COMPLEXES AS THE FOUNDATION FOR DESIGNING A MOLECULAR PLATFORM FOR CATALYSIS

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A lot of important chemical reactions in biological systems occur owing to the active centers of enzymes, such as cytochrome p450, peroxidases, methane monooxygenases, etc. Their versatility and importance inspired the interest in the design of molecular platforms for catalysts capable of operating under mild conditions. An effective approach to the development of catalysts is the use of dimeric structures including porphyrin-like macrocycles and transition metals, as a simplified model of the active center of the enzyme. Such structures are advantageous due to several reaction centers (metal, ligand, bridging fragment).

This work focuses on the synthesis, spectral, coordination and redox properties of μ-nitride and μ-carbide dimeric complexes of transition metals with macroheterocyclic ligands. Such compounds are shown to be possible for constructing the molecular platforms for oxidation catalysis. Regularities of axial bonding of N-bases with compounds under study are established. the nature of the metal, macroheterocyclic ligand and bridging fragment are noted to affect the coordinating ability of the dimeric complexes. Interaction of the compounds and tBuOOH affords various highly oxidized species able to oxidize peroxide and substrates (β-carotene, methylene blue, adamantane) under mild conditions. The redox properties of the studied compounds depending on the coordination sphere (the presence/absence the axial ligands) are examined electrochemically. Factors allowing us to tune the catalytic properties of the dimeric complexes are revealed. The synergistic effect of different metals, macrocyclic and bridging fragments in one molecule is of interest from the point of view of a detailed study of the "structure" *vs* "property" relationship. The results of the work will expand the range of model compounds aiming at creating molecular platforms prospectively useful for practical application.

$X = C; N$
$M_1, M_2 = Fe, Ru, Mn$
$R = {}^tBu$

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DEVELOPMENT OF NEW PYRIDINE-CONTAINING MACROCYCLIC CHELATORS FOR RADIOPHARMACEUTICS

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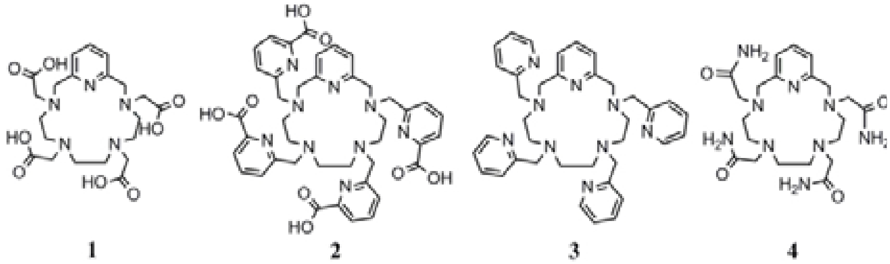
One of the advanced methods for the treatment and diagnosis of oncological diseases is the use of radiopharmaceuticals. There are strong complexes of bifunctional chelators with a radionuclide ion, attached via a linker to a vector biomolecule. Currently, there are no chelators that meet all the requirements for them, so the development of new ligands for radionuclide cations is an urgent task. The use of pyridine-containing azacrown compounds as chelators can provide high thermodynamic stability of the obtained complex compounds, as well as their chemical inertness under physiological conditions.[1]

The aim of this work is to develop new chelate derivatives of pyridine-containing azacrown compounds capable of efficiently binding various metal ions.

As a result of the work, 4 target macrocyclic ligands were obtained with carboxyl, picolinate, pyridyl, and amide chelating groups (Scheme 1). Their structure was confirmed by NMR spectroscopy, mass spectrometry and elemental analysis. All chelators form complexes with a stoichiometric metal-ligand ratio of 1:1, which was confirmed by MALDI mass spectrometry. The structures of the complexes in solution were thoroughly investigated using 1H NMR spectroscopy showing formation of complexes with a rigid structure. Radiolabeling studies for ligands **1**, **2**, **4** with ^{68}Ga and ^{177}Lu showed that radiolabeling with RCY >70% was achieved for **1-2** complexes with ^{68}Ga and ^{177}Lu at room temperature. Experiments in fetal bovine serum and a 1000-fold molar excess of EDTA revealed that the most stable complexes are formed by the ligand 1 with ^{177}Lu. Given the rapid radiolabeling of the ligand **1** with the radionuclide ^{177}Lu at room temperature, it can be considered for further studies for potential use as a component of a radiopharmaceutical.



Scheme 1. Target macrocyclic ligands

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Acknowledgements
The reported study was funded by the Russian Science Foundation project № 23-13-00424.

DIMERIC OR MONONUCLEAR CYCLOPALLADATED CATALYSTS: WHICH IS MORE ACTIVE IN SUZUKI-MIYAURA REACTION?

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The high catalytic activity of cyclopalladated compounds (CPC) in C–C bond formation reactions is well known.[1,2] A change in the coordination environment of a metal center of a catalyst, for example, the opening of bridges in dimeric CPCs, can serve as one of the ways to increase its catalytic activity. However, this approach is not always justified. There are cases of higher catalytic activity of the initial dimeric palladacycles in comparison with their numerous derivatives.[3]

The aim of the work was to study the catalytic activity in the Suzuki–Miyaura (SM) reaction of the dimeric *C,N*-palladacycle based on available *N,N*-dimethylbenzylamine and compare it with that for its known mononuclear derivatives.[4] Surprisingly, dimer **1** had not previously been used as a catalyst for the SM cross-coupling. Preliminary results showed that the catalytic activity of dimeric CPC **1** in the SM reaction 4-bromanisole with $PhB(OH)_2$ is comparable to that described earlier for mononuclear carbene derivatives under the same conditions. Subsequent experiments showed that dimer **1** exhibits high catalytic activity under mild conditions in a cross-coupling with a number of aryl bromides and aryl chlorides, including sterically hindered substrates.

Thus, palladacycle **1** is a more available, but just as effective catalyst for the SM reaction as its derivatives. We call for the need for mandatory verification of the catalytic activity of the initial dimeric CPCs.

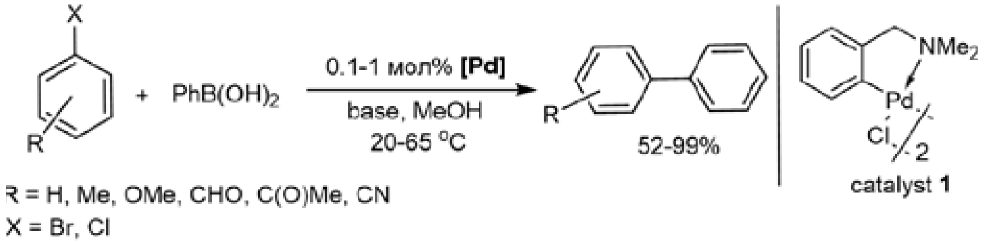

Figure 1. Catalytic activity of dimeric catalyst **1** in Suzuki-Miyaura cross-coupling

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TETRAPHENYLPORPHYRINATE-PENTHAMETHYLCYCLOPENTADIENIDE SANDWICH COMPLEXES – THE FIRST AIR-STABLE Ln(III) ORGANOMETALLICS

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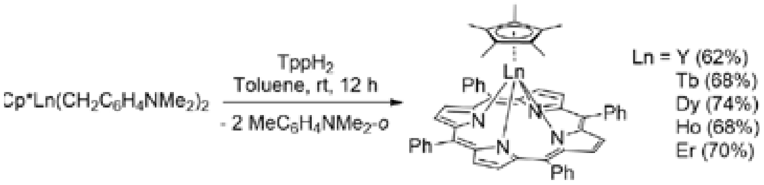
An efficient synthetic approach to the first air-stable Ln(III) organometallics supported by 5,10,15,20-tetraphenylporhpyrin ligand (Tpp) was elaborated. Sandwich tetraphenylporphyrinate-penthamethylcyclopentadienide complexes TppLnCp* (Ln = Y, Tb, Dy, Ho, Er) were synthesized by the reaction of half-sandwich bis(dimethylaminobenzyl) precursors $Cp^*Ln(CH_2C_6H_4NMe_2)_2$ with equimolar amounts of 5,10,15,20-tetraphenylporhpyrin ($TppH_2$) in toluene at ambient temperature and isolated in 62–74% yields. X-ray analysis revealed the strictly linear structure of base-free complexes featuring Cp^*_{Centr}–Ln–Tpp_{Centr} bond angles close to180° and Cp^*_{Centr}–Ln and Tpp_{Centr}–Ln bond distances of 2.325–2.365 and 1.012–1.063 Å. TppLnCp* proved to be stable under aerobic conditions and can be sublimed in vacuum (>290 °C, ~$5\cdot10^{-2}$ Torr).



Scheme 1. Synthesis of sandwich complexes TppLnCp*.

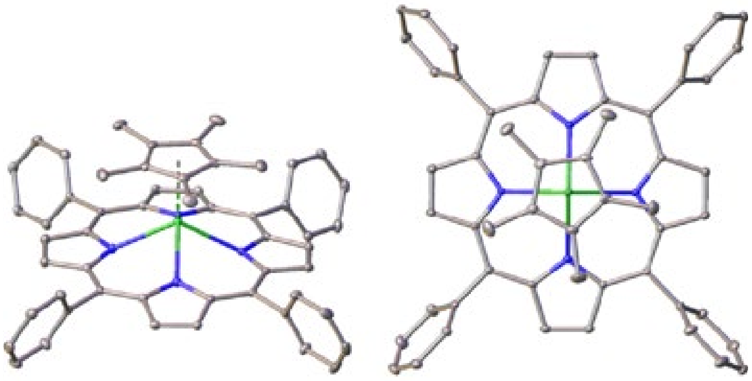


Figure 1. General view of **TppLnCp*** (a, side; b, top); C = gray, N = blue, Ln = green.

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NEW CATALYSTS FOR THE ELECTORCHEMICAL REDUCTION OF PROTON

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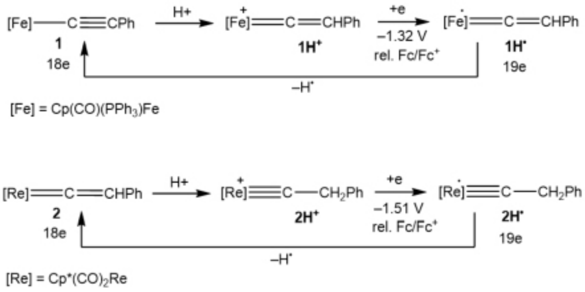
The activity of manganese phenylvinylidene Cp(CO)(Ph_3P)Mn=C=C(H)Ph and diphenylallenylidene $Cp(CO)_2Mn$=C=C=CPh_2 complexes in catalyzing the electrochemical reduction of proton in an acidic medium,[1] as we have described earlier, gives promise that a similar activity can be exhibited by other transition metal complexes, the protonated forms of which contain a C–H bond conjugated with the metal–carbon multiple bond. Therefore, we studied the activity of the iron σ-phenylethynyl complex Cp(CO)(Ph_3P)Fe–C≡CPh (**1**), the rhenium vinylidene complex Cp*$(CO)_2$Re=C=C(H)Ph (**2**), and the manganese isonitrile complexes $Cp(CO)_2$Mn=C=NR (**3**, R=Me; **4** R = *Bu^t*) in such a catalysis. Complexes **1** and **2** were found to be active in the ERP: they are quantitatively protonated by HBF_4•OEt_2 in CH_2Cl_2 to form a cationic iron vinylidene [Cp(CO)(Ph_3P)Fe=C=C(H)Ph]BF_4 (**1H$^+$**) and a cationic rhenium carbyne [Cp*$(CO)_2$Re≡C–CH_2Ph]BF_4 (**2H$^+$**), respectively (see Scheme 1). Catalytic currents were observed upon the electrochemical reduction of (**1H$^+$**) and (**2H$^+$**) to corresponding 19e radicals (**1H▪**) and (**2H▪**); the current magnitudes were governed by the structure of the catalyst and the acid content in a solution (see data in Scheme 1). The key step in these catalytic cycles is the homolysis of C_β-H bonds in 19e radicals (**1H▪**) and (**2H▪**), which is accompanied by hydrogen evolution and regeneration of the starting complexes **1** and **2**.



Catalytic current (change in rel.%)
(CH_2Cl_2, 25 °C, GC electrode, 0.1 M $Bu^n{}_4NPF_6$, 1 mmol/L, 200 mV/s)

HBF_4, equiv.	**1H$^+$**	**2H$^+$**
0	1.8 μA (100%)	1.3 μA (100%)
1	-	5.7 μA (440%)
2	3.8 μA (210%)	-
3	-	10.3 μA (790%)
5	4.8 μA (265%)	14.1 μA (1085%)
10	6.7 μA (370%)	17.5 μA (1345%)

Scheme 1. Proposed scheme for the catalytic reduction of proton

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CYCLORUTHENATED THIOPHENE-IMINES: NOVEL ANTICANCER AGENTS

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The potential for using cyclometallated compounds, including palladium, platinum, ruthenium, iridium, and osmium is extremely huge: oxidation catalysts, cross-couplings, sensors, dyes for DSSC, antitumor therapy. And if the potential for using ruthenium compounds as dyes for DSSC has been exhausted with the advent of perovskite solar cells, then no excellent results have yet been achieved in antitumor therapy, which leaves room for studying new structures.

In this work we limited ourselves to a series of halogen-substituted derivatives of thiophene-2-carbaldehyde and unsubstituted aniline, including thiophene with a donor diphenylaminophenyl and an acceptor nitro substituent. 2,2'-Bipyridine was used as a ligand filling the remaining coordination sites of the ruthenium atom.

Nine new ruthenium complexes were obtained. The crystal structures of all ruthenium complexes were established by means of single crystal X-ray diffraction. Antiproliferative activity was assessed against several human cancer cell lines, including MCF7 breast carcinoma, A549 non-small cell lung carcinoma, and A2780 and A278Cis cisplatin-resistant variant. Also, for complexes with 2,2-bipiridine ligands UV spectra were obtained.

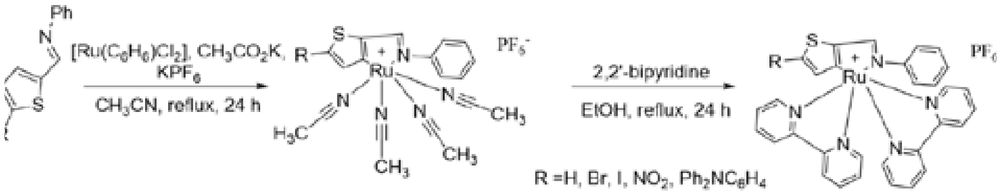

Figure 1. Synthesis scheme

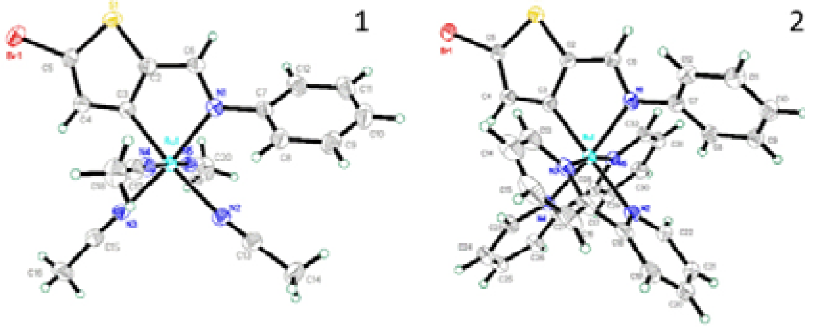

Figure 2. Structure of ruthenium complexes with acetonitrile (1) and 2,2-bipiridine (2) ligands

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η⁵-FLUORENYL RHODIUM COMPLEXES: ARE THEY A MYTH OR REALITY?

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Half-sandwich complexes of rhodium with cyclopentadienyl ligands and their benzo-fused analogues are important catalysts for a wide range of organic transformations, including C-H activation reaction, hydrogenation, hydrofunctionalization etc[1]. Complexes with benzo-fused ligands usually have higher catalytic activity than cyclopentadienyl ones because of prone to haptotropic rearrangements[2]. For example, the η^5-indenyl complexes of rhodium can be used to create highly efficient catalysts for C-H activation, including in the enantioselective case[3]. At the same time, fluorenyl complexes of rhodium are nearly unexplored while similar complexes are known for other 9 group metals.

Herein we report our attempts to synthesize η^5-fluorenyl complexes of rhodium. We discovered that these compounds are highly unstable and only η6-fluorene complexes could be synthesized. Even in the case of highly kinetically stabilized octasubstituted fluorene, only η^6-coordination takes place (Figures 1 and 2).

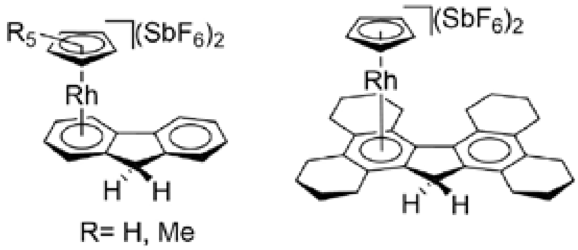

Figure 1. Synthesized fluorene complexes of rhodium.

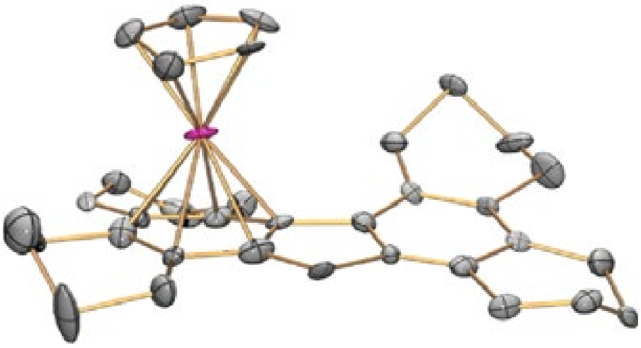

Figure 2. X-Ray diffraction structure of η^6-complex with octasubstituted fluorene

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COMPLEXATION OF TRINUCLEAR SILVER (I) 3,5-BIS(TRIFLUOROMETHYL)PYRAZOLATES WITH PYRIDINE-PYRAZOLE DERIVATES

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The complexation of trinuclear silver(I) and copper(I) pyrazolate ($[MPz]_3$) with N- or P-containing ligands allows the formation of complexes with different structures, which are of interest due to their photophysical properties.[1,2,3] For example, the interaction of $[AgPz]_3$ with N^N-chelating ligands results in complexes with various structures depending on the ratio of reagents.

Herein, we present the results of an investigation of the complexation of cyclic trinuclear silver(I) 3,5-bis(trifluoromethyl)pyrazolate with pyridine-pyrazole derivatives (L), acting as a 2,2'-bipyridine analog. The ratio of $[AgPz]_3$ to L does not affect the complexation, and in all cases, a dinuclear complex is formed due to strong Ag-Ag metalophilic interactions and NH-N hydrogen bonds. Interestingly, the presence or absence of toluene in the cocrystal or the absence of a cocrystallized solvent molecule leads to differences in photoluminescence behavior. The complex containing toluene exhibits blue emission, while the absence of the solvent results in yellow emission.

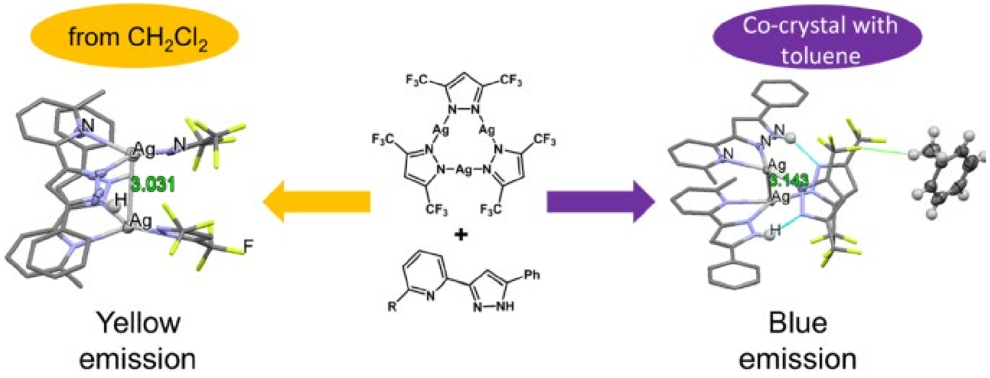

Figure 1.

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Acknowledgements
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ONE-POT SYNTHESIS OF BENZOPHOSPHOLENES BASED ON THE REACTIONS OF DIALKYLPHOSPHITES WITH CARBONYL COMPOUNDS AND PHENOLS

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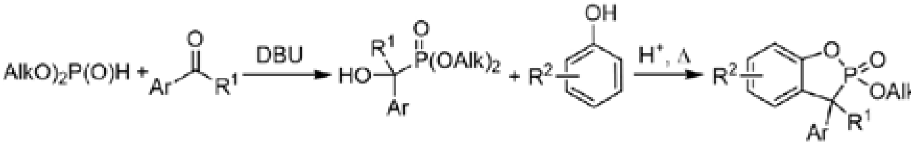
Benzoxaphospholenes are five-membered phosphorus-containing heterocycles exhibiting high biological activity.[1] Some of them possess an anti-inflammatory, antitumor, and antiviral activity.[2] In addition, these compounds can act as antioxidants.[3]

Here we report a new approach for the synthesis of benzooxaphospholenes based on the sequence of Abramov and Friedel-Crafts reactions. The approach includes the formation of P-C and C-C bonds, followed by intramolecular transesterification with ring-closure in *one-pot* procedure. Moreover, this method shows a wide substrate scope and good to high yields of the target products. Furthermore, the proposed procedure can be carried out in both solvent and solvent-free conditions. Thus, the reducing the number of synthetic steps and the by-products allows to consider this approach as atom-economical.



Scheme 1. General scheme of two-step synthesis of benzophospholenes

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SYNTHESIS AND PROPERTIES OF HETEROLEPTIC DIADS AND TRIADS ON THE SUBPHTHALOCYANINE AND PORPHYRIN PLATFORMS

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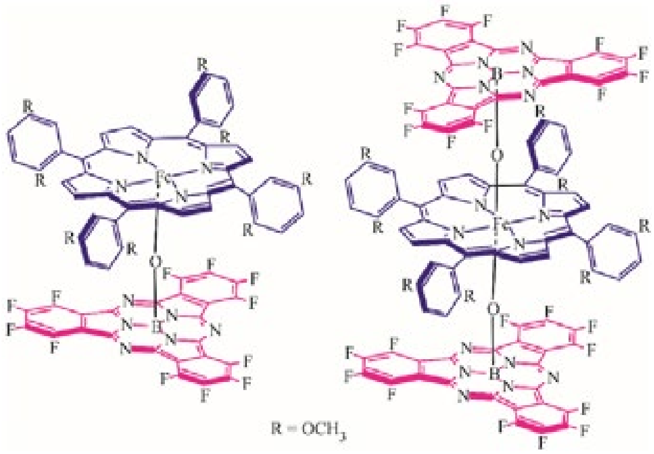
Metalloporphyrins, metallophthalocyanines and subphthalocyanines are structurally related derivatives of cyclic oligopyrroles. he different π-conjugation of the chromophore of these macrocycles fules their various optical and electronic properties. These compounds absorb light variously, participate in excitation energy transfer and photoinduced electron transfer. Such properties are especially interesting for efficient photosynthetic systems and their applying in the field of light harvesting, photovoltaics and molecular photonics. Integrating the chromophores in the molecule that exhibits complementary absorptions in the visible region, allows us the synthesis of various types of hybrid compounds with an extended absorption region and new properties arising due to chromophore interactions, including charge transfer interactions.

This paper reports on the synthesis and spectral properties of μ-oxo heterodyads and heterotriads on a subphthalocyanine and porphyrin platforms. The compounds ynder study were identified using mass spectrometry and UV-vis, ^{1}H NMR spectroscopy. The redox properties of the multichromophore compounds were examined spectrophotometrically and electrochemically. According to fluorescent spectroscopy data for the heterotrimer the lifetime and quantum yield of fluorescence were determined. The results of the work are of great interest to prepare and study the light-sensitive donor-acceptor systems aiming at using them in high-tech fields.



Acknowledgements
This work was supported by the Russian Science Foundation (Project number no. 23-23-00421).

SELECTIVE SYNTHESIS OF NEW FLUORESCENT LIGAND FOR HEAVY METALLS

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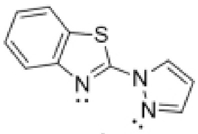
Benzotiazole derivative of pyrazole **1** are complexing ligands for various heavy metal ions.

Pyrazoles of similar structure can be obtained by reaction of cross-conjugated eninones **2** and corresponding hydrazines **3**, but direct reaction of the starting compounds usually leads to a mixture of isomers[2]. Thereby, a selective method for the synthesis of new benzothiazole substituted styryl-pyrazoles **4 a-f** in high yields was developed.

The obtained products **4a-g** have brightly expressed fluorescence. However, the emission maximum of these substances in the form of their complexes with various metal ions is shifted bathochromically or absent[3]. This effect seems to be determined by the nature of the metal ion. This effect may allow these substances to be used as analytical probes for the qualitative and assay of heavy metal content.



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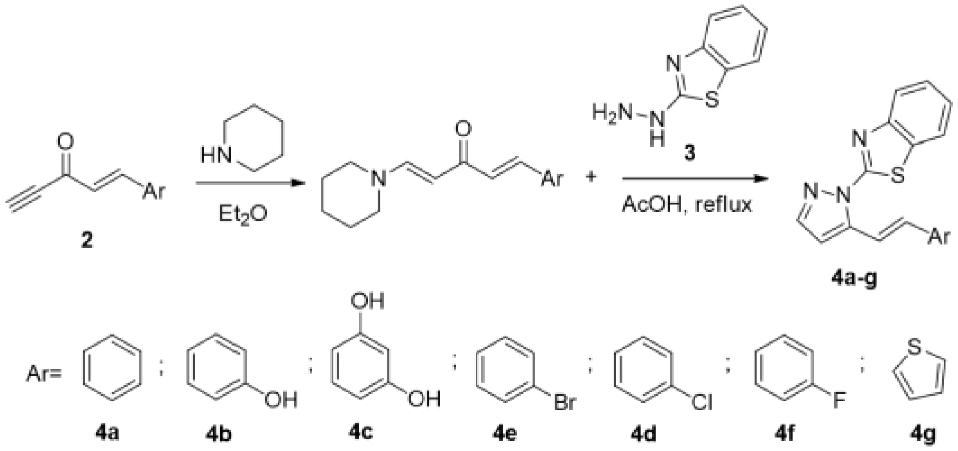

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This study was performed under financial support by the Russian Science Foundation (project no. 22-13-00185, https://rscf.ru/project/22-13-00185/).

SYNTHESIS OF FERROCENE-CONTAINING DERIVATIVES OF 1,4-DISUBSTITUTED 1*H*-1,2,3-TRIAZOLES

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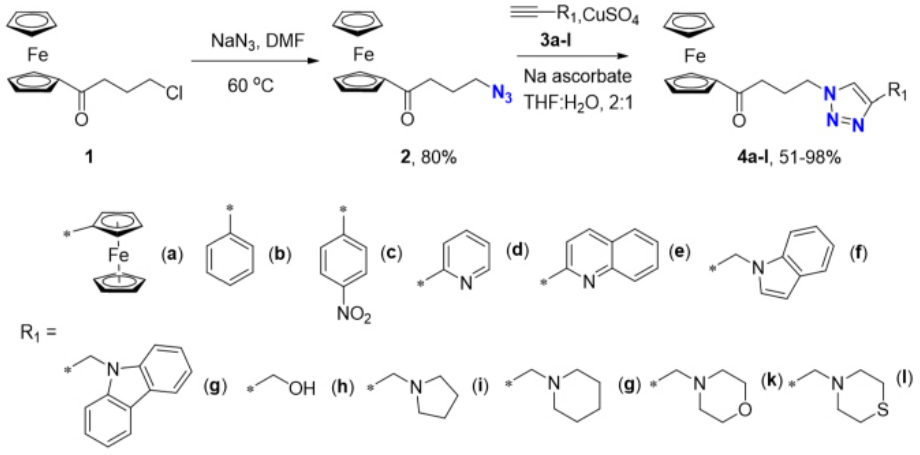
1*H*-1,2,3-Triazole is a versatile scaffold in medicinal chemistry for development of multifunctional hybrid molecules. Triazole-containing derivatives showed in vitro and *in vivo* Alzheimer's disease activities.[1] Ferrocene derivatives of 1*H*-1,2,3-triazoles have been less studied as agents for the treatment of neurodegenerative diseases.

Thus, the desired ferrocenyl-1,2,3-triazole derivatives **4a-l** were synthesized using Cu-catalysed azide–alkyne cycloaddition (click-chemistry) in the presence of Na ascorbate, as shown in Scheme 1. 4-Azidobutanoylferrocene **2** was obtained during the reaction of 4-chlorobutyryl ferrocene **1** with NaN_3 at 60 °C in DMF.

Initial experiments revealed that ferrocene-containing derivatives of 1,4-disubstituted 1,2,3-triazoles were promising candidates for further research as multifunctional drugs to treat Alzheimer's disease.



Scheme 1. Synthesis of 1,2,3-triazole-containing ferrocenes.

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POSTER PRESENTATIONS

CHEMISTRY OF POLYMERS

POLY(VINYL ALCOHOL) CRYOGELS FORMED IN THE PRESENCE OF ACIDS USED IN COSMETOLOGY

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During recent years poly(vinyl alcohol) cryogels – heterophase macroporous gels prepared by the “freeze-thaw” method, became materials of a great sceintific ana applied interests[1]. Since these materials are non-toxic, biocompatible, possess good mechanical properties, and also have macroporous structure, their application areas are constantly expanding. In particular, PVA cryogels are gradually finding wide application in the biomedical field and cosmetology.

In this work poly(vinyl alcohol) cryogels were prepared in the presence of various concentrations of low-molecular additives used in the cosmetology. Rheological and thermal properties of the resultant cryogels were measured. The dynamics of the release of these additives from the cryogel matrix has also been studied.

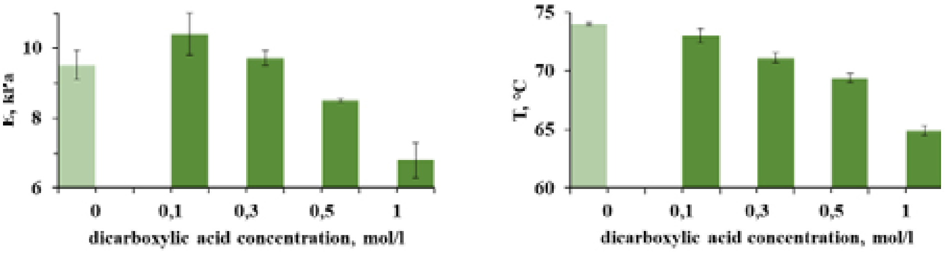

Figure 1. Dependences of the compression modulus of elasticity E and fusion temperature Tf of PVA cryogels on the concentration of oxalic acid in the initial polymer solution.

It was shown that the release of additives from the gel matrix occurs without diffusion barriers. Thus, PVA cryogels can be used as "depot forms" for these compounds and can find application in cosmetology.

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CATALYTIC PROPERTIES OF CATIONIC PALLADIUM ACETYLACETONATE COMPLEXES IN MYRCENE TELOMERIZATION

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Terpenes can be used as starting substrates in the processes of "green chemistry", as they are easily renewable substances of natural origin. One of them is myrcene (obtained by pyrrolysis from β-pinene (Figure 1)), which is widely used to produce various products, for example, polymers, pharmaceuticals, insect repellents and others[1]. Structurally, myrcene is a substituted 1,3-diene, therefore it is capable of entering into a telomerization reaction (Figure 1). However, at the moment there are two works in the literature on the telomerization of myrcene [2,3].

Palladium-catalyzed telomerization of diene hydrocarbons is a promising direction for chemical transformations, as it is characterized by 100% atomic economy. Earlier4, we found that catalytic systems based on palladium cationic acetylacetonate complexes are promising for the telomerization of butadiene with methanol. Thus, in this report, the results of studies of the catalytic properties of these systems in the reaction of the telomerization of myrcene with diethylamine and pyrrolidine are discussed. Screening of phosphine ligand nature as well as varying of reaction conditions were performed. It was found that the process of telomerization of myrcene with secondary amines in the presence of catalytic systems based on palladium cationic acetylacetonate complexes requires additives of a co–catalyst, such as $BF_3{\cdot}OEt_2$ ($[Pd]_0$:$[BF_3{\cdot}OEt_2]_0$ = 50-110).

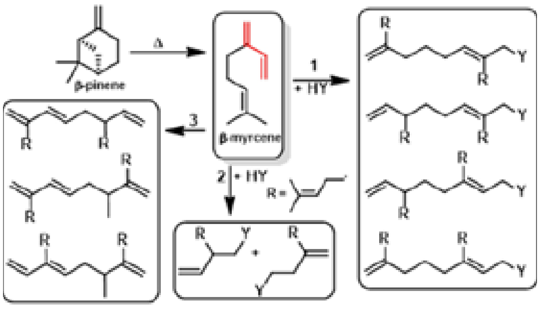

Figure 1. Scheme of different variants of the reaction of myrcene with HY
(1 – telomerization, 2 – hydroamination, 3 – dimerization)1

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This work was supported by the Government Assignment for Scientific Research from the Ministry of Science and Higher Education of the Russian Federation (FZZE-2023-0006)

POLY(NORBORNENE-2,3-DICARBOXYLIC ACID ANHYDRIDE) – REACTIVE MODIFIER-CO-HARDENER FOR EPOXY SYSTEMS

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Epoxy binders, adhesives and sealants are becoming more widespread due to their advantages, which are high mechanical, adhesive, low shrinkage and high heat resistance. However, the main disadvantage of epoxy binders is low crack resistance and poor impact characteristics. To solve this problem, a variety of modifiers are introduced into epoxy systems. This paper considers the use of a reactive polymer capable of being involved in the curing process as a modifier. It can be expected that the participation of the modifier in the chemical reaction will prevent the formation of large particles in the phase separation of these systems during the curing process.

The binder based on epoxy oligomer DER-330 (Dow Chemical, USA) was modified with specially synthesized poly (norbornene-2,3-dicarboxylic acid anhydride) (poly(NDA), TIPS RAS, Russia) of different molecular weights. The main hardener was isomethyltetrahydrophthalic anhydride (IMTHPA, Chimex Limited JSC, Russia). The curing accelerator was 2-methylimidazole (Chimex Limited JSC, Russia). The modifier was introduced into the system through dissolution in the hardener. The miscibility of poly(NDA) with DER-330 and IMTGFA was investigated in pairs by laser microinterferometry. To determine the curing enthalpy, the temperature of maximum curing rate and the glass transition temperatures of the cured samples, the method of differential scanning calorimetry (DSC) was used. DSC experiments were carried out on a 2920 MDSC instrument (TA Instruments, USA).

An increase in the molecular weight of poly(NDA) leads to a shift in the onset temperature of chemical interaction between poly(NDA) and DER-330 and the onset temperature of poly(NDA) dissolution in IMTGFA towards higher temperatures. Replacing a part of IMTGFA as the main hardener with poly(NDA) of different molecular weights resulted in a change in the thermal effect and maximum cure rate temperature of DER-330 compared to the unmodified system. The glass transition temperature of the cured modified systems is not inferior to that of the unmodified system.

Acknowledgements
This work was supported by the grants the Russian Science Foundation, RSF 24-73-00330, https://rscf.ru/en/project/24-73-00330/

POLYISOBUTYLENE-BASED BLOCK COPOLYMERS BY MECHANISTIC TRANSFORMATION FROM CATIONIC TO RADICAL PROCESS

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Polyisobutylene (PIB) is a rubbery polymer, which is synthesized exclusively via cationic polymerization. Due to unique properties of the polymer, such as low gas permeability, chemical resistance and biocompatibility, a number of PIB-based copolymers has been developed for various applications, including biomedical materials.[1-3] Mechanistic transformation is a promising approach in polymer synthesis that combines different polymerization modes to create novel copolymer structures, unavailable through single polymerization mechanism. Such approach seems even more interesting in a combination with facile and environmentally friendly polymerization techniques, such as visible light-induced polymerization. The latter is a powerful synthetic tool, which allows the one to conduct fast reactions with spatiotemporal control and with low energy and solvent requirements.

In this work, the simple strategy for the preparation of PIB-based block copolymers with styrene and methyl methacrylate via mechanistic transformation from cationic to photo-induced radical polymerization is reported4. This strategy involves the synthesis of 2-bromo-2-methylpropanoyl-terminated difunctional PIB macroinitiator via consecutive cationic polymerization, in situ preparation of hydroxyl terminated polyisobutylene and its acylation by 2-bromo-2-methylpropanoyl bromide (Figure 1). The following $Mn_2(CO)_{10}$– triggered photo-induced radical polymerization utilizing this macroinitiator produces multiblock copolymer with styrene (Figure 1, A) and triblock copolymer with methyl methacrylate (Figure 1, B) in bulk conditions.

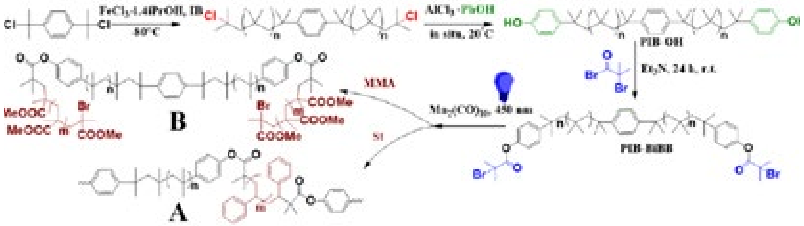

Figure 1. Synthetic strategy to multiblock copolymer of isobutylene with styrene and triblock copolymer PMMA-PIB-PMMA via mechanistic transformation

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MOLECULAR MOTION AND PHASE TRANSFORMATIONS IN PLASTIC FULLERENE C_{60}

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A special place in the field of orientationally disordered condensed systems is occupied by the so-called plastic crystals - plastic mesophases possessing orientational dynamic disorder. The fullerene molecule C_{60} is a vivid representative of plastic crystals, which attracts the attention of researchers from the moment of its prediction [1] and discovery [2] up to the present time. Despite the fact that the very prediction of fullerene existence was made by a group of D.A. Bochvar in INEOS RAS [2], the Nobel Prize was awarded to a group of American researchers in the mid-1980s. Despite the large number of papers and reviews[3] devoted to the studies of fullerenes, knowledge about the C_{60} molecule still has many gaps. As experience shows, the most adequate method for studying the structure, phase transitions, and molecular mobility of the fullerene C_{60} molecule is Raman spectroscopy.

This work presents the results of the state-of-the-art study by Raman spectroscopy of molecular motion and phase transformations of crystalline fullerene C_{60} under excitation with the 633 nm line using low and ultra-low laser powers up to 10^{-4} mW in a wide temperature range of 93-723 K. The approach allowed to separate the thermal and light effects of the laser on the system and to detect new insights of the T01 phase transition in the C_{60} crystal. Moreover, for the first time, the reversibility of photopolymerisation at varying laser power was demonstrated.

The results presented are a logical continuation of the approach developed by us to study phase transitions and molecular mobility of plastic crystals packed from globular molecules by Raman spectroscopy, which was previously performed on a series of carboranes[4].

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SP^2 -CARBON IN THE LUNAR SOIL OF THE AS "LUNA-24" SAMPLE

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The last decade has seen a renewed interest in studying the composition of the lunar soil (regolite). Among the non-destructive structural physicochemical methods used for this purpose, Raman spectroscopy occupies a special place. The use of microscopes allows to perform structural studies of particles by micro-Raman-mapping at the micro level with a spatial resolution of about 1-5 mkm. The efficiency of the aforementioned non-destructive spectral method was demonstrated by us earlier in the study of the Chelyabinsk meteorite earlier(1-3), and lunar soil extracted by the automatic station "Luna-24" in the Sea of Crises from a depth of 1.85 m.[4] It was shown for the first time that the carbon material found in its composition in direct contact with pyroxene is sp^2-carbon of various modifications, which are similar to terrestrial materials, namely: amorphous sp^2 carbon (Fig. 1-1), Karelian shungite (Fig. 1-2), and turbostratite graphite (Fig. 1-3). The obtained data allowed us to conclude about the impact origin of the investigated sample of regolith.

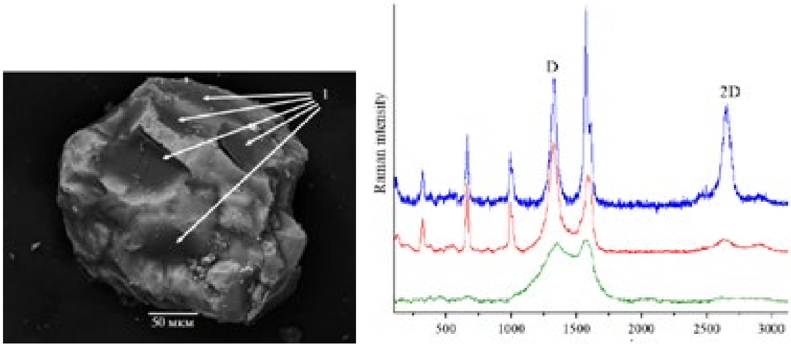

Figure 1. Raman spectra of various modifications of carbon identified in linar material.

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A NEW METHOD OF HYDROPHOBIZATION OF POLYETHYLENE TEREPHTHALATE FABRIC FOR BLOOD VESSEL PROSTHESIS

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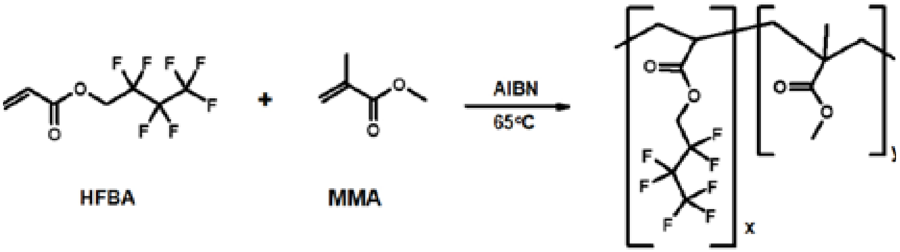
Among the known polymers, polyethylene terephthalate (PET) is one of the most commonly used materials for the production of vascular prostheses. It possesses the necessary physical and chemical properties[1], but it does not have a high enough hydrophobicity to prevent adhesion of red blood cells and other blood elements to the prosthetic vessel. This can lead to their destruction, thrombosis, calcification, and stenosis of the vessel[2].

Currently, it is believed that the creation of a superhydrophobic coating on the surface of the prosthesis ($\theta > 150°$) can help prevent complications. However, the researchers' attempts to develop a method for applying a stable coating to PET fabric with an edge wetting angle of more than 150° have not yet been successful.

We found that radical copolymerization on the surface of Dacron PET tissue used for the manufacture of vascular prostheses, 2,2,3,3,4,4,4-heptafluorobutylacrylate (*HFBA*) with methyl methacrylate (*MMA*) at a ratio of 10:1



in the presence of *AIBN* at 65°C for 8 hours leads to the formation of a superhydrophobic polymer coating with a wetting angle of $\theta \approx 155°$ (Fig. 1, c).

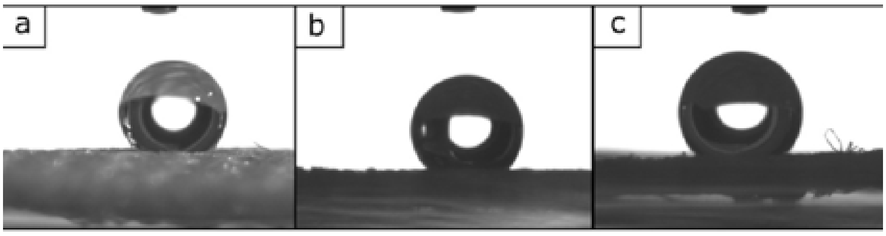


Figure 1. Images of water droplets on the surface of Dacron tissue samples with hydrophobic HFBA/MMA copolymerization: a) at a ratio of 1:0, b) at a ratio of 5:1, c) at a ratio of 10:1, respectively

A distinctive feature of this method is that it is carried out under normal conditions, which greatly simplifies the process of hydrophobization. The surface examination by EMS-SEM and SEM analysis of the sample confirmed the presence of an ultrathin structured fluorinated polymer coating, which exhibits stability both in an aqueous medium and in organic solvents.

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SYNTHESIS AND STRUCTURE OF [Sb(DMSO)(μ_2-O)Cl]$_n$

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Recently, the possibility of using antimony(III, V) compounds has been shown as reagents and catalysts for organic synthesis, medicinal, antiseptic and antimicrobial drugs, electrodes for sodium and lithium-ion batteries.[1,2]

The interaction of triorganylstibine with acids leads to partial or complete elimination of organic substituents from the antimony atom. The composition of the resulting products is determined by the nature of the organoantimony compound, acid, solvent and temperature.

We carried out the reaction of tris(2,6-dimethoxyphenyl)stibine with hydrochloric acid. The product was recrystallized from dimethyl sulfoxide (DMSO). The [Sb(DMSO)(μ_2-O)Cl]$_n$ was isolated in 90% yield. The complex is formed according to the following scheme:

$$Ar_3Sb + 3\ HCl \rightarrow SbCl_3 + 3\ ArH,\ Ar = 2,6\text{-}(MeO)_2C_6H_3,$$

$$n\ SbCl_3 + n\ H_2O + n\ DMSO \rightarrow [Sb(DMSO)(\mu_2\text{-}O)Cl]n + 2n\ HCl.$$

In the IR spectrum of the [Sb(DMSO)(μ_2-O)Cl]n complex there is a band of stretching vibrations ν(SO) at 1032 cm^{-1}, the shift of which to longer wavelengths compared to "free" DMSO indicates the coordination of the solvent through oxygen atom. The IR spectroscopy data are consistent with the X-ray results.

The antimony atoms in [Sb(DMSO)(μ_2-O)Cl]n have a distorted trigonal bipyramidal coordination with the axially located oxygen atoms of the DMSO molecule and chlorine. The O–Sb–Cl bond angles are 163.8, 164.1°. In the equatorial plane there are bridging oxygen atoms and a lone electron pair of an antimony atom. Interatomic distances μ_2-O–Sb 1.948, 1.970 Å, Sb–O$_{ax}$ 2.194, 2.242 Å.

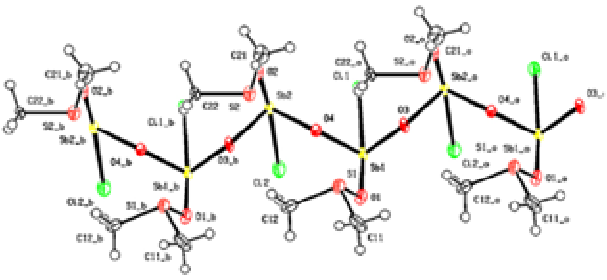

Figure 1. Fragment of the polymer chain [Sb(DMSO)(μ_2-O)Cl]$_n$

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SYNTHESIS OF POLYSILOXANE (BUTYLENE OXIDE) URETHANE UREAS BASED ON OLIGODIAMINOSILOXANE AND CYCLOALIPHATIC DIISOCYANATES IN THE PRESENCE OF BISMUTH (III) NEODECANOATE

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Polysiloxaneurethanes are of great interest because they combine the unique properties of polysiloxanes (low glass transition temperature, low surface energy, hydrophobicity, high gas permeability, biological inertness) and polyurethanes (high mechanical strength, abrasion resistance). Toxic organotin catalysts, which can have a negative impact on human health and the environment, are widely used in the synthesis of polyurethanes. In the present work, using the previously described technique[1] cross-linked polysiloxane (butylene oxide) urethane ureas (PSBUUs, fig. 1), model polybutylene oxide urethanes and polysiloxane ureas based on oligosiloxane diamine, H_{12} MDI and isophorone diisocyanate (IPDI) in the presence of a less toxic catalyst, bismuth (III) neodecanoate[2,3], were synthesized. The obtained polymers form colorless transparent films. It was shown that the introduction of an oligobutylene oxide block into PSBUUs leads to an increase in the strength compared to the model polysiloxane ureas with the same length of the siloxane fragment. In PSBUUs with a siloxane component content of 47-53% (wt.), the presence of two glass transition temperatures corresponding to the glass transition temperatures of the organic and siloxane phases was found.

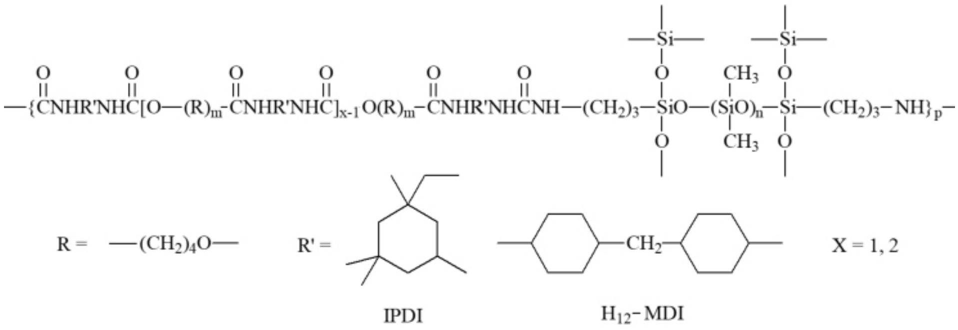

Figure 1. A formula for the polysiloxane (butylene oxide) urethane ureas.

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Acknowledgements
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INFLUENCE OF THE CATALYST ON THE SYNTHESIS AND PROPERTIES OF POLYSILOXANE (PROPYLENE OXIDE) URETHANE UREAS BASED ON H_{12}-MDI

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Polysiloxane urethanes are polymers that combine the unique properties of polysiloxanes (low glass transition temperature, low surface energy, hydrophobicity, high gas permeability, biological inertness) and polyurethanes (high mechanical strength, abrasion resistance). Organotin catalysts are widely used in the synthesis of polyurethanes, but they have a negative impact on human health and the environment. Bismuth-based catalysts are less toxic and can replace organotin catalysts in many cases[1]. In this work, cross-linked polysiloxane (propylene oxide) urethane ureas (PSPUUs) based on H_{12}-MDI (figure 1) were synthesized using the previously described method[2]; chloroform as a solvent was used. The reaction was carried out in the presence of three different catalysts: diethyltin dicaprylate (DETC), dibutyltin dilaurate (DBTL), and bismuth neodecanoate (Bi-NDE). It is known[1,3], all three catalysts accelerate the reactions of both urethane formation and polymer crosslinking. The main characteristics of the obtained polymers are given in the table 1. Aging the samples for a month resulted in a slight improvement in mechanical properties and may be due to the continuation of the crosslinking.

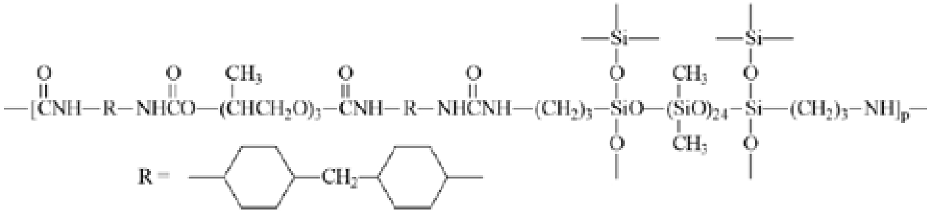

Figure 1. A formula for the polysiloxane (propylene oxide) urethane ureas.

Table 1. Main characteristics of PSPUUs.

PSPUU	m/M_n	n/M_n	Catalyst	Gel-fraction, %	ε, %	σ, MPa	Gel-fraction*, %	ε*, %	σ*, MPa	T_g*, °C
I	3/200	24/2100	DBTL	90	58	10.0	93	34	11.0	120/81
II	3/200	24/2100	Bi NDE	85	300	6.5	91	160	7.0	116/59
III	3/200	24/2100	DETC	90	53	10.0	92	44	10.0	127/94

* After a month of aging under normal conditions.

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AUTOCATALYTIC SYNTHESIS OF CARBOXYLATED POLYIMIDES FOR IN SITU APPLICATIONS

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Carboxylated polyimides (CxPIs) have great potential for the development of gas separation membranes, high-temperature resistant coatings, ion-conducting materials, aerogels, nanocomposites, etc. However, the synthesis of CxPIs has traditionally involved a long and expensive two-step process through the formation of unstable poly(amic acid) followed by thermal or chemical imidization.

A new strategy has been developed, which consists in a one-step high-temperature synthesis of CPIs based on 3,5-diaminobenzoic acid (DABA), whose carboxyl groups provide the autocatalytic effect[1]. The efficient synthesis of a wide variety of CxPIs without an additional catalyst allows to use the obtained solutions *in situ* in the production of various functional materials. In particular, varnishes based on CxPIs form a primary protective coating of silica optical fiber that are characterized by superior performance compared to their commercial counterpart in terms of manufacturing technology, thermal and hydrolytic stability.

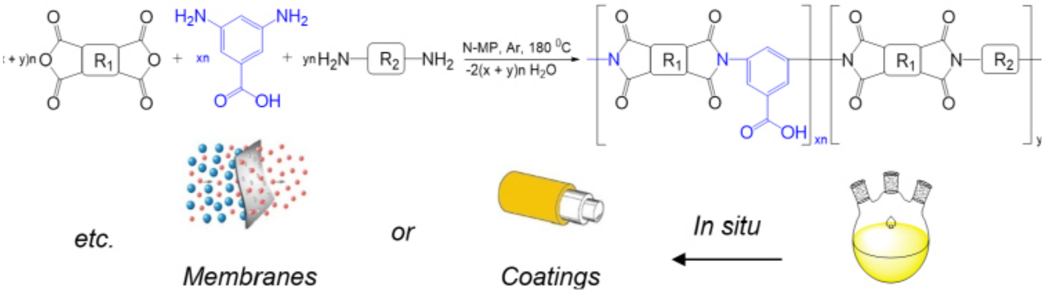

Figure 1. Scheme of synthesis of carboxylated polyimides and their in situ applications.

The results obtained show the significant potential of the developed method for the synthesis of CxPIs and their application as coatings, gas separation membranes and in other high-performance materials.

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COMPOSITES BASED ON MAGNESIUM-SUBSTITUTED HYDROXYAPATITE AND POLYSACCHARIDES

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In connection with the development of tissue and cell engineering, the production of biopolymers suitable for creating a matrix on which cells can form tissue structures for subsequent implantation in places of damaged organs is developing. Matrices are used for effective treatment of cells as a substrate on which they can be fixed[1].

The aim of this work is to synthesize composites and determine the influence of organic biopolymers on the composition and morphology of doped hydroxyapatite.

Synthesis of Mg-HA-chitosan/Mg-HA-chitin composites was carried out in the presence of chitosan/chitin by precipitation from an aqueous solution at room temperature. The study of the microstructure and surface features of the obtained Mg-HA-chitosan/Mg-HA-chitin was carried out using a JSM-6390/6390LV scanning electron microscope from JEOL, Japan.

Using optical microscopy, it was revealed that the Mg-HA-chitosan and Mg-HA-chitin aggregates have a lamellar elongated shape, characteristic of magnesium-containing hydroxyapatite crystals (Fig. 1)[2].

Synthesized composites based on HA, doped with magnesium in the presence of chitin and chitosan polymers have a constant composition, the presence of functional groups of HA and polymers is confirmed by IR spectroscopy. The presence of characteristic phases is established by X-ray diffraction. For the use of composites as materials with high biodegradation, it is better to use a HA-chitosan composite. The effect of organic polymers on the structure and properties of hydroxyapatite has been proven.

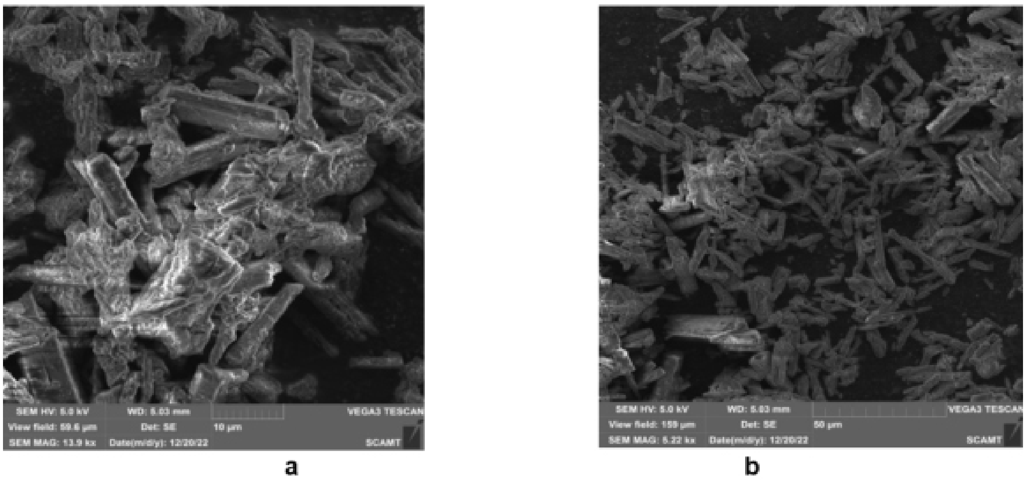

Figure 1. Micrographs of Mg-GA composites with chitosan (a) and chitin (b).

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Acknowledgements
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TRIBOLOGICAL PROPERTIES OF PHENOL-FORMALDEHYDE COMPOSITE MATERIALS CONTAINING POLYETHYLENE TEREPHTHALATE

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For the production of highly loaded parts of friction units of various mechanisms, it is preferable to use reinforced polymer composite materials (PCM) based on thermosetting plastics, which have a higher load capacity and increased heat resistance compared to antifriction thermoplastics such as polyamide, ultra-high molecular weight polyethylene, and polyethylene terephthalate (PET).[1]

The aim of the study was to create new antifriction reinforced PCMs based on thermosetting martices and thermoplastic fillers. In the work, PCMs based on a resol phenol-formaldehyde (r/f) binder and PET (used both as a reinforcing fibrous component and as a modifying dispersed additive under dry friction conditions on steel) were obtained for the first time and their tribological properties were studied.

Samples of p/f PCM, reinforced with PET fabric, during friction in the absence of lubrication on the counter-body "steel bushing", have higher tribological properties compared to composites reinforced with cellulose cotton fabrics. Maximum wear resistance values and minimum friction coefficient were recorded for samples of p/f PCM, reinforced with cotton fabrics and modified with dispersed PET obtained by cryogenic grinding of industrial granules.

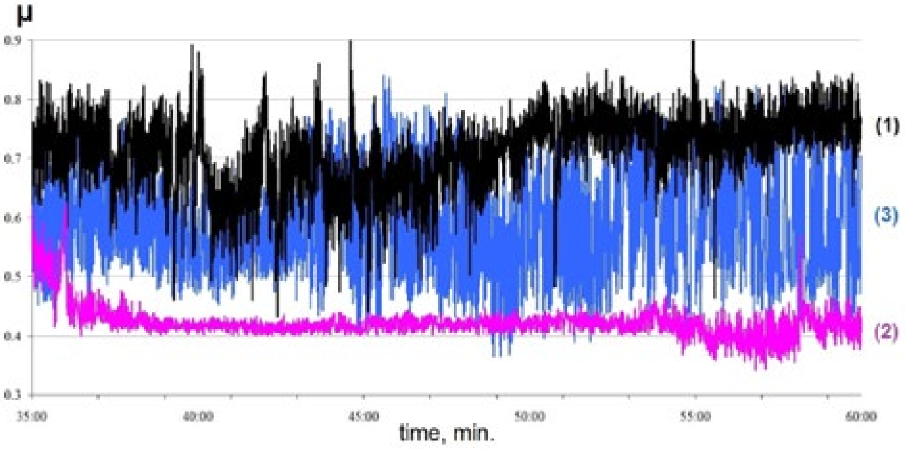

Figure 1. Frictional dependencies of p/f textolites with cotton fabric (1), with cotton fabric and dispersed PET modifier (2), with PET fabric (3).

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OPTICAL PROPERTIES OF POLY(N-VINYL SUCCINIMIDE) MOLECULES IN ISOTROPIC AND ANISOTROPIC SOLVENTS

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The unflagging interest in investigations of poly(N-vinyl succinimide) (PVSI) is caused by the use of its derivatives in many fields of medicine. Researchers continue to explore the potential of their use, synthesizing novel modified polymers and copolymers on their basis with broader application possibilities[1-3]. At the same time the information on PVSI molecular properties especially optical one, is extremely scanty.

The dynamic flow birefringence (FB) is one of the methods that are sensitive to conformational changes in macromolecules [4,5]. The study of the optical properties of PVSI is a promising study capable to expand the understanding on the organization of monomer unit of macromolecule, on the influence of the solvent nature on optical anisotropy of segment, anisotropy of the monomer unit and the anisotropy of the macroform.

Poly(N-vinyl succinimide) was synthesized by classical radical polymerization in solution. A set of PVSI with a wide range of molecular masses ($100<M\times10^{-3}<3350$) was obtained. In this study, optical properties of PVSI molecules were investigated in virtually optically isotropic (dimethylformamide) and optically anisotropic (benzyl alcohol) solvents. Shear optical coefficient $\Delta n/\Delta\tau$, anisotropy of the segment $(\alpha_1\text{-}\alpha_2)_0$ and anisotropy of the monomer unit ($a\|–a\perp$) were determined. A significant difference in the optical characteristics of PVSI molecules in anisotropic and isotropic solvents has been established. The difference is associated with the additional contribution of benzyl alcohol molecules to the optical anisotropy of PVSI molecules in solution. This is a manifestation of the Frisman-Dadivanyan effect[6].

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SYNTHESIS OF WIDE BANDGAP CONJUGATED π-COPOLYMERS INCORPORATING 9H-CARBAZOL-3-YL DITHIENO[3,2-F:2',3'-H]QUINOXALINE UNITS VIA DIRECT ARYLATION POLYCONDENSATION FOR PHOTOVOLTAIC APPLICATION

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The exhaustion of traditional fossil energy sources and the looming environmental challenges have propelled polymer bulk heterojunction solar cells (BHJS) into the spotlight as a viable, renewable, and eco-friendly energy solution, owing to their low cost, lightweight, and large-area fabrication capabilities. Notably, conventional polymer binary solar cells have recently achieved an efficiency of over 19%. There is an expectation that the efficiency of BHJS should reach around 25% for commercialization. Therefore, it is pertinent to focus on the development of highly efficient BHJS.[1,2]

We have designed new wide bandgap copolymer of A-D-A'-D type with strong carbazole-3-yl dithieno[3,2-f:2',3'-h] quinoxaline and benzodithiophene-4,8-dione acceptors and thiophene donor unit denoted P1 and compared its optical and electrochemical properties with well-known copolymer PM6,[3] which consists of same acceptor unit. The P1 exhibits deeper highest occupied molecular orbital and higher dipole moment than PM6, which is attributed to the weak donor unit in P1. Employing a narrow bandgap non-fullerene acceptor Y6, the organic solar cells based on P1 and PM6 under identical processing conditions showed overall power conversion efficiency of 13.48 and 14.81%, respectively. Although the power conversion efficiency of device based on P1 is lower than that for PM6, but its open circuit voltage is higher than that for PM6. Employing P1 as second donor, optimized ternary organic solar attained power conversion efficiency of 17.11%, which is higher than that for binary counterparts. The increased power conversion efficiency for ternary organic solar cells is associated with balanced charge transport, suppressed recombination process, faster charge extraction owing to the more appropriate morphology as well as the energy transfer from guest donor P1 to PM6.

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POLYMERIC STATIONARY PHASES WITH VARIABLE POLARITY FOR GAS CHROMATOGRAPHIC SEPARATIONS OF AROMATIC COMPOUNDS AND ITS SULFUR ANALOGUES

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The most often discussed thermodynamic functions of sorption for chromatographic systems are enthalpy ΔH and entropy ΔS of sorption of analytes of different classes which are the instruments for evaluation of properties of polymers which may be used in gas chromatography (GC) as stationary phases. However, the sorption system in GC separation processes is not sufficiently formalized, the phenomenon of sorption is often investigated separately from other processes, not as a part of general chemical thermodynamics of the system. The present paper is devoted to the investigation of the mixed stationary phases for GC prepared by the physical mixing of two polymers with different polarity: non-polar polydimethylsiloxane and polar polyethylene glycol. Several GC capillary columns were prepared, containing 100% PDMS, 20% PDMS+80% PEG, 40% PDMS+60% PEG, 60% PDMS+40% PEG, 80% PDMS+20% PEG, 100% PEG, and all the polymeric mixtures were investigated using inversed GC (IGC). It is expected that the resulting stationary phase should demonstrate the properties being the linear combination of the properties of the individual polymers. To work out this question, values of enthalpy ΔH and entropy ΔS of sorption for alkanes from hexane to dodecane, alcohols, ethers and ketones together with Rohrschnieder constants including those for pyridine, benzene and nitrobenzene were determined for each individual polymer and for all the mixtures. It was shown that the efficient polarity of the prepared mixtures differs from the linear combinations of the individual values. The compensation temperatures were calculated for comparison of the sorption mechanism of sorbates in all the polymeric mixtures. The prepared columns were evaluated for separation of aromatic compounds and their sulfur-containing analogues, demonstrating selectivity sufficient for baseline separation (Fig.1).

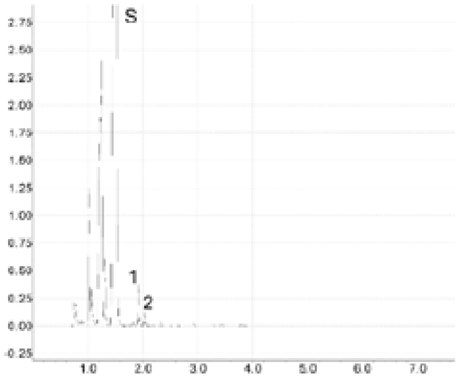

Figure 1. Separation of test mixture on the column 40% PDMS+60% PEG.
S – solvent, 1 – benzene, 2 – thiophene

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STUDY OF AMINOLYSIS OF CYCLOCARBONATES BY ALCOXYSILANES

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Polyurethanes are among the most common and popular polymers. However, due to the toxicity of the industrial synthesis method, research into the development of alternative ways of synthesizing these materials has recently become very relevant. Among the chemical processes described in the literature that lead to the formation of a urethane group without the participation of isocyanates [1], aminolysis of cyclocarbonates is considered the most promising, since the reaction is not sensitive to moisture, and the starting components do not have the same toxicity as isocyanates and phosgene, which is used in their synthesis.

Many works have been devoted to the study of this method [2], but the use of silicon-containing reagents in this process remains low. Based on this, the purpose of our study was to study the kinetic patterns of the aminolysis reaction of organic cyclocarbonates with organosilicon alkoxysilanes with γ-aminopropyl substituents. As initial components we selected cyclocarbonates of different structure: linear dicyclocarbonate (based on propylene oxide), linear-branched tricyclocarbonate (based on trimethylolpropane and propylene oxide), branched tricyclocarbonate (based on trimethylolpropane), aromatic dicyclocarbonate (based on bisphenol-A) and amines: γ-aminopropyltriethoxysilane and γ-aminopropylmethyldiethoxysilane. The process was carried out without using solvents. The conversion of cyclocarbonates was determined using IR spectroscopy.

As a result of the kinetic studies, it was shown that a number of factors have a positive effect on the aminolysis reaction rate - temperature, catalyst, and excess amine. New silyl-modified urethane oligomers, which are promising binders, were obtained and their adhesive properties to various surfaces (glass, metal, wood) were studied (Fig. 1).

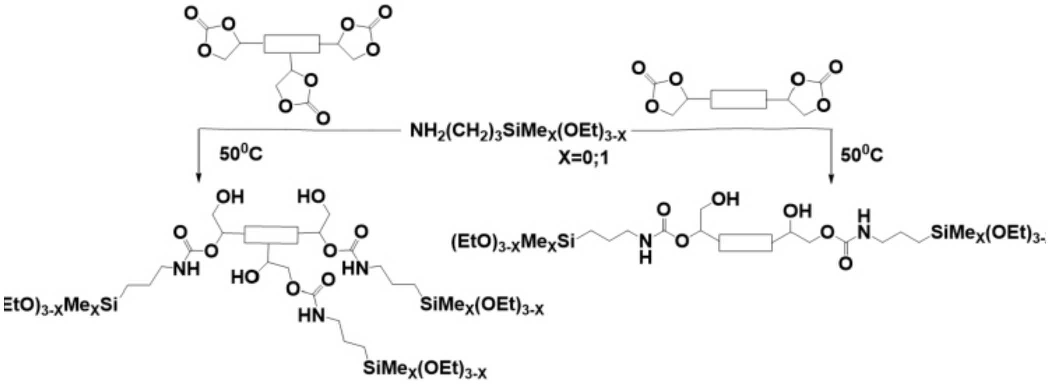

Figure 1. Synthesis of silyl-modified urethane oligomers

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CATALYTIC ACTIVITY OF NOVEL LN CYMANTRENECARBOXYLATE COMPLEXES WITH FERROCENE PHOSPHINE OXIDO LIGAND IN POLYMERIZATION OF VINYL MONOMERS

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It is known that cymantrene (CymH = (η^5-C_5H_5)Mn$(CO)_3$) derivatives can serve as polymerization catalysts.[1] At the same time, carboxylate complexes of the lanthanides can influence the stereoregularity of this process.[2]

Earlier we have shown that neodymium cymantrenecarboxylate complex $[Nd_2(CymCO_2)_6(DMSO)_4]$ can be the catalyst of stereoregular polymerization of 2,3-dimethyl-1,3-butadiene.[3] Continuing further our research in the field of organometallic carboxylates, we obtained a new series of heteroleptic organometallic *3d-3d′-4f*-complexes $[Ln(CymCO_2)_2(DppfO_2)_2]X\cdot$*Solv* (Ln = Nd, Dy, Ho, and Er; $DppfO_2$ is the Fe(η^5-$C_5H_4P(O)Ph_2)_2$ ligand; X = Cl^- or NO_3^-, *Solv* are the lattice solvent molecules). Both kinds of organometallic ligands in the bulky cations $[Ln(CymCO_2)_2(DppfO_2)_2]^+$ are bidentate (Fig.1, left).

All the constituents of the obtained complexes can potentially affect the polymerization processes. Activities of complexes of Nd (**1**) and Ho (**2**) with X = Cl^- in the processes of polymerization of methyl methacrylate and styrene in the presence of $(PhCOO)_2$, as well as under UV-light or thermal activation in the presence of CCl_4, are studied and discussed (Figure1, right).

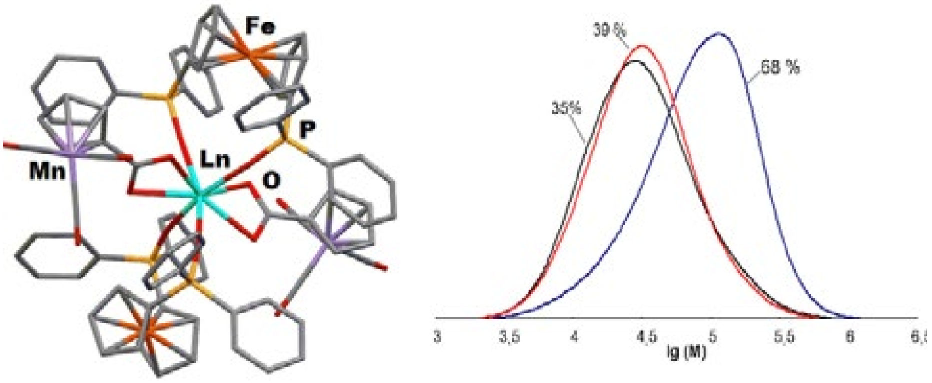

Figure 1. Structures of complex cations in compounds $[Ln(CymCO_2)_2(DppfO_2)_2]X$ (left) and the curves of the molecular weight distribution of polystyrene samples synthesized in the presence of **1** (0.05 mol.%) and CCl_4 (0.25 mol.%) at 110°C; the yields are given in percent values (right).

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TRANSDERMAL DRUG DELIVERY SYSTEMS BASED ON CROSSLINKED HYALURONIC MICRO- AND NANO-PARTICLES

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Design of modern highly effective antimicrobial drug delivery systems able to achieve maximum therapeutic effect is currently in development. Avoidance of chaotic drug distribution in the bloodstream makes encapsulated forms of antibiotics more preferable. Polysaccharides are of particular interest in the development of micro- and nano-sized delivery systems of antimicrobial agents', as they are safe, biocompatible and stable. Majority of bacteria and prokaryotes do not have the ability to phagocytose micro- and nanoparticles, but are able to dissolve and destroy various used to design micro corpuscular depot forms of drugs. This is a result of specific enzymes releasement upon bacterial vital activity[1]. Destruction of the polysaccharides chain does not occur when the absence of these enzymes. This approach is widely used to impart bacteriostatic properties to various transdermal therapeutic systems. Present study uses the enzymatic activity of bacteria as a basis used to impart antibacterial properties to various fillers and transdermal therapeutic drug delivery systems based on hyaluronic acid. Hyaluronic acid is widely used in medicine due to its unique properties[2]. It is the crucial component of living beings' extracellular matrix as well as various organs and tissues.

Micro- and nano-particles based on cross-linked with 1,4-butanediol diglycidyl ether hyaluronic acid gel nanoparticles obtained in a biphasic system formed by aqueous solutions of two immiscible polymers. Polyvinylpyrrolidone aqueous solution was used as a dispersed medium. Particles prepared in a cooled reactor with continuous ultrasonic treatment. The chemical structure of the products was determined by FTIR spectroscopy and MALDI-ToF mass- spectrometry. The particle size and distribution were investigated via dynamic light scattering. The antimicrobial activity of the samples was assessed using the disk diffusion method in *in vitro* experiments over a week. The standard test strain of gram-positive bacteria Staphylococcus aureus 209P was used as an experimental model.

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POLYPHENYLENEPYRIDINES AND NITROGEN-CONTAINING CARBON MATERIALS BASED ON THEM

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Global warming and environmental pollution due to the huge consumption of fossil fuels require the development of new energy generation technologies. A fuel cell based on the cathodic oxygen reduction reaction is considered an ideal energy supply system due to its high energy conversion efficiency, environmental friendliness and the possibility of large-scale application. At the same time, platinum is considered the best catalyst for this reaction, but suffers from high cost. In this regard, the development of affordable alternative porous materials, in particular nitrogen-containing carbon materials, which can be comparable in activity or even better than the platinum catalyst for the oxygen reduction reaction, is relevant. Conjugated polymers built by covalently linked aromatic rings in π-conjugated skeletons seem to be the most promising in terms of use as precursors of electrode materials for fuel cells[1]. Carbon materials based on such polymers have nanoporous structures, large surface areas and high chemical stability. Such nitrogen-containing polymers were obtained mainly by metal complex catalysis. In the present work, conjugated nitrogen-containing polymers were synthesized using a simpler and more technologically advanced method, where pyridine rings were obtained as polymer-forming fragments.

Heat-treated in argon at 450, 800 and 1000 °C, porous polymer samples (specific surface area according to BET up to 1150 m^2/g) were studied by X-ray photoelectron spectroscopy, according to which nitrogen in them is mainly found in the form of graphite- and pyridine-like nitrogen-containing systems.

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COMPOSITE MATERIALS BASED ON PLGAS AND CARBONATED APATITE

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Interest in composite materials combining synthetic bone mineral substitutes (BMS) and biodegradable polyesters for orthopedic applications is growing. Poly(lactic-co-glycolic acid)s (PLGAs) are vital in biomedical fields, with their biodegradation and mechanical properties affected by the lactate/glycolate (L/G) ratio, molecular weight, and microstructure. Incorporating glycolic acid into poly(L-lactide) increases hydrophilicity and degradation rates. PLGAs allow for adjustable biodegradability; for instance, glycolate-rich PLGA 10/90 is used for sutures, while PLGA 85/15 suits surgical devices. However, conventional methods of producing PLGAs often fail to achieve optimal copolymer statisticity due to differences in reactivity between lactide and glycolide as well as newly developed segmer assembly polymerization method, do not allow to obtain high-MW PLGAs. Using L-methylglycolide (L-MeGL), a comonomer with intermediate reactivity, appears promising for enhancing PLGA statisticity[1].

Calcium phosphates, especially hydroxyapatite (HAp) and β-tricalcium phosphate (TCP), are crucial for bone support and regeneration. HAp is FDA-approved, but its high crystallinity limits biodegradability and can cause cytotoxicity, whereas TCP resorbs too quickly. Carbonated apatite (CAp) offers a promising alternative, mimicking bone apatite with better resorption rates and neutralizing acidic byproducts from polyesters. A significant challenge in bone tissue engineering is finding materials that balance mechanical strength, bioactivity, and bioresorption. Plate-like CAp with a high aspect ratio can enhance composite strength through reinforcement, making it an optimal solution.

We present new biodegradable materials from the PLGA family: copolymers of L-lactide and L-methylglycolide (L-MeGL) in molar ratios of 85:15 and 70:30, named L-PLMG 85/15 and L-PLMG 70/30. These were synthesized via ring-opening copolymerization using Sn(Oct)2, while L-PLGA 85/15 served as a reference. NMR studies revealed distinct microstructures, with L-PLMG copolymers showing improved hydrolytic stability due to the absence of oligo(glycolate) fragments. Composites incorporating 25% and 50% carbonated apatite were created from various polymers. L-MeGL-based copolymers exhibited greater thermal stability and higher flexural moduli compared to PLLA and PLGA 85/15. They also maintained strength better in phosphate buffer solutions. Preliminary studies suggest L-MeGL copolymers may outperform PLGA 85/15 in biomedical applications, including surgical devices.

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APPLICATION OF CONTROLLED POLYMERIZATION METHODS IN THE SYNTHESIS OF VISCOUS AND DEPRESSANT ADDITIVES TO PETROLEUM PRODUCTS

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Modern issues of petroleum industry are aimed for stable economic development and oriented on improvement characteristics of oils and fuel. One of the ways of improvement technological characteristics and the expansion of their working life in internal combustion engines consists in the introduction of multifunctional polymer-based additives into their composition[1,2].

There are three methods of controlled radical polymerization have been chosen: Atom Transfer Radical Polymerization – ATRP, Reversible Addition-Fragmentation Chain-Transfer – RAFT and Nitroxide-Mediated Radical Polymerization – NMRP. These methods allow sinthesize (meth)acrylic based polymers for impovement low temprature, thermooxidative and viscosity properties. Via ATRP process CuBr/TPMA system has been used. Molecular-weight characteristics has been regulated with 2-cyano-2-propyldithiobenzoate and 2-cyano-2- propyldodecyltrithiocarbonate in RAFT-polymerization. C-phenyl-N-tertbutylnitron has been used as polymerization agent via NMRP process.

The influence of molecular weight characteristics and architechture of polymers is analyzed for the degree of thickening and viscositytemperature properties of industrial oil. It has been shown that linear polymers with low molecular weights and polydispersity, regardless of the chosen production method, have greater resistance to mechanical, thermal and thermo-oxidative degradation. The oil thickened with branched polymers has self-compensating properties with respect to the viscosity index during mechanical degradation of the additive in the oil.

The influence of molecular weight characteristics, structure, composition and topology (meth)acrylic polymers has been studied for low-temperature, thermo-oxidizing and lubricating properties of DF. It has been established that copolymers with introduced nitrogen- and oxygencontaining heterocyclic components obtained by any of the selected methods are capable of effectively improving the low-temperature properties of DT at a concentration of 800-1600 ppm. It was revealed that the topology of copolymers plays an important role in the effectiveness of depressor additives, low-temperature parameters of DT improve with an increase in the branching of polymers obtained on a mono-, bi- and trifunctional initiator (by the ATRP method) by more than 10°C.

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3D PRINTING WITH POLYPHENYLENE SULFIDE COMPOSITE

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The scope of 3D printing application is becoming wider every year, which is why the demand for filaments based on superstructural polymers is expanding. The paper studies the effect of dispersed fillers in the filament composition on the mechanical and thermal properties of printed products.

The matrix material was a linear polyphenylene sulfide powder, the filler was 4.5 mm chopped glass fiber and finely dispersed quartz flour (15 µm). Random ethylene-glycidyl methacrylate copolymer was used as a plasticizer.

The components were mixed and the filament was obtained (Table 1) on a twin-screw extruder. The obtained filaments were used to print samples of the form B1 bar and A1 tensile specimen, the dimensions of which were taken from ISO 20753. The samples were printed using nozzles with a diameter of 0.8 mm at a layer thickness of 0.4 mm and a printing speed of 60 mm/min.

The physical and mechanical tests, including tensile tests and unnotched Izod impact strength tests, were carried out in accordance with ISO 527 and ISO 180, respectively. Tensile tests of the obtained samples were carried out on a universal electromechanical testing machine with wedge-shaped grips and a deformation rate of 5 mm/min. Unnotched Izod impact strength tests were carried out on a pendulum impact machine with a pendulum energy of 7.5 J.

To evaluate the heat resistance of the samples, tests were carried out to determine the bending temperature under load in accordance with ISO 75-1. The tests were carried out with a heating rate of 2 °C/min and a generated stress of 1.8 MPa.

Thus, the properties of products printed with filaments of different compositions were determined, and the most optimal composition was identified, which has high mechanical characteristics and is relatively easy to manufacture.

Table 1. Filament compositions

Number	Fiberglass, wt%	Quartz flour, wt%	Plasticizer, wt%
1	-	-	-
2	10	-	-
3	20	-	-
4	30	-	-
5	-	10	-
6	-	20	-
7	-	30	-
8	10	20	-
9	20	10	-
10	-	-	10

Acknowledgements
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THE EFFECT OF ALUMINUM HYDROXIDE ON THE THERMAL CONDUCTIVITY OF SILICONE COMPOUNDS

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The development and application of silicone materials with high thermal conductivity are of great importance for various industries. They find their application in the production of electronic components such as processors, microchips and other devices, where it is necessary to quickly dissipate heat and prevent overheating, thus increasing their efficiency.

Such materials are in high demand nowadays, and the requirements for heat conductivity are constantly increasing. In this regard, new materials have been developed very intensively in recent years to meet consumer demand. The most widely used method of increasing the thermal conductivity of compounds is the introduction of fillers with high thermal conductivity. The rapid cheapening of electronics also makes demands on the cost of polymeric materials, so the development of organosilicon compounds with inexpensive fillers is undoubtedly of interest.[1-3]

The effect of surface-modified and unmodified aluminum hydroxide of different dispersity on the thermal conductivity and thermal resistance coefficient of the compositions has been investigated. Viscosity and gel-time of compounds, physico-mechanical properties of the cured systems at different volume concentrations of fillers were compared. The use of surface-modified aluminum hydroxide greatly facilitates the dispersion process, improves the compatibility with the binder, affects the rheological characteristics and allows to achieve higher values of filler volume concentration.

It is established that when filling the compositions with aluminum hydroxide it is possible to increase the thermal conductivity of the material from 0.24 (for unfilled compound) to 0.75 W/(mK). It was shown that the use of surface-modified aluminum hydroxide can increase the thermal conductivity of the silicone compound by 60% and reduce the coefficient of thermal resistance by half compared to the unmodified one. The use of more highly dispersed modified aluminum hydroxide leads to problems in dispersion, increased viscosity and dusting during the preparation of compositions.

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HIGH NITRATE-SELECTIVE METAL-POLYMER MEMBRANES BASED ON CARDO POLYBENZIMIDAZOLE FOR ELECTRODIALYSIS

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Ion exchange membranes with high monovalent ion selectivity are essential for extracting valuable components from natural and waste waters[1]. One of the approaches to their fabrication is the creation of nanostructured materials with ion-conducting channels. In this study, materials based on cardo polybenzimidazole (PBI-O-PhT) containing Zn^{2+}, Cr^{3+} and Cu^{2+} ions were obtained and used for the first time for electrodialysis separation.

The formation of crosslinked structure due to metal-benzimidazole coordination bonds was demonstrated. The obtained metal-polymer membranes have ionic conductivity comparable to commercial ones, reaching 0.32 $mS \cdot cm^{-1}$, and high values of nitrate ion transport numbers (99.2%).

It is shown that the obtained membranes achieve incredibly high values of selectivity coefficients for anion separation. The highest and most stable values were obtained for the copper-containing membrane PBI/Cu-50, which are $P(NO_3/SO_4) = 729$, $P(Cl/SO_4) = 109$ and $P(NO_3/Cl) = 6.66$.

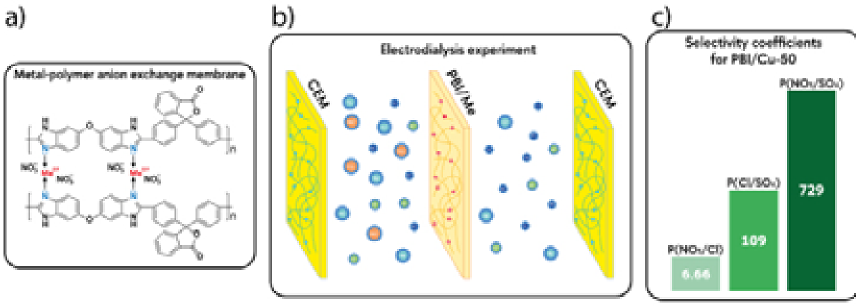

Figure 1. Structure of metal-polymer membranes (a), scheme of electrodialysis experiment (b), selectivity coefficients for PBI/Cu-50 (c).

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PHTHALONITRILE MONOMERS WITH A SILAZANE FRAGMENT AS ACTIVE THINNERS IN THE PREPARATION OF POLYMER MATRICES

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Thanks to advances in new fiber reinforced plastics (FRP) it is already possible to use them in many industries. Due to the high specific strength of the FRP, it is relevant to replace metal parts with fiber reinforced plastics, which significantly reduces the weight of the final product. With a further increase in the proportion of fiber reinforced plastics applied in aircraft construction, the replacement of metal parts in engines is the most promising. But it is currently limited by the insufficient thermal stability of the matrices. Therefore, obtaining new thinners for FRP suitable for operation at temperatures above 300 °C is relevant. As a result of the study of phthalonitrile matrices, it was concluded that FRP based on them are promising for high-temperature applications.

According to existing literature data, silicon-containing phthalonitrile derivatives have relatively low melting points, therefore they may potentially be used as active thinners of mixtures of phthalonitrile monomers in the preparation of polymeric matrices for FRP.[1] Structures with siloxane bridges are characterized by hydrolytic instability. Silozane linkers, in turn, are resistant to hydrolysis. However, to date, there is only one publication dealing with phthalonitrile compounds containing the Si-N bond.[2] The compounds described in the publication are capable of entering into a polycondensation reaction in the absence of catalysts and have a sufficiently high thermal stability. Based on this, the aim of this work was to synthesize and determine the properties of a number of promising silicon-containing monomers and FRP based on them.

During the work, the syntheses of 4-(4-aminophenoxy)-phthalonitrile (*p*-APN) and 3-(4-aminophenoxy)-phthalonitrile (*m*-APN) were carried out. After optimizing the synthesis technique, the reactions of the obtained compounds with $SiMe_2Cl_2$, $SiPhMeCl_2$, and $SiPh_2Cl_2$ were carried out. The hydrolytic stability of the obtained compounds was studied. The thermal properties of hydrolytically stable synthesized products containing a phthalonitrile fragment and a Si-N bond were investigated by the DSC method. As a result, it was found out that $SiMe_2Cl_2$ and $SiPhMeCl_2$ derivatives are hydrolytically unstable, and the melting points of phthalonitrile derivatives of $SiPh_2Cl_2$ are higher than the melting points of the initial p-APN and *m*-APN, which limits the use of the studied compounds as active thinners.

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PHYSICOCHEMICAL PROPERTIES OF POLY(VINYL ALCOHOL) CRYOGELS PREPARED FROM THE POLYMER SOLUTIONS IN A MIXTURE OF DIMETHYL SULFOXIDE AND DIMETHYLFORMAMIDE FOLLOWED BY REPLACEMENT OF THE ORGANIC SOLVENTS FOR WATER

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Physical (non-covalent) poly(vinyl alcohol) (PVA) cryogels are the macroporous gel materials formed through cryotropic gelation, which involves freezing, incubation in a frozen state and subsequently thawing of solutions of this polymer. The choice of solvent for the preparation of PVA cryogels can significantly affect their properties. With that, only water and dimethyl sulfoxide (DMSO) can serve as solvents for highly deacetylated (99-100%) poly(vinyl alcohol).

PVA cryogels produced in aqueous media are well-studied. The patterns of cryotropic gelation for PVA solutions in DMSO are similar to those in the PVA-water system; however, the macroporous morphology and physicochemical properties of cryogels fabricated from the PVA aqueous solutions differ significantly from those derived from the DMSO solutions. Cryogels produced from the PVA solutions in DMSO tend to be less rigid and have lower fusion points compared to cryogels formed from the aqueous polymer solutions of the same PVA concentrations. For applications in medical and biological fields, it is essential to replace the organic solvent (DMSO) for water, which results in a significant increase in the rigidity and heat endurance of the cryogel samples.

In addition to aqueous and DMSO solutions of the polymer, PVA cryogels can also be derived from mixtures of these two solvents. In turn, this study reports, for the first time, PVA cryogels producing from the polymeric solutions in the mixtures of DMSO and dimethylformamide (DMF). It was found that a volumetric ratio of 75% DMSO to 25% DMF was optimal for the preparation of PVA solutions that had polymer concentration suitable for the formation of PVA cryogels possessing desired strength.

It has been established that PVA cryogels formed in a DMSO/DMF mixture exhibit greater elasticity compared to those produced from the DMSO solutions alone. Moreover, PVA/DMSO/DMF cryogels undergo substantial shrinkage during hydration, leading to a significant increase in their Young's modulus and shear modulus. This is attributed to a decrease in the thermodynamic quality of the solvent due to the desolvation of the polymer relative to DMSO, caused by the presence of the non-solvent DMF in the initial polymer solution, which enhances polymer-polymer interactions. Additionally, cryogel samples formed in the PVA/DMSO/DMF mixture have a higher light transmittance compared to cryogels produced in DMSO and aqueous environments.

RING-OPENING METATHESIS POLYMERIZATION OF CIS-5-NORBORNENE-EXO-2,3-DICARBOXYLIC ANHYDRIDE IN THE PRESENCE OF A CHAIN TRANSFER AGENT - 1-HEXENE

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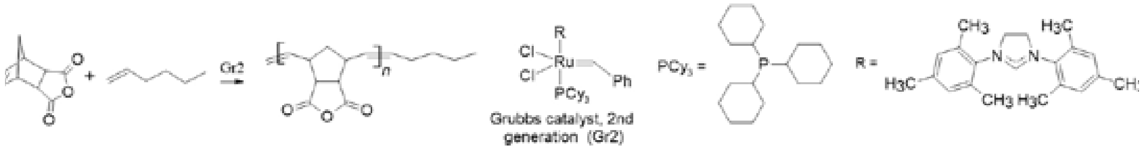
One of the methods for regulating the properties of new polymeric materials is to create them using polymers keepped chemical reactivity after their production. After post-polymerization reactions such polymers added to another material are capable of changing the product final properties. This polymers are synthesized from monomers containing two or more reaction centers participating in reaction various types. For example, *exo*-5-norbornene-2,3-dicarboxylic acid anhydride (NDA), been capable to cure epoxy resins due to the anhydride group[1], polymerizes by ROMP to poly(NDA)[2] due to the strained cycloolefin fragment. As far as poly(NDA) is solubility only in polar solvents[3], no detailed study of the metathesis polymerization its in a DMF medium has been conducted. Therefore, the aim of this work is to study the possibility of obtaining poly(NDA) with different molecular weights by ROMP of NDA under the action of the 2nd generation Grubbs catalyst in the presence of the chain transfer agent - hexene-1. The initial *exo*-NDA was obtained by the Diels-Alder reaction. Poly(NDA)s were synthesized according to Scheme 1 in an absolute DMF medium at different ratios of the initial reagents.

The resulting products were isolated by precipitation in methanol or water, after which the low-boiling components were removed in vacuum at 70°C for 3 hours. The structure of the products was confirmed using IR, ^{1}H, ^{13}C NMR spectroscopy, as well as two-dimensional correlation ^{1}H-^{13}C HSQC spectroscopy. The chemical shifts of the terminal double bond protons were determined, and the M_n^{NMR} of the reaction products were determined according to ^{1}H NMR data. Poly(NDA)s were characterized by GPC (eluent was DMF) and DSC. It was shown that an increase in the amount of hexene-1 in the reaction mass leads to a decrease in M_n^{NMR} and M_n^{GPC}. According to DSC data, T_g increases with an increase in M_n of the polymerization products.



Scheme 1. Synthesis Poly(NDA) by ROMP of exo-5-norbornene-2,3-dicarboxylic acid anhydride (NDA)

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Acknowledgements
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SUPRAMOLECULAR NANOCONTAINERS WITH MITOCHONDRIAL-TARGETING FUNCTION BASED ON CALIXRESORCINE CAVITAND

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The uniqueness of supramolecular systems is the ability to not only mimic nature objects but also perform various technological functions. One significant application of these systems is as drug delivery systems (DDS). Several requirements for DDS include low toxicity, prolonged circulation in the bloodstream, high drug loading capacity, specificity[1]. The specificity of DDS is achieved by optimizing their size and functionalization with target ligands. Among them, those oriented towards intracellular specificity are promising, for example, mitochondria-targeted (MT) ligands. Their action occurs due to the highly negative charge of the mitochondria membrane in cancer cells, which can provide the effectiveness of DDS[2]. Our approach to obtaining MT DDS includes the formation of supramolecular polymer-calixresorcine cavitand complexe, in which the polymer provides the size of DDS required to maintain the EPR effect[3] and reduces the toxicity of DDS. The cavitand is modified with MT ligands and also provides the binding of a cargo. The complex of PAA and cavitand, bearing triphenylphosphonium (TPP) groups was developed (Figure 1). The TPP groups possess the ability to target mitochondria due to their delocalized charge and lipophilic nature.[4] DDS particles have an average hydrodynamic diameter of 190 ± 2 nm and a positive charge (+21.6 ± 4.95 mV). We studied the hemo- and cytotoxicity of DDS, as well as its ability to reduce the mitochondrial membrane potential of M-HeLa cells and induce their apoptosis via the intrinsic mitochondrial pathway. The results of the study demonstrate the potential of the systems as MT DDS.

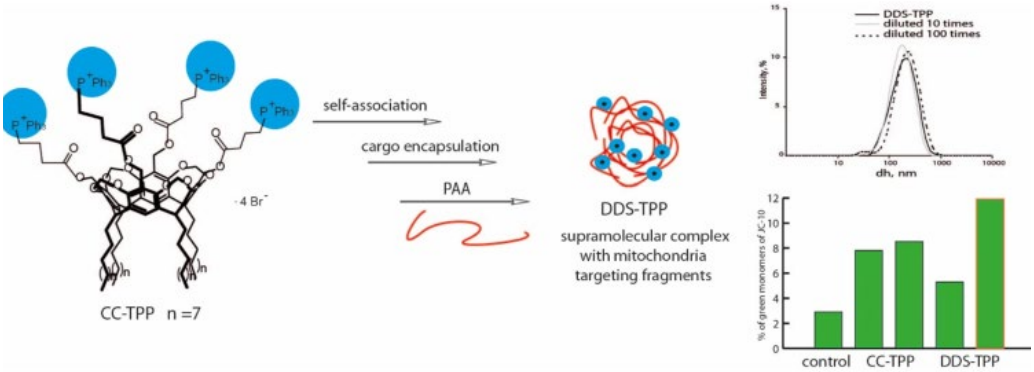

Figure 1. The structure of CC-TPP, the proposed scheme of DDS-TPP formation, the intensity-averaged distribution of DDS-TPP particles (DLS data), and the percentage of M-HeLa cells with “green” fluorescence of JC-10 (cytometry data).

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3D-PRINTABLE BIO-SOURCED NANOCOMPOSITE HYDROGELS BASED ON NATURAL POLYMER AND CELLULOSE NANOCRYSTALS

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Last time, environmental concerns led to the rapid growth of the use of renewable and biodegradable materials, as well as the development of resource-saving and waste-free technologies such as three-dimensional (3D) printing. One area of particular interest is the development of 3D printed hydrogels made from natural and biodegradable polymers such as polysaccharides that will decompose at the end of their useful life, without leaving any pollution behind.

Typically, 3D-printed products made from traditional hydrogels have low mechanical strength, with elastic moduli in the tens of kPa or less, and low toughness (low ability to resist defect growth), with fracture energy of less than 10 J/m^2) which limit the area of their applications. To enhance the mechanical strength and toughness of hydrogels, several strategies were proposed including the formation of double network structures[1] and the introduction of reinforcing fillers[2].

In the work it was studied at the investigation of the behavior of HPG-MA/CNC hydrogels containing soft network of hydroxypropyl guar (HPG) molecular chains that can be photocrosslinked in situ during 3D printing and percolated carboxylated cellulose nanocrystals (CNC) reversibly crosslinked by calcium ions that act as a hard sacrificial network. Such double network hydrogels demonstrate the pronounced increase in stiffness and toughness compared to the corresponding single-component networks, without loss of maximum extensibility. The toughening mechanism of the prepared gels consists in the ability of non-covalent bonds within rigid network and between the soft and rigid networks to dissociate and reassociate dynamically, dissipating energy and protecting the soft HPG-MA network from stress overshoot.

This makes the photocrosslinkable HPG-MA/CNC-Ca hydrogels promising as a novel type of “green” ink for 3D printing, in which both components feature low toxicity, biocompatibility, and biodegradability, and are widely available from renewable biosources.

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Acknowledgements
The financial support provided by the Russian Science Foundation (project number 23-13-00177) is acknowledged.

CHITOSAN/HYDROXYAPATITE COMPOSITES: PRODUCTION USING CO2-BASED SOLVENT AND INVESTIGATION OF PHYSICO-CHEMICAL PROPERTIES

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Nowadays, scientists pay great attention to the development of biocompatible scaffolds based on polymer nanocomposites for biomedical technologies. Such materials with predetermined porosity and specific mechanical characteristics that have antimicrobial and proliferative activity can be effectively utilized in bone tissue regeneration.[1,2] Thus, a promising direction is fabrication of chitosan/hydroxyapatite scaffold encapsulated with copper nanoparticles. These composite can be produced in three steps using a «green» self-neutralizing solvent – water/subcritical carbon dioxide biphase system.[3]

The research was aimed at identification of the optimal conditions for synthesis composites based on chitosan, hydroxyapatite and copper nanoparticles in a biphase water/subcritical CO_2 system, and study their functional properties.

Samples were prepared at different conditions: using *in situ* and *ex situ* synthesized hydroxyapatite; 1.5% and 2% chitosan solutions; 30°C and 70°C temperature reduction of copper nanoparticles. Infrared spectroscopy and X-ray diffraction analysis were utilized for determination of the composite stability. Morphological features of the obtained biomedical device were examined using high-resolution microscopy. All the samples had an average pore diameter of 100 microns and a porosity of approximately 75%. Studies on the mechanical properties of composite materials have shown a significant increase in the compression modulus when hydroxyapatite was added.

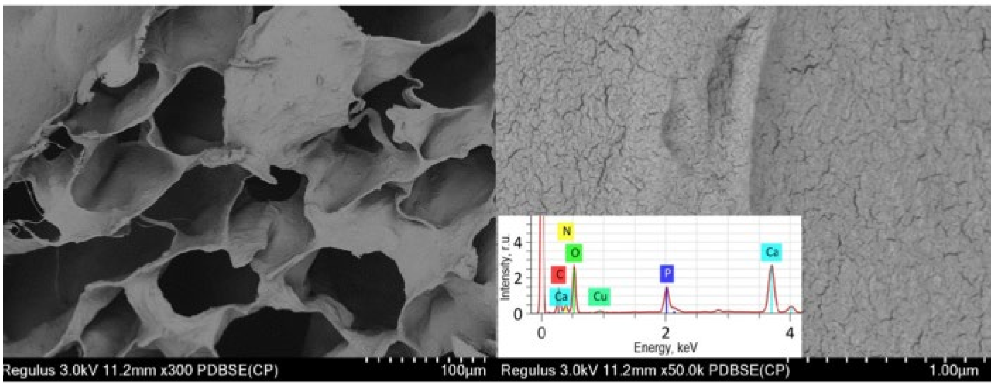

Figure 1. SEM micrographs of chitosan/hydroxyapatite composite, encapsulated with copper nanoparticles

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INTERACTION OF POLYORGANOSILOXANES WITH ELEMENTAL SULFUR

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It is known that aromatic compounds readily react with elemental sulfur to form polyaryl sulfides.[1] However, such reactions have not been carried out with polyorganosiloxanes. The interaction of polyorganosiloxanes with elemental sulfur was carried out at a temperature of 160-200 °C after mechanochemical activation according to scheme 1.

IR spectroscopy data show a shift in the absorption bands in the obtained thio derivatives compared to the IR spectra of the original polymers. According to X-ray diffraction data, the difference in the interplanar distance of the obtained and initial polymers is 0.3–0.7 Å, which does not imply the placement of sulfur atoms in the interchain space. However, the complete loss of solubility of the polyvinylsiloxane-based polymer indicates that polysulfide bridges are nevertheless formed between polymer molecules by the type of vulcanization. Apparently, the interaction of sulfur with polyvinylsiloxane occurs with the formation of polysulfide bridges outside the interchain space.

When polyphenylsiloxane interacts with sulfur, soluble and insoluble fractions of polymers containing sulfur are formed. The soluble fraction was studied using NMR spectroscopy. In the ^{13}C NMR spectrum, a signal appears at 150 ppm, corresponding to the presence of a C–S bond in the phenyl radical.

Three chlorinating agents were used to cleave the S–S bond in polythioethylsiloxane: PCl_5; Cl_2; SO_2Cl_2. Under the action of the described chlorinating agents, there was an increase in the chlorine content and a decrease in the sulfur content in the final product. The increase in chlorine content is apparently due to simultaneous chlorination of the double bond. However, the interaction of the polymer with phosphorus pentachloride is ambiguous. Two products were obtained: polythioethylsiloxane, which does not contain chlorine, and polythiophosphate.

$$[RSiO_{1,5}]_n + nS_x \rightarrow [S_xRSiO_{1,5}]_n \text{, где } R=C_2H_3-;\ C_6H_5-.$$

Scheme 1. Interaction of polyorganosiloxanes with elemental sulfur

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FUNCTIONAL POLYLACTIDE MICELLES FOR TARGETED DELIVERY OF PACLITAXEL

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Minimization of non-specific side effects and enhancement of therapeutic activity of drugs by targeted delivery of drugs to the patient's tumor tissue are important areas of modern medicine. One method to improve the efficiency of delivery of hydrophobic drugs to cancer cells is the use of nanocontainers such as micelles, which are typically composed of amphiphilic diblock copolymers. Polylactide is often used as a hydrophobic block, and polyethyleneglycol (PEG) is used as a hydrophilic block. Such a copolymer is capable of self-organizing in an aqueous solution into micelles with a polyester core and a PEG shell. Such micelles are not suitable for passive delivery due to their small size (about 30 nm), so it was proposed to modify them to ensure active delivery. The possibility of including maghemite nanoparticles in polymer micelles was previously demonstrated, but the ternary system micelle – targeting agent – antibiotic was not obtained.

Thus, the aim of this work is to investigate the possibility of creating a nanocontainer for the targeted delivery of a hydrophobic antibiotic based on micelles of a block copolymer of lactide and ethylene glycol with maghemite nanoparticles. Paclitaxel (PTX) was used as a water-insoluble antitumor drug. A sample of the copolymer was dissolved in tetrahydrofuran (THF), then PTX, previously dissolved in ethanol, and a sample of maghemite were added to the solution. Then THF was distilled off in a vacuum rotary evaporator, and the resulting polymer film was dispersed using ultrasound in bidistilled water. As a result, aqueous solutions of micelles were obtained with a PTX and maghemite content of 10 wt. % and 0.5 wt. %, respectively. Their hydrodynamic diameters were determined using the dynamic light scattering method. The stability of the obtained micelles to enzymatic hydrolysis was studied. After 24 hours from the moment the enzyme was added, the individual size of the micelles ceased to be recorded, which is a consequence of the enzymatic effect.

The following conclusions were obtained in the course of the work. After solubilization of paclitaxel and magnetic particles, the micelles retain a size acceptable for use as a dosage form for antitumor drugs. The resulting nanosystems are resistant to enzymatic hydrolysis for several hours, but then undergo degradation, which is an advantage of polylactide micelles as carriers for drugs. Thus, polylactide micelles are a promising material for creating magnetically sensitive systems for targeted drug delivery.

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SELF-HEALING POLYURETHANES FROM BIOBASED SOURCES

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The reversible Diels-Alder reaction (DA) is one of the most powerful tools for creating thermally remendable polymers. The introduction of DA adducts into the polymer structure gives them the ability to heal damage repeatedly. The healing process is easy to engage with thermal stimuli. A new series of self-healing polyurethanes (PUs) was synthesized with a trifuranic diol compound derived from furfuryl glycidyl ether (FGE), the byproduct of vegetable stock processing, and bismaleimide curing agent (BMI). The structure of the obtained polymers was studied by IR spectroscopy. The thermal properties and reversibility of the DA-bonds were investigated using the DSC method. Visual estimation of self-healing capability was examined by SEM imaging. For quantification of self-healing process efficiency, the measurement of elastic modulus and tensile strength was performed. The influence of the content of dynamic DA adducts on the properties of polyurethanes and the efficiency of self-healing was shown. The effect of recycling on mechanical properties and self-healing efficiency was investigated as well.

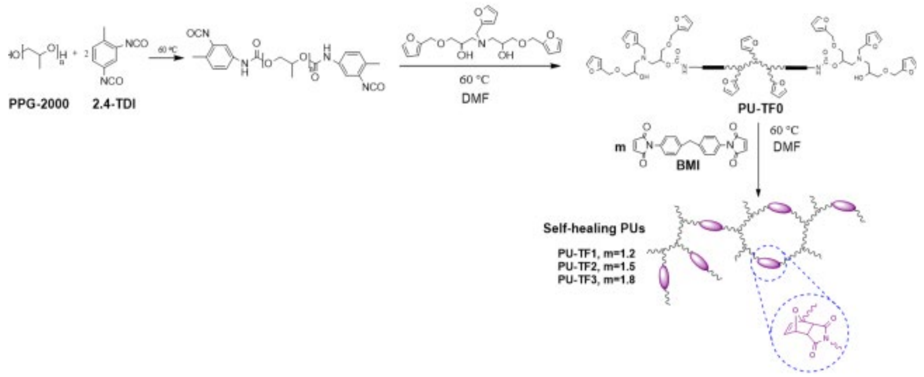

Figure 1. Synthesis of self-healing polyurethanes

Acknowledgements
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SYNTHESYS OF NONCONJUGATED TADF-POLYMERS FOR MAIN CHAIN NATURE IMPACT STUDY

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The rapid proliferation of various wearable electronic devices necessitates the utilization of high-performance organic light-emitting diodes (OLEDs), which involves the exploration of novel materials.[1,2] Three generations of OLED materials exist: fluorescent organic materials (1st generation), phosphorescent organo-metallic complexes (2nd generation), and organic molecules featuring thermally activated delayed fluorescence (TADF; 3th generation). It is known that the latest material class can attain 100% internal quantum efficiency due to its ability to enhance emission from the singlet state via reverse intersystem crossing and a small energetic gap between singlet and triplet states.

Polymeric light-emitting diodes (PLEDs) constitute a promising subset of OLED technologies consisting of polymers endowed with electroluminescent properties enhanced by TADF. Several PLEDs with various acceptor content have been synthesized and characterized.[3-5] Synthetic scheme includes concurrent obtaining of precursors. Acceptor prototype is synthesized via sequential cyanuric acid substitution using 4-bromostyrene and phenylboronic acid.[6] Donor prototype is synthesized via Buchwald–Hartwig reaction under various conditions. Polymers are obtained by free-radical polymerization and hydrosililation addition to polymethylsiloxane-60. Purity and structures are identified by GPC and 1H NMR analysis accordingly. The optical study and TADF properties of polymers are carried out for THF solutions and films.

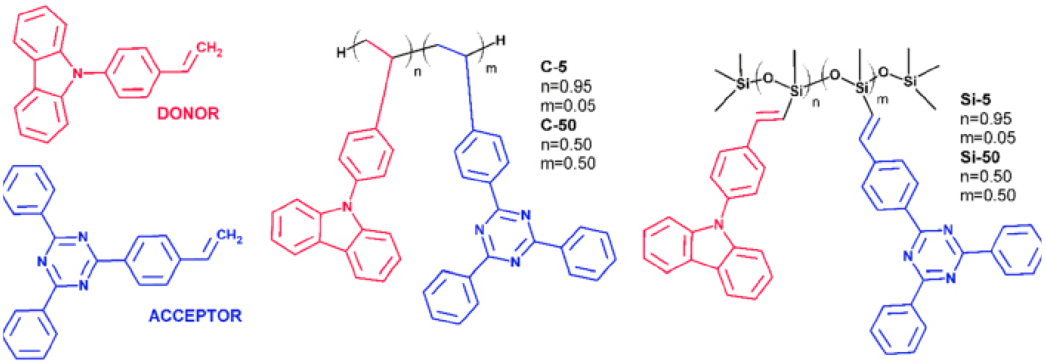

Figure 1. Precursors and polymers structures.

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SYNTHESIS OF LITHIUM-CONDUCTING POLYAMIDE-POLYMETHACRYLATE BLOCK COPOLYMERS

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Single-ion-conducting polymers are a promising replacement for traditional electrolytes in the manufacture of safe high-capacity solid-state lithium batteries[1]. It is possible to combine good mechanical properties with ionic conductivity in a polymer material by achieving microphase separation of block copolymers[2]. To ensure incompatibility of the blocks, which facilitates separation, the synthesis of a polymer containing strong polyamide and ion-conducting polymethacrylate blocks is proposed.

A polyamide with terminal amino-groups was synthesized by low-temperature polycondensation in NMP of 9,9-bis(4-aminophenyl)fluorene and terephthaloyl chloride. The polyamide is modified by interaction of terminal amino groups with 4-cyanopentanoic acid dithiobenzoate. This allows the polyamide to be used as a chain transfer agent in the RAFT polymerization of methacrylates. Ion-conducting A-B-A copolymers with a central polyamide block and terminal polymethacrylate were obtained by RAFT copolymerization of polyethyleneglycol methacrylate with lithium 1-[3-(methacryloxy)propylsulfonyl]-(trifluoromethanesulfonyl)-imide. It has previously been shown that the copolymers of these methacrylate monomers have good ionic conductivity but poor mechanical properties[3].

The use of controlled RAFT polymerization makes it possible to synthesize copolymers with terminal ion-conducting A-blocks bearing desired length and a narrow molecular weight distribution. The influence of these parameters on the properties of copolymers is studied.

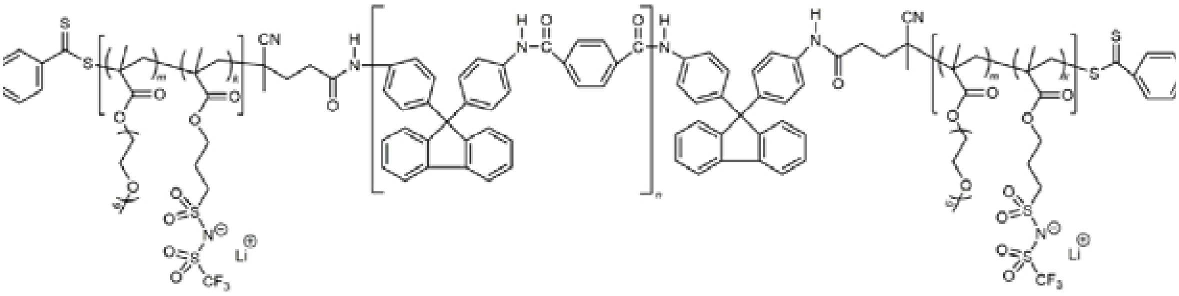

Figure 1. Lithium-conducting polyamide-polymethacrylate block copolymer

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THE TUNABLE PROPERTIES OF MAGNETIC ALGINATE BIOPOLYMER BEADS

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The object of this study is sodium alginate beads. The polymer is a salt of alginic acid - an unbranched copolymer composed of two residues of polyuronic acids: D-mannuronic and L-guluronic. It is obtained, for example, from algae such as Laminaria hyperborea and Laminaria japonica, as well as Sargassum vulgare. Sodium alginate is widely used in various industrial applications. Sodium alginate is a widely used ingredient in various industrial applications. In the food industry, for example, it is commonly used as a stabilizer and thickening agent, while in medicine, it serves as an antacid. In addition, alginate has potential applications in the oil industry. Magnetically responsive alginate beads could be used to create plugs for controlling water flow in well.

The swelling of the beads under different conditions was studied. As a result, macrogels formed from beads concentrated in the region of the magnetic field were obtained. The regularities of swelling and destruction of beads with changes in the conditions of their preparation and the composition of the solution in which they swelling were investigated. First of all, the swelling of beads in NaCl and $NaHCO_3$ solutions was considered, since groundwater in oil production contains a large amount of salts. It was noticed that with preliminary drying of the beads, a large relative change in the size of the beads during swelling can be achieved. It is shown that to obtain a macrogel with good mechanical properties for the formation of a plug, plastic deformations are necessary, therefore, pre-dried beads of two types were used: treated in an $NaHCO_3$ solution for 10 minutes and 20 minutes. This way, "cement and bricks" are obtained - plastic and elastic beads for "building" plugs. Such densely packed plugs are able to effectively block water flows. Finally, It is shown that in water-alcohol mixtures and hydrocarbons (decane), the degree of swelling of the beads decreases, since the quality of the solvent deteriorates.

Thus, magnetic alginate beads were obtained, and their swelling in salt solutions was studied. Macrogels from swollen beads concentrated in the region of the magnetic field were obtained. Strong macrogels were obtained by combining beads with different crosslinking densities and degrees of swelling. The obtained beads can be used for selective blocking of water flows in an oil well by forming a macrogel plug.

Acknowledgements
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COORDINATION POLYMERS OF SILVER(I) NITRATE WITH SOME AMIDES AS LIGANDS: FEATURES OF SYNTHESIS, MOLECULAR AND CRYSTAL STRUCTURE

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Over the past decade, there has been a strong increase in the interest of researchers in studying the structures and properties of metal-organic frameworks and coordination polymers. High value of specific surface area, features of crystal and molecular structure and high stability make them promise multifunctional materials. Thus, coordination polymers based on silver(I) and various amides can be used as heterogeneous catalysts [2] and antimicrobial agents [1].

In present work the conditions of synthesis and crystallization of coordination compounds based on silver(I) nitrate and some amides have been selected: carbamide, N,N'-dimethylcarbamide, acetamide. A composition, crystal and molecular structure of isolated target products have been determined by use of set of physical-chemical analisys methods: $[Ag_2(Ur)_2(NO_3)_2]_n$, $[Ag_2(Me_2Ur)(NO_3)_2]_n$ and $[Ag(AA)(NO_3)]_n$. These compounds were shown to form 1D, 2D and 3D polymer chains. Coordination number of central Ag(I) atom varies from 2 to 6. In case of acetamide and N,N'-dimethylcarbamide the monodentate coordination through the donor oxygen atom is realised, and bridging bidentate coordination through the oxygen and nitrogen atoms in case of urea. Nitrate-ion behaves as bridging bidentate ligand.

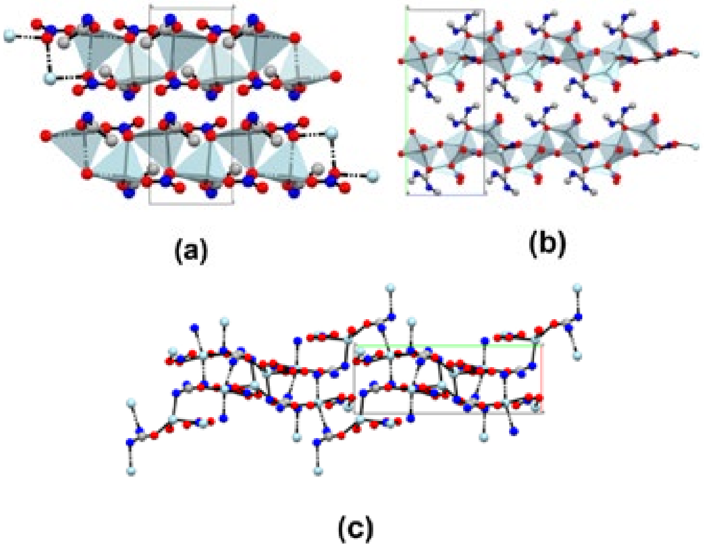

Figure 1. Cryctal and molecular structure of isolted compounds: $[Ag(AA)(NO_3)]_n$ (a), $[Ag_2(Me_2Ur)(NO_3)_2]_n$ (b), $[Ag_2(Ur)_2(NO_3)_2]_n$ (c)

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ORGANOSILICON RUBBERS AS STABILIZERS IN THE PRODUCTION OF STABLE POLYMER SUSPENSIONS

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Synthetic and artificial polymer suspensions are currently widely used in various fields of science and technology. However, their production is associated not only with the problem of insufficient stability in the process of their production, but also with an environmental problem - wastewater pollution with water-soluble surfactants used as stabilizers. The solution to this problem may be the use of new types of surfactants as stabilizers.

Water-insoluble organosilicon surfactants produced by the domestic industry - polydimethylsiloxane rubbers of the SKTN brand of different molecular weights - are proposed as such surfactants.

Studies of the colloidal-chemical properties of polydimethylsiloxane rubbers of the SKTN brands have shown that they are characterized by high surface-active properties and reduce the interfacial tension at the toluene surfactant/water interface and form thick interfacial adsorption layers, the values of which exceed 100 nm. This means that due to their structure they are capable of forming strong interphase adsorption layers on the surface of polymer particles and ensuring their stability.

Organosilicon surfactants have been studied as stabilizers in heterophase polymerization of acrylic monomers. It has been shown that when using SKTNs during heterophase polymerization of methyl methacrylate, it is possible to obtain stable polymer suspensions with diameters up to 1 μm and a narrow RCD at low surfactant concentrations (up to 2%). In addition, SKTNs were used to obtain artificial polymer suspensions. In this case, the formation of an interphase adsorption layer on the surface of polymer particles occurred at the stage of their preparation during emulsification of a polymer solution containing SKTNs. The strength of the interphase layer of the polymer suspension turned out to be sufficient to obtain stable polymer suspensions of polar polymers, such as polymethyl methacrylate and polyetherimide, with particle diameters from 0.2 to 0.9 μm.

BEHAVIOR OF POLY(VINYL ALCOHOL) CRYOGELS IN THE MEDIA OF CONCENTRATED INORGANIC ACIDS

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PVA cryogels are the non-covalent gels that are formed by freezing a polymer solution, maintaining it in a frozen state, and then thawing. The following factors influence on the physicochemical characteristics of cryogels: the molecular characteristics of the polymer used, its concentration in the initial solution, the conditions of cryogenic processing, and the presence of additives introduced in the initial PVA solution.[1,2]

In this work, the formed poly(vinyl alcohol) cryogels were placed in solutions of inorganic acids (hydrochloric, sulfuric, phosphoric) of different concentrations. After saturating for three days, the volumes of the samples, elastic moduli and fusion temperatures of the respective cryogels were measured. Then the cryogels were placed in excess distilled water and rinsed for a week with periodical replacement of water, after which the physicochemical characteristics were again evaluated (Figure 1).

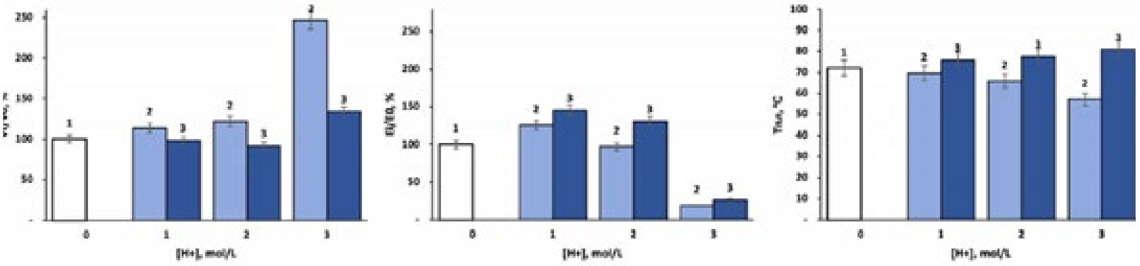

Figure 1. The effect of different concentrations of hydrochloric acid solutions on the physicochemical characteristics of PVA cryogels: a) – volume dependence, b) – elastic modulus dependence, c) – fusion temperature dependence. (1 – formed PVACG, 2 – PVACG after exposure to HCl solutions, 3 – PVACG after rinsing in distilled water).

It was found that, saturation PVA cryogels in solutions of inorganic acids results in the to changes in their physicochemical properties, which are not recovered to their original state after rinsing with water.

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SYNTHESIS OF RUTHENIUM-DOPED PHOTOCATALYSTS FROM RUTHENIUM SILOXANE

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Recently, more and more attention has been attracted by heterogeneous catalysts with a high dispersion of the active phase - " single atom catalysts" - which determines their high activity and economic prospects.[1] Single atoms of noble metals, as a rule, are connected to the surface through oxygen bridges, due to which they retain catalytic activity for a long time. Metallosiloxanes are compounds contained in their transition path M-O-Si (where M is a metal atom). In a broad aspect, the study of this class of compounds began in the 40s of the 20th century and continues to this day, which allows us to take into account a number of approaches to their synthesis at the present time.[2] The possibilities of constructing the structure and composition of such compounds determined the potential areas of their application, one of the main ones is catalysis, due to the presence of a coordinatively unsaturated metal atom as a result.3 Such compounds are capable of easily hydrolyzing (including thermally) with the formation of moisture in the air, and also interacting with the substrate containing hydroxyl groups on the surface (Figure 1). In this paper, the possibility of using ruthenium siloxane as a source of noble metal for modifying the surface of photocatalysts and the photocatalytic activity of the samples are investigated.

As a result of the work, a method for obtaining ruthenium siloxane, nanocrystalline TiO_2, and ruthenium-doped titanium dioxide was developed. The physicochemical properties of the obtained TiO_2 and its photocatalytic properties were studied. Figure 1 shows a micrograph, a diffraction pattern with an XPS spectrum of a 0.2Ru-TiO_2 sample, and the dependence of the concentration of the violet crystalline dye on the time of photocatalytic decomposition. The highest value of photocatalytic activity is observed for the 0.2Ru-TiO_2 sample.

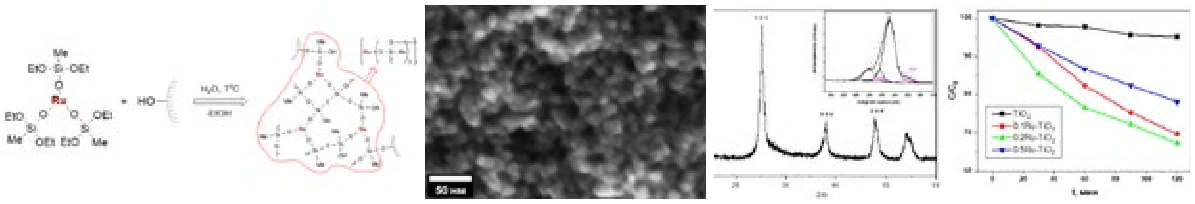

Figure 1. Scheme of ruthenium siloxane crosslinking, micrograph, diffraction pattern with XPS spectrum of 0.2Ru-TiO_2 sample and photocatalytic properties.

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STUDY OF THE BIOCIDAL PROPERTIES OF ORGANOSILICON DERIVATIVES OF GUANIDINE AND QUATERNIZED AMMONIUM BASES

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At the moment, there is an acute problem of the spread of infectious foci in public places and the formation of resistant biofilms of microorganisms on medical equipment. One of the most effective solutions to these problems will be the creation of antibacterial coatings.

In addition, coatings made from antibacterial materials, due to their anti-corrosion properties, can also solve the serious engineering problem of biofouling on marine infrastructure surfaces[1].

We have developed methods for the synthesis of organosilicon derivatives of tetramethylguanidine (TMG) and quaternary ammonium compounds based on tetramethylethylenediamine with different alkyl tail lengths (TMEDA-C10, TMEDA-C16). The antibacterial effect of coatings based on organosilicon derivatives of quaternary ammonium bases with different lengths of hydrophobic tail and tetramethylguanidine, as well as quaternary ammonium bases based on tetramethylguanidine, was compared. The indicators of the antibacterial effect of all coatings are high, and the highest indicator corresponds to quaternized tetramethylguanidine salts.

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SYNTHESIS AND INVESTIGATION OF HYDROLYTIC POLYCONDENSATION OF SILANES CONTAINING SYDNONYL SUBSTITUENTS

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In modern chemistry of organosilicon polymers, the direction of obtaining polysiloxanes with various functional groups that give new properties to materials based on them is actively developing. Sydnons have a unique electronic structure, unusual physico-chemical properties and have a wide range of biological activity. Their introduction into the structure of polyorganosiloxanes can significantly change the physical and mechanical properties of organosilicon polymers and expand their scope of application. The hydrosilylation process (HSP) is widely used both for the production of functionalized silane monomers and for the modification of organosilicon polymers.

In the present work, the processes of hydrosilylation of the olefin derivative of 4-phenylsidnone by silanes containing hydrolysis-capable groups (chlorine, ethoxy) and the subsequent process of hydrolytic polycondensation (HPC) of new silane monomers were studied. Platinum $[Pt]^0$ and rhodium $Rh[P(C_6H_5)_3]_3Cl$ catalysts have been studied as a catalyst for HSP. Mono-, di-, and trifunctional organosilicon monomers were isolated. The reaction proceeds quantitatively at room temperature for several hours regioselectively (β-addition).

Depending on the functionality of the monomer, various siloxane structures (linear and polycyclic) were obtained with HPC. All the compounds obtained were characterized by NMR (^1H, ^{13}C, ^{29}Si) and GPC methods (Fig.1).

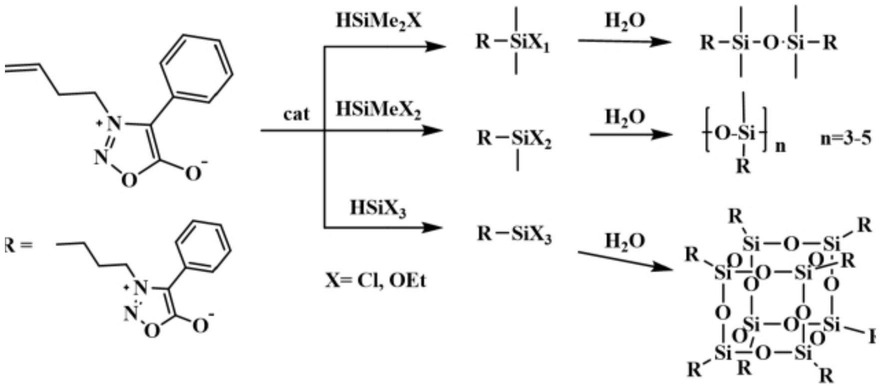

Fig. 1 Scheme of hydrosilylation and polycondensation reactions.

STABILIZATION EFFECT OF THE FE- AND AL-SILOXANES IN POLYIMIDE-NANOCOMPOSITES AGAINST ATOMIC OXYGEN

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The structure and properties of metallosiloxane nanocomposites based on the organosoluble polyimide (PI) synthesised from 4,4'-(9-fluorenylidene)dianiline and 3,3',4,4'-diphenyloxide tetracarboxylic acid have been studied. During the sol-gel process, the nanoparticles are formed from (methyldiethoxysiloxy)aluminium (Al-siloxane) and tris(methyldiethoxysiloxy)iron (Fe-siloxane) precursors. The atomic oxygen (AO) resistance results showed that PI-Fe-siloxane nanocomposites exhibited higher AO resistance than PI-Al-siloxane composites. SEM imaging revealed that the protective mechanism against destructive AO impact is the formation of a protective oxide layer. Based on the FTIR spectroscopy studies of the curing of metallosiloxanes in their pure state and in the polymer matrix, the sustainability to microcracking observed for the protective layer on the surface of PI filled with Fe-siloxane-based in compared to that of the PI-Al-siloxane film was rationalised. Namely, its morphology and continuity are determined by a residual amount of M-O-Si bridges in nanocomposites and directly increase the stability of PI composites against atomic oxygen irradiation by an order.

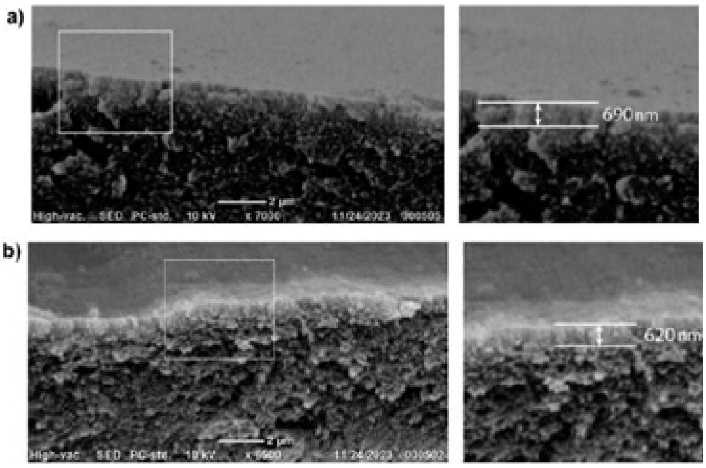

Figure 1. SEM images of the cross section filled films prepared using 25 wt.% of Al-siloxane (a) or Fe-siloxane (b) after the AO irradiation (fluence F is 6×10^{20} O atoms/cm^2).

Acknowledgements
This work was supported by the Russian Science Foundation (project No. 23-13-00244).

THE NEW LUMINOPHORES ARE BASED ON THE STRUCTURAL FRAMEWORK OF 2,1,3-BENZOTHIADIAZOLE AND INCORPORATE PHENYL, THIOPHENE AND A VARIETY OF TERMINAL SUBSTITUENTS

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Luminophores, as functional materials, are successfully used in various fields of science and technology. Among these materials, derivatives of 2,1,3-benzothiadiazole play a significant role due to their unique optical and electronic properties. The luminescent properties of these molecules can be tuned by incorporating different donor substituents.[1]

The main goal of this work is to investigate the relationship between the chemical structure and properties of these systems. A series of conjugated compounds based on 2,1,3 benzothiadiazole were synthesized, which contain donor thiophene and benzene moieties in their structures, as well as various terminal substituents. Optimal methods for obtaining these compounds through Pd-catalyzed cross-coupling reactions (Suzuki) were developed in two different ways. The spectral properties of the compounds obtained in dilute solutions were also investigated. It was found that the end groups have a negligible effect on optical properties. When alkyl groups are added, a slight shift of the luminescence maximum towards longer waves is observed. These molecules also have a high quantum yield of 86-90%. The influence of alkyl substituents on the thermal properties was investigated using TGA/DSC techniques. The melting point of derivatives that have terminal alkyl groups decreases compared to the unsubstituted compound.

Thus, BTD derivatives exhibit a high level of chemical and thermal stability, a high quantum yield, and a wide Stokes shift. These properties make BTD-based phosphors versatile and suitable for a variety of applications.

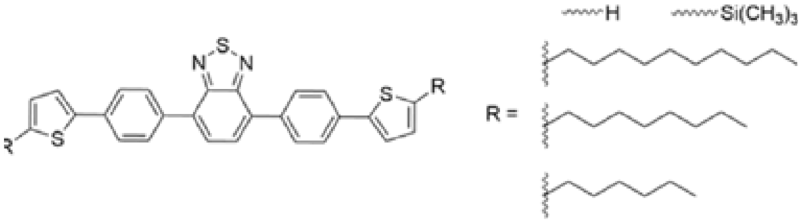

Figure 1. Chemical structure of the obtained compounds

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EFFECT OF TEMPERATURE ON HYDROLYTIC DEGRADATION OF POLY(L-LACTIDE)

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Polylactide (PLA) is a biodegradable and biocompatible polymer with tailored properties, which is widely used for fabrication of medical devices, in regenerative medicine and drug delivery. The key advantage of PLA-based products is that they do not require additional surgical intervention for removal of the implant. The degradation profile of PLA materials can be adjusted by changing its stereochemical structure, i.e. L/D ratio, crystallinity and molecular weight. To develop effective medical devices, it is important to assess the degradation rate of the polymer and final implant. However, at body temperature PLA-based materials can degrade for 2-5 years and even more. So, the evaluation of the full degradation profile may be a challenge, especially in time-limited projects focused on development of new medical devices. Therefore, an urgent issue is development of the standard methods for an accelerated degradation at elevated temperatures, followed by a calculation of the degradation profile at body temperature.

To study the dependence of the rate constant of poly-L-lactide hydrolysis on incubation temperature dog-bone samples with work length of 40 mm were 3D-printed from REC 3D PLA filament ($Mw = 170$ kDa, $PDI = 2.3$). The devices were placed in a phosphate buffer saline ($pH = 7.4$) at incubation temperatures of 37, 45, 55, and 75 °C. At desired time points, analysis of mass of the samples and molecular weight of the poly-L-lactide was performed. It was found that the molecular weight of poly-L-lactide decreases by 50% after 112, 49, 17, and 1 day of incubation at temperatures of 37, 45, 55, and 75 °C, respectively. A complex approach[1] was used to fit the experimental data, and the rate constants of random non-catalytic and autocatalytic hydrolysis were calculated. The calculated rate constants for random noncatalytic hydrolysis (k^r_n) were found to be $2.5*10^{-6}$, $1.0*10^{-5}$, $3.3*10^{-5}$ and $8.0*10^{-4}$ day^{-1} as the temperature increased, while the rate constants for random autocatalytic hydrolysis (k^r_a) were $7.6*10^{-6}$, $2.3*10^{-5}$, $7.1*10^{-5}$ and $1.0*10^{-3}$ $(mol^{-1} * m^3)^{½} * day^{-1}$. The calculated reaction rate constants were verified for matching with the Arrhenius and Vogel-Fulcher-Tamman equations. The first showed correlation coefficients of 0.995 and 0.997 for non-catalytic and autocatalytic hydrolysis, respectively, while the second showed lower correlation coefficients of 0.939 and 0.942, respectively.

Based on the experimental data, it can be concluded that an increase of the incubation temperature significantly accelerates degradation, which can be described by the Arrhenius law. The correlation coefficient close to 1 for Arrhenius equation indicates the reliability of the approximation methods and possibility for subsequent extrapolation of the results on any desired temperature. These results pave the way for development of the methods for accelerated degradation of PLA-based products.

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Acknowledgements
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ELECTRORHEOLOGICAL FLUIDS BASED ON QAS-PDMS MODIFIED MONTMORILLONITE IN SILICON OIL

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Electrorheological (ER) fluids represent a class of stimuli-responsive soft materials with tunable physical properties. A typical ER fluid is composed of solid polarizable particles dispersed in a dielectric medium. When an external electric field (EEF) is applied, the particles in ER fluids begin to form chain-like structures, which result in significant alterations to the material's rheological properties and a reversible transition from a viscous to a viscoelastic fluid. The ER effect observed in suspensions of MMT dispersed in polydimethylsiloxane can be attributed to the presence of a considerable number of polar groups at the phase boundary and defects of isomorphic substitution in MMT sheets. Due to its high aspect ratio (approximately 500) and extensive surface area (800-1400 m^2/g), the utilization of montmorillonite as a filler enables the attainment of an ER response at relatively low concentrations (1-8 wt%) of the filler. Moreover, bifunctional QAS-PDMS modifiers promote the formation of a more robust mechanical network of interlocks within the composite.

The objective of this study was to examine the rheological and electrorheological properties of suspensions comprising polydimethylsiloxane (PDMS) and montmorillonite, modified with quaternized PDMS. The concentration of the modified filler was varied from 1 to 8 wt%. Furthermore, small- and wide-angle X-ray diffraction (XRD) patterns were recorded to observe the sample structures. It was demonstrated that in the absence of an electric field effect (EEF), suspensions with a filler concentration of up to 2 wt% exhibited properties consistent with Newtonian fluids. An increase in filler concentration results in the emergence of yield stress, with the magnitude of this stress dependent on the filler concentration. In the presence of an electric field, the ER fluid exhibits plastic behavior. Moreover, the yield stress increases significantly, while the viscosity only shows a slight increase. Furthermore, it was demonstrated that the ER effect in the studied samples only manifests at specific intensities of the applied electric field. The minimum intensity of the electric field at which the ER effect can be observed depends on the concentration of the filler. Conversely, the maximum voltage at which the ER effect vanishes is determined by the value at which electric breakdown occurs (approximately 7 kV/mm). Furthermore, it has been established that the sedimentation stability of the modified montmorillonite suspensions depends on the concentration of the dispersed phase.

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SYNTHESIS OF A BLOCK COPOLYMER FROM LADDER-LIKE POLYPHENYLSILSESQUIOXANE WHICH IS OBTAINED IN AN AMMONIA MEDIUM AND POLYDIMETHYLSILOXANE

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Siloxane block copolymers are unique macromolecules obtained by binding two polysiloxane blocks. One of the main representatives of such compounds is "Blocksil", a copolymer of rigid-chain ladder polyphenylsilsesquioxane (L-PPSQ) and flexible-chain polydimethylsiloxane (PDMS). Such block copolymers can be used as radiation-, thermo- and corrosion-resistant coatings, as the basis of polymer composite materials for various purposes, including adhesives, sealing and filling compositions. However, the main disadvantage of the "Blocksil" type block copolymers is the difficulty of obtaining them, in particular the rigid polyphenylsilsesquioxane block.

Earlier, we demonstrated an effective method for producing L-PPSQ in an ammonia medium. Using this approach, it is possible to obtain polymers with various molecular weight characteristics that are regulated in a wide range.[1]

During this work, a number of L-PPSQ blocks with molecular weights from 10 to 500 kDa was obtained. Based on a low molecular weight block, a block copolymer of L-PPSQ and PDMS was obtained by the hydrosilylation reaction (Fig. 1). A study of the mechanical properties of the sample showed that it has a high deformation value (up to 400%), which significantly exceeds the values characteristic of L-PPSQ.

All the samples synthesized in the work were examined by a complex of physico-chemical analysis methods: IR, NMR spectroscopy, GPC.

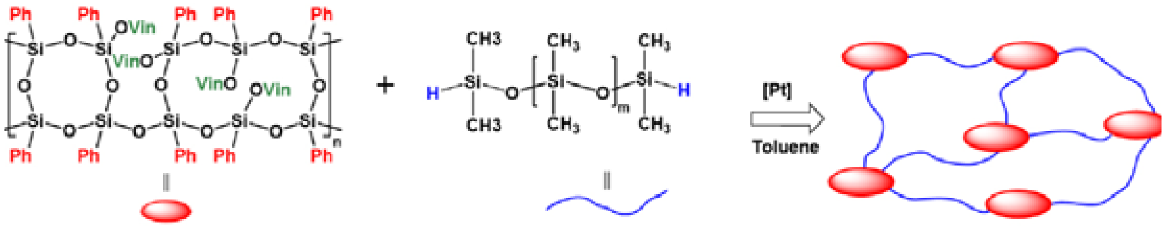

Figure 1. Formation of block-copolymer by hydrosilylation

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NANOPARTICLES BASED ON ALIPHATIC BIODEGRADABLE POLYESTERS FOR DELIVERY OF X-RAY CONTRAST AGENTS

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The development of polymeric micro- and nanoparticles as advanced systems for targeted delivery of drugs and physiologically active substances has garnered increasing attention in recent years. These systems can enhance the bioavailability, solubility and permeability of many hydrophobic drugs. Biodegradable polymers, particularly lactide-based polymers, such as diblock- and triblock-copolymers of lactide with polyethylene oxide, are widely used in the formulation of nanoscale forms of hydrophobic drugs. The degradation properties and rates of these particles can be controlled by varying the molecular weight, enantiomeric composition (i.e., L- and D-lactide content in the polymer chain), copolymerization with other cyclic esters (e.g., glycolide, ε-caprolactone), and modification of terminal groups and post-processing techniques.[1,2]

In medicine, there is a pressing need to develop new agents that provide efficient diagnosis of a wide range of pathological processes in the human body. However, most diagnostic agents exhibit several side effects due to the toxic impact on healthy tissues caused by uncontrolled dosing during prolonged exposure.[3]

The primary goal of this study is the production of polymeric nanoparticles loaded with iodinated ethyl esters of fatty acids synthesized from vegetable oils. This approach opens new possibilities for improving therapeutic strategies for targeted impact on specific tumor cells. These esters represent an oily X-ray contrast agent that is widely used for intravascular administration in the diagnosis and treatment of primary and metastatic tumors of various organs via oily chemoembolization.

In the initial phase of the research, a synthesis method for iodinated esters from vegetable oils, predominantly containing glycerides of linoleic and oleic acids, was developed. The fatty acid composition of the raw material was determined by capillary gas chromatography with mass spectrometric detection, analyzing the resulting volatile ethyl esters of fatty acids. The structure of the synthesized iodinated ethyl esters was characterized using NMR spectroscopy and mass spectrometry with electrospray ionization.

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COLLAGEN-BASED COMPOSITES MODIFIED WITH SILVER NANOPARTICLES AND DIHYDROQUERCETIN: SYNTHESIS AND STRUCTURAL STUDIES

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The development of environmentally friendly methods for obtaining new medical materials based on collagen is an urgent and actively developing area due to collagen biocompatibility and the possibility of modification with active antimicrobial and antioxidant components. Such components may include metal nanoparticles with antibacterial activity and flavonoids with antioxidant properties.

New hybrid materials based on collagen (Coll), collagen-chitosan scaffolds (CollChit) and conjugates of dihydroquercetin (DHQ) with silver nanoparticles (AgNPs) prepared by metal-vapor synthesis (MVS), were obtained.

The materials were characterized by scanning electron microscopy, powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS). An evaluation of the crystallite sizes of Ag by the Sherrer method with PXRD data gives 23 nm for Coll-AgNPs and 12 nm for Coll-AgNPs@DHQ. In contrast to AgNPs with a single Ag^0 state, XPS measurements detected three Ag states in AgNPs@DHQ and Coll-AgNPs@DHQ conjugates.

The AgNPs@DHQ sample showed general cytotoxicity inhibiting the metabolic activity and vitality of both normal and tumor human cell types. The study showed good prospects for the biomedical use of the Coll-AgNPs@DHQ system, which exhibited good biocompatibility, selective antitumour properties and antioxidant activity.

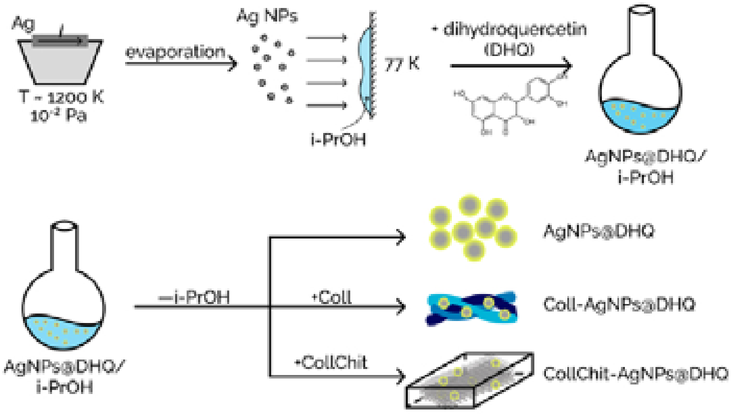

Figure 1. Scheme for obtaining collagen-based composites

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STUDYING ANTI-VIRAL COMPONENTS OF MEDICINAL PLANTS IN SOUTH FERGANA

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Herbal preparations have high potential as possible treatments for viral diseases.[1] The antiviral properties of many plants have been confirmed in modern experiments.[2]

Using HPLC and instrumental neutron activation analysis of the aerial parts *of Matricaria recutita L.*(1), *Taraxacum officinale Wigg. sL*(2), *Cichonum intubus L.* (3) , *Herba Origani vulgaris* (4) , *Tribulus terrestris L.* (5), *Leonurus cardiaca L.* (6) and *Melissa officinalis L.* (7), growing in the Fergana Valley, the amount of chemical components with antiviral activity was studied.

Table 1. Number of antiviral components in the composition plants

Medicinal plants	Concentration substances in plants (in mg/g)				
	Cysteine	Histidine	Vitamin C	Quercetin	Rutin
Tribulus terrestris L.	8.39235	0.083024	7.1	1.51	39.12
Melissa officinalis L.	6.339891	3.431227	28.8	45.50	54.2
Matricaria recutita L.	15.25574	0.680297	54.2	4.65	11.3

Table 2. Amount of microelements in the composition of the parts.

bioelements	Concentration of antiviral components in medicinal plants (in mg/ g)						
	1	2	3	4	5	6	7
Zn	105	51.5	100	47.2	53	50	47.2
Se	0.53	0.3	0.16	<0.01	0.7	0.38	<0.01
Fe	1870	2970	469	324	1500	1500	324
Mg	2360	6210	8850	7640	4850	8830	3660

Based on the studied medicinal plants, a dietary supplement was prepared, used as a means of antiviral and immunomodulatory effects, which included plants containing the optimal amount of antiviral components: due to Se (antioxidant), virus killers are formed in the body, Fe is necessary for immunization cells and Zn counteracts the proliferation of viruses, forming with amino acids (histidine and cysteine) an antiviral protein with zinc fingers (ZAP), which destroys viruses by binding to their RNA in a certain area, also strong antioxidants (Vitamin C , quercetin and vitamin P) enhance the antiviral the activity of the prepared dietary supplement, which makes it promising to use it in the treatment and prevention of viral diseases.

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CISTANCHE MONGOLICA PLANT EXTRACT THE EFFECT OF R. PORSOLT'S METHOD ON THE DURATION OF FORCED SWIMMING OF WHITE MICE

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Fluoxetine Lannaxer (Austria) 20 mg capsule drug was taken as a comparative drug for the experiments. Experiments on the antidepressant activity of fluoxetine in most foreign articles 10; Since it was carried out at doses of 20 and 30 mg/kg, we used the same doses in our experiments. Pharmacological activity of the studied substances was administered 60 minutes before the start of the experiment. In experiments conducted on white mice, Cistanche mongolica plant extract 50; 100 and 200 mg/kg and comparative drug fluoxetine 10; Oral doses of 20 and 30 mg/kg were studied [1,2]. The experiment was studied for 6 minutes. Active and inactive times were calculated in seconds. Indicators of the obtained results are shown in Table 1.

Table 1. Effects of Cistanche mongolica plant extract and comparator fluoxetine on the duration of forced swimming in albino mice

№	Substances and groups	Doses are in mg/kg	A period of mobility	A period of inactivity	The result is in %
1.	Control group		233,2	126,8	
2.	Cistanche mongolica	50	265	95	+25,1
		100	294,6	65,4	+48,4
		200	239,8	120,2	+5,2
3.	Fluoksetin	10	264	96	+24
		20	228,3	131,7	-4
		30	70,5	289,5	-39,2

It is based on experiments that compounds with antidepressant activity, regardless of the mechanism of action, prolong the active period and shorten the inactive (immobilization) period. These experiments are a pre-clinical specific method of determining antidepressant activity. Therefore, this method is widely used to determine the presence or absence of primary antidepressant activity.

Based on the obtained results, Cistanche mongolica plant extract demonstrated antidepressant activity at all studied doses, especially 100 mg/kg fluoxetine showed 2-fold higher activity compared to 10 mg/kg fluoxetine.

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SYNTHESIS OF BENZIMIDAZOLE- AND BENZOTRIAZOLE-CONTAINING SILSESQUIOXANES BASED ON (BENZAZOLYL) TRIMETHOXYSILANES

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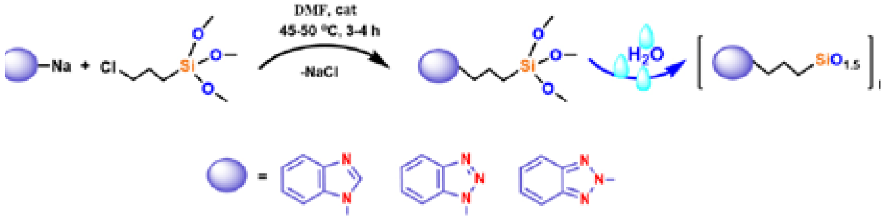
Silsesquioxanes are a promising and unique class of silicon compounds that occupy a significant niche in polymer chemistry. Silsesquioxanes exhibit properties of both inorganic and organic compounds – thermal and chemical stability due to the high energy of inorganic siloxane bonds of the main chains compared to carbon-carbon bonds in organic compounds, excellent compatibility with organic materials, and multifunctionality due to a variety of organic side chains. Materials based on them are of great interest and have a wide range of applications, for example, as protective coatings, insulating layers, precursors for the production of ceramics, optical materials, proton-conducting membranes, etc.[1] Therefore, the search for new monomers and polymer structures based on them with valuable properties remains an urgent task in the chemistry of organosilicon compounds.

We obtained soluble silsesquioxane derivatives of benzimidazole and benzotriazole by the hydrolytic polycondensation reaction of the corresponding trifunctional methoxysilanes using deionized water in the absence of acidic or basic catalysts (Scheme 1). The monomers were synthesized by the nucleophilic substitution reaction of the halogen atom in (chloralkyl)trimethoxysilanes with the *N*-sodium derivative of the corresponding benzannelated azole. As a result, 1-[3-(trimethoxysilyl)propyl]-1*H*-benzimidazole was obtained for the first time and two isomers, 1-[3-(trimethoxysilyl)propyl]-1*H*– and 2-[3-(trimethoxysilyl) propyl]-2*H*-1,2,3-benzotriazoles, which have a benzenoid and quinoid form, respectively, were isolated. The composition and structure of the synthesized compounds were confirmed by elemental analysis data and a set of physico-chemical research methods (IR and ^{1}H, ^{13}C, ^{29}Si, 15N NMR spectroscopy, mass spectrometry, X-ray diffraction, GPC, TGA and DSC).



Scheme 1. Synthesis of functional (benzazolylpropyl)trimethoxysilanes and silsesquioxanes based on them

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THE EFFECT OF ZINC PHOSPHATE ON THE FORMATION OF COATINGS FROM POLYVINYL ACETATE DISPERSION

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Due to the stricter environmental requirements, organo-diluted paint and varnish materials are being replaced with water-dispersion. But materials with the use of toxic solvents still have high anticorrosive protection. At the same time, effective anticorrosive materials contain toxic chromates in their composition, which negatively affect human health and the environment. The development of an aqueous dispersion material with a non-toxic anticorrosive agent could solve the entire range of problems that arise. As a result, the aim of the research is to develop a technology and formulation for the production of anticorrosive water-dispersion materials with non-toxic pigments.

The objects of the study are the aqueous dispersion of polyvinyl acetate (PVA) and zinc phosphate.

To evaluate the effect of zinc phosphate on the aggregate stability and properties of coatings formed from PVA dispersion, studies of the surface energy of the coatings obtained were carried out.[1] PVA dispersion was combined with an aqueous extract of zinc phosphate. The coatings were obtained at different exposure times of the obtained systems. It is shown that there is a change in surface energy due to an increase in the polar component during 10 days of exposure, which indicates a redistribution of surfactants (surfactants) in the system that stabilize the dispersion.[2] Microscopic studies confirm the presence of larger aggregates in the system at a given exposure time. Thus, the influence of zinc phosphate on the properties of the obtained aqueous dispersion materials is shown, which must be taken into account when developing them.

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INFLUENCE OF DIETHYL ZINC ON ETHYLENE POLYMERIZATION CATALYZED BY ALPHA-DIIMINE NICKEL COMPLEXES

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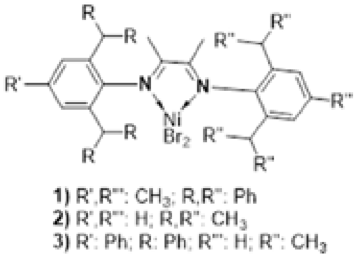
Nickel(II) complexes have long been known as catalysts that enable the direct production of branched polyethylene from ethylene. Due to the "chain walking" mechanism, it is possible to create polyethylenes with varying degrees of branching by adjusting the ligand environment and reaction conditions. Most studies in this field focus on identifying the relationships between the complex structure and the properties of the resulting polyethylene, while the effect of various additives on the ethylene polymerization process is usually underexplored and is primarily limited to phosphine derivatives. To fill this gap, we have attempted to study the influence of diethylzinc as an additive to catalytic systems based on well-studied nickel precatalysts with α-diimine ligands, first synthesized by Brookhart[1].

Diethylzinc has previously been mentioned in the literature as a chain transfer agent used in dual-catalyst systems, where one catalyst generates linear polyethylene, and the other produces branched polyethylene, leading to the formation of bimodal polyethylene[2,3]. However, its effects as an additive to an individual catalyst have been explored only superficially. In our study, we demonstrated that the properties of polyethylene produced by the nickel complex with high steric bulk (complex 1) are only slightly affected by the presence of diethylzinc in the catalytic system. However, as the steric bulk of the ligand decreases in complexes 2 and 3, the presence of 150 equivalents of diethylzinc results in the production of more amorphous polyethylene, with nearly complete disappearance of crystalline structures in the case of complex 3 (enthalpy of melting -2 J/g). The influence on catalyst activity was also observed to be positive, with an increase of up to 25% for all precatalysts.



1) R',R''': CH_3; R,R'': Ph
2) R',R''': H; R,R'': CH_3
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Figure 1. Alpha-diimine nickel complexes were used for tests

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HYBRID COMPOSITES BASED ON CHITOSAN MODIFIED BY CONJUGATES OF Ag AND Cu NANOPARTICLES WITH DIHYDROQUERCETIN

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The creation of hybrid materials based on natural polymers with metal nanoparticles providing a prolonged anti-inflammatory effect is an urgent problem of tissue engineering[1]. Metal nanoparticles have antibacterial activity, while flavonoids are characterized by antioxidant activity. The combination of these components with biocompatible polymers can lead to the production of biologically active materials effective for medical use.

The method of metal-vapor synthesis (MVS) is effective for obtaining biologically active metal nanoparticles and their oxides[2]. For the first time, chitosan-based composites containing conjugates of silver/copper nanoparticles with dihydroquercetin were synthesized using the MVS method.

The analysis of the surface of materials by X-ray photoelectron spectroscopy showed that copper systems contain two oxidized metal states Cu^{+} and Cu^{2+}. For a silver-containing composite, it is determined that metal nanoparticles are in the Ag^{0} and Ag^{+} states.

Conjugates of metal nanoparticles with dihydroquercetin have demonstrated activity against gram-positive and gram-negative microorganisms. They have shown high efficacy and selectivity against tumor cells, which makes them promising components in the creation of new generation medical supplies.

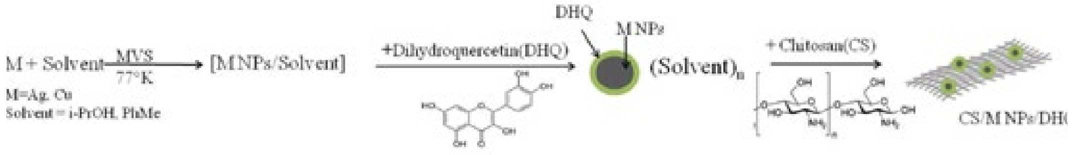

Figure 1. Scheme for obtaining chitosan-based materials with conjugates of Ag and Cu nanoparticles and dihydroquercetin

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SYNTHESIS AND RESEARCH OF TARGETED DRUG DELIVERY SYSTEMS BASED ON NANOPARTICLES AU AND FEOX

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Chemotherapy, one of the main methods of treatment in oncology, has a number of limitations associated with undesirable side effects. Metal nanoparticles are very effective in cancer therapy, providing specific selectivity in influencing cells and being a means of drug delivery. Conjugation of chemotherapeutic agents with metal nanoparticles can provide significant benefits in cancer therapy.[1]

The method of metal-vapor synthesis (MVS) was used to create targeted drug delivery systems based on mono- and bimetallic nanoparticles Au, Fe and AuFe, as well as their conjugates with methotrexate. In the case of MVS of Fe nanoparticles, the use of toluene as an organic reagent led to a partial reduction of iron to FeO, and acetone to oxidation to Fe^{3+}. During the interaction of AuFe bimetal nanoparticles obtained in toluene with methotrexate, the Au^0 states are recorded. In the conjugate of methotrexate with AuFe obtained in acetone, the presence of Au^+ and Au^{3+} states is observed.

The study of antibacterial activity showed moderate inhibitory activity of conjugates against gram-negative and gram-positive bacteria. Monometallic conjugates exhibit cancer-specific cytotoxicity by affecting the functionality of lysosomes in lung cancer cells. Bimetal conjugates in low concentrations have a high inhibitory potential for lung adenocarcinoma, cervical and colorectal adenocarcinoma cells, and their use has virtually no effect on normal fibroblasts .

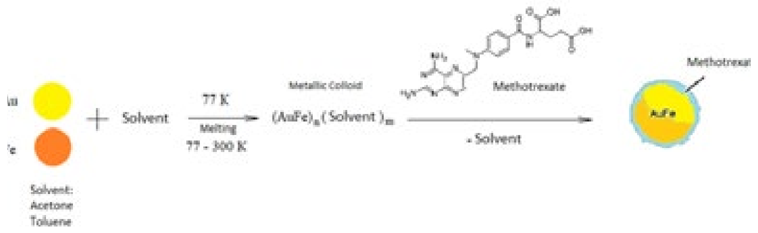

Figure 1. The general principle of obtaining nanocomposite materials using the method of metal-vapor synthesis

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POLYAMIDE-IMIDES AS NOVEL HIGH PERFORMANCE PRIMARY PROTECTIVE COATINGS OF SILICA OPTICAL FIBERS

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Novel thermostable primary protective coatings with high operational reliability have successfully been developed on the basis of polyamide-imides (PAIs). PAIs with different chain rigidity and molecular weight were synthesized by low temperature polycondensation of various tetracarboxylic acid dianhydrides and terephthaloyl chloride with 9,9-bis(4-aminophenyl)fluorene or 2,2-bis(trifluoromethyl)benzidine in NMP. The effect of temperature, the order and duration of the interaction of reagents on the yield, molecular weight and properties of the resulting polymers has been studied.[1] A synthetic approach yielding high-molecular-weight PAIs (Mw = 84–365 kDa, η_{inh} = 0.6–2.6 dL/g) in contrast to the conventionally utilized methods has been developed. All synthesized polymers exhibited high heat resistance (Tg = 260–360 °C), thermal-oxidative stability (T10% ~500 °C) and formed quite tough films (σ =100–190 MPa, E = 0.9–4.2 GPa, ε = 9–30%).[2]

Coatings with good adhesion to silica optical fiber and a desired thickness of ~10 μm were produced from a solution in NMP without the traditional use of a coupling agent in one deposition cycle (Figure 1). It was established that the structure and molecular weight of PAI, as well as the deformability of film therefrom, are crucial for obtaining tough durable coatings. The best results were obtained for optical fibers protected by highly elastic PAIs (elongation at break ~16–30%, Mw ~ 200 kDa) based on 2,2-bis(trifluoromethyl)benzidine. The optical fibers with such coatings can withstand 300 or 350 °C for 72 and 3 h accordingly retaining >80% of the original bend strength, which is a warranty for stable fiber life for a long time.[2]

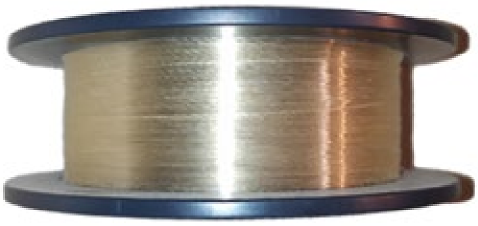

Figure 1. The ready-made silica optical fiber on a reel

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THERMALLY STABLE POLYMER MATERIALS BASED ON THE TANDEM DIELS-ALDER REACTION

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The Diels-Alder reaction (DA) is a versatile cornerstone in organic chemistry, facilitating the construction of intricate structures. This reaction allows for a substantial elaboration of compounds in one "click”, providing the ability to revert to the original reagents if needed.[1] Reversible DA (rDA) reaction is commonly used to develop of self-healing materials. Despite the vast potential of the rDA reaction, there are several drawbacks. Self-healing materials derived from the DA reaction between furan and maleimide derivatives typically undergo cleavage at temperatures ranging from 120-140°C and healing between r.t. and 60-80°C.[2] In addition, at temperatures above 70°C, the rate constant for the reverse DA reaction increases, and the equilibrium shifts towards the starting furan and maleimide, hindering achieving high conversion in polymerization. All of these features may impose limitations on the broader applications of such materials. At the same time, the DA reaction is an attractive strategy for modern organic synthesis which aligns with the principles of atom-economy and green chemistry.

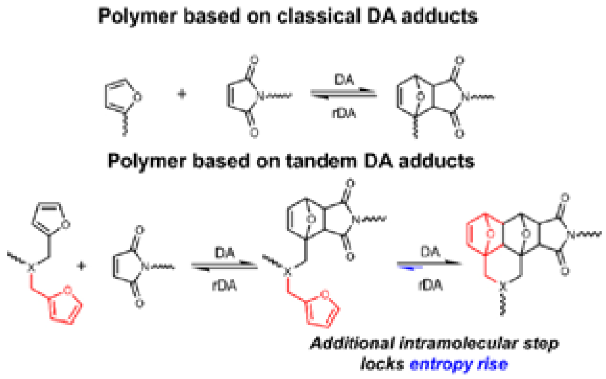

Figure 1. Types of polymer materials based on the Diels-Alder reaction.

This work aimed to develop a new synthetic approach that would allow us to achieve a high conversion in polymerization by the DA reaction and at the same time significantly increase the depolymerization temperature of such materials. Using relatively simple thermodynamic explanations, supported by quantum chemical calculations and experimental data, we have shown that it is possible to obtain thermally stable polymer materials based on the tandem DA reaction.

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COMPOSITE BIODEGRADABLE NANOPARTICLES BASED ON LACTIDE POLYMERS FOR DRUG DELIVERY

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Amphiphilic PDLA-PEG block copolymers can self-assemble into biocompatible nanoparticles of 10 to 300 nm, making them promising carriers for drug delivery, particularly for anticancer agents due to their enzymatic and hydrolytic degradation properties[1]. We propose that co-assembly of polylactide and PDLA-PEG to create composite nanoparticles offers a flexible and straightforward method for modifying particles with fluorescent dyes or radionuclides for diagnostics, imaging, and therapy. An example of this method for introduction of IR780 dye in PDLA-PEG was described earlier[2]. This study aimed to investigate how the addition of polylactide affects the characteristics of mixed nanoparticles based on amphiphilic polylactide-b-polyethylene glycol ($P(D,L)LA_{17}$-*b*-PEG_{113}).

For preparation of the composite nanoparticles block copolymer $P(D,L)LA_{17}$-*b*-PEG_{113} and $P(D,L)LA_{94}$ homopolymer were synthesized. Aqueous suspensions were obtained by nanoprecipitation technique using acetone:water = 1:1 volume ratio. The weight ratio of $P(D,L)LA_{17}$-*b*-PEG_{113} to $P(D,L)LA_{94}$ was varied from 1:2 to 100:1. Size distribution of the nanoparticles was studied by dynamic light scattering (DLS). The morphology and chemical composition of particles was assessed by electron microscopy and NMR spectroscopy, correspondingly.

According to the DLS data the $P(D,L)LA_{17}$-*b*-PEG_{113} without the addition of $P(D,L)LA_{94}$ forms two fractions of particles with hydrodynamic diameters (D_h) of 24 and 250 nm. Using TEM it was found that narrowly dispersed particles of 7-10 nm in size with spherical morphology are predominant. When $P(D,L)LA_{94}$ is added to $P(D,L)LA_{17}$-*b*-PEG_{113} in a 1:1 ratio, also two fractions are formed, but with higher diameters of 106 and 825 nm. The SEM analysis showed that the particles have a spherical morphology and rather wide size distribution (500-1500 nm). An increase in the ratio of $P(D,L)LA_{94}$ to $P(D,L)LA_{17}$-*b*-PEG_{113} to 2:1 leads to a decrease in sized of particles in both fractions to 68 and 531 nm compared to the ratio of 1:1, as well as the disappearance of the fraction with Dh 825 nm. With a decrease in the ratio of $P(D,L)LA_{94}$ to 1:10 or less, the D_h of the obtained particles exceeds 500 nm, and aqueous suspensions are characterized by low stability. NMR analysis showed that the fraction of particles with sizes of 500 nm and larger consists mainly of polylactide, while $P(D,L)LA_{17}$-*b*-PEG_{113} acts as a stabilizer. Further research will be focused on finding the optimal ratio and process conditions for reproducible production of composite particles with predetermined sized and morphology.

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ROTATIONAL DIFFUSION OF $Sc_2@C_{80}CH_2Ph$ STUDIED BY EPR SPECTROSCOPY

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A dilute solution of scandium dimethallofullerene in toluene was studied by continuous wave (CW) and pulsed EPR methods over a wide temperature range [1-3]. The endofullerene $Sc_2@C_{80}(CH_2Ph)$ has a single unpaired electron delocalized between two scandium ions. The strong hyperfine interaction (HFI) of the electron spin (S=1/2) and the two equivalent nuclear spins ($I_{Sc}=7/2$) of the scandium ions provides 64 well resolved EPR transitions. Each of these lines is characterized by its own parameters related to the state of the total spin of the magnetic nuclei (I=0,1,..7) and its projection.

In the liquid phase, CW EPR studies show that the lines in the EPR spectrum differ in amplitude and width due to the wide distribution of the resonance fields and the strong HFI. It has been shown that the width (and amplitude) of the EPR lines has a non-linear dependence on the ratio of the HFI (510 MHz) and the Zeeman interaction (9.8 GHz). Low temperature (20-120K) measurements were performed using the spin-echo method. It is found that the phase relaxation depends on the total spin state I of the scandium nuclei. The obtained results are rationalized as the effect of rotational diffusion of the fullerene (in liquid phase) and of the endohedral fragment inside the fullerene framework (in both phases, liquid and frozen solvent).

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EMBEDDING OF MANGANESE OXIDES INTO SUBSTRATES OF COMPLEX MORPHOLOGY USING A CARBONYL PRECURSOR

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The work proposes a method for impregnating manganese oxides into a substrate of complex morphology in a single-stage synthesis. Carbon aerogel was chosen as a model substrate of complex morphology. Aerogels are a class of materials with unique properties, the main ones being low density, high porosity and high specific surface area. Aerogels can be used as thermal insulation materials, adsorbents, filters, chemical and electrochemical catalysts. Of particular interest are aerogels containing metals or metal oxides, due to the possibility of their use in catalytic and filtration processes.

The problem of introducing the oxide phase into the complex morphology of carbon aerogel is a complex task. It is known that it is possible to obtain a composite carbon aerogel containing metal oxide nanoparticles using a method in which carbon aerogel is immersed in a metal oxide sol, after which a sol-gel process is carried out to form a metal oxide in the pores of the carbon aerogel. However, the presence of a liquid solvent results in non-uniform deposition of the precursor due to capillary effects. A solution may be the use of a supercritical fluid as a solvent. In such a medium, uniform precipitation of the precursor is possible throughout the depth of the carbon aerogel.

In this work, such an approach, that allows the introduction of nanosized, highly dispersed manganese oxide particles into carbon aerogels using the thermal-oxidative decomposition of $Mn_2(CO)_{10}$ dissolved in supercritical CO_2 was demonstrated.[1] It is shown that the proposed procedure preserves the branched porous structure of the material with a high specific surface area of more than 600 m^2/g. The resulting composite aerogels contain 4–16 wt. % manganese.

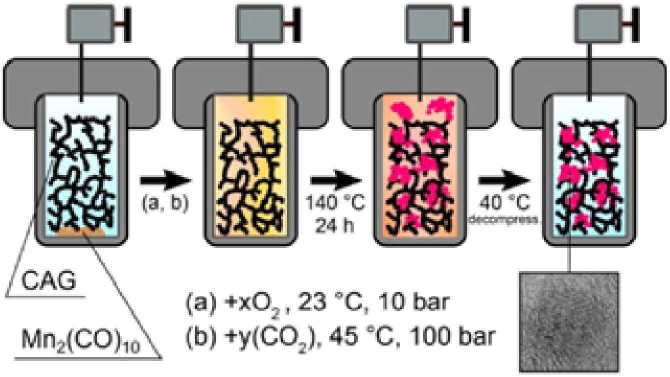

Figure 1. Schematic representation of the experiment

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INFLUENCE OF GRAPHENE OXIDE NANOSTRUCTURE ON ULTRAFAST WATER DIFFUSION: ATOMISTIC SIMULATION

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Graphene oxide (GO) is promising membrane material due to its high water permeability[1]. However, the exact physical mechanisms, governing this process at the molecular level, remain poorly understood. We use classical molecular dynamics with the reactive potential ReaxFF to study the mobility of water molecules intercalated in GO and analyze the influence of its structure on diffusion processes.

We show, that in the presence of pristine of graphene channels[2] within GO the water transport is particularly active along the interface between oxidized and pristine regions. Water diffusion involves random "jumps" along this interface over distances of 1-2 nm. Remarkable, diffusion along these interfaces is not significantly affected by the level of oxidation or interlayer distance, but it requires heterogeneity in the distribution of oxygen groups.

While previous computational studies primarily focused on diffusion within either graphenic or oxidized regions, our findings underscore the critical role of the boundary between these regions. Diffusion along such boundaries represents a previously unreported mechanism, that may provide a plausible explanation for the high water mobility observed in GO.

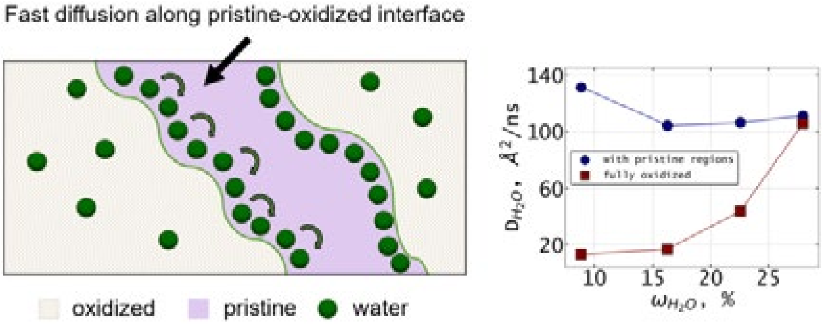

Figure 1. a) Water diffusion scheme between oxidized and pristine graphene.
б) Water diffusion coefficient for total mass fraction in: heterogeneously oxidized GO (dark-blue line) and homogeneously oxidized GO (red line).

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Acknowlegments
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PROPERTIES OF COMPOSITES BASED ON POLYPHENYLENE SULFIDE AND LONG GLASS FIBERS

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Polyphenylene sulfide (PPS) is a thermoplastic semi-crystalline polymer used as a matrix for composites in aerospace applications and is also known as an engineering superconstruction polymer with good thermal stability, high mechanical properties, excellent chemical resistance and is not affected by moisture.[1]

Glass-filled composites are widely used as construction materials, and in the case of superconstruction polymers with the highest strength and thermal stability characteristics, exceptional materials are possible for the most demanding applications in aerospace, electrical and other fields. The fibers most commonly used are cut short glass fibers. Such fibers simplify material processing and facilitate the production of composites based on them in extrusion and injection moulding, but they have reduced mechanical strength characteristics compared to long glass fiber thermoplastics (LGFT).

In this work, composites based on polyphenylene sulfide and long glass fibers were obtained by extrusion method. Continuous glass fiber in the form of roving was used as glass fiber. The roving was fed into the extruder and cut by screws during the extrusion process, thereby obtaining composite pellets with elongated fibers. From the obtained pellets, standard samples were made for mechanical testing by injection moulding. Long glass fiber thermoplastics (LGFT) showed improved mechanical performance compared to short glass fiber composites.

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CO_2 HYDROGENATION REACTION ON CATALYSTS BASED ON DOUBLE COMPLEX FE-CO SALTS

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In recent decades, there has been an urgent need to reduce greenhouse gas emissions into the atmosphere. Since the 2000s, the focus of research has shifted to the chemical use of CO_2 to create valuable products, as it is a widely distributed, non-toxic and renewable raw material. An effective way of CO_2 use is to hydrogenate it to hydrocarbons and, in particular, methane. Methane obtained by hydrogenation of emitted CO_2 can be returned to industrial processesas fuel, thereby CO_2 can be involved in a closed production cycle, eliminating its emissions into the atmosphere.

Fe and Co, as well as bimetallic Fe-Co samples, are usually used as catalysts for the CO_2 hydrogenation process. The method for producing a bimetallic catalyst should ensure the synergy of the active phases[1]. In works[2,3], the synergy of Fe and Co in the composition of active centers was achieved by the formation of the active phase by thermolysis of double complex salts of iron and cobalt. The new catalyst was obtained by thermolysis of $[Co(NH_3)_6]_4[Fe(CN)_6]_3$, optimized for CH_4 formation by enriching of Co:Fe ratio, was prepared by the same technique, presented in works[2,3].

Dependence between CO_2 conversion and CH_4 selectivity for catalysts, designed for C_{5+} hydrocarbons (C_{5+} Cat.) and CH_4 (CH_4 Cat.) producing in CO_2 hydrogenation process presented on fig. 1. Selectivity to CH_4 values for CH_4 Cat., were 3 and more times higher against data for C5+ Cat.at the same CO_2 conversion.

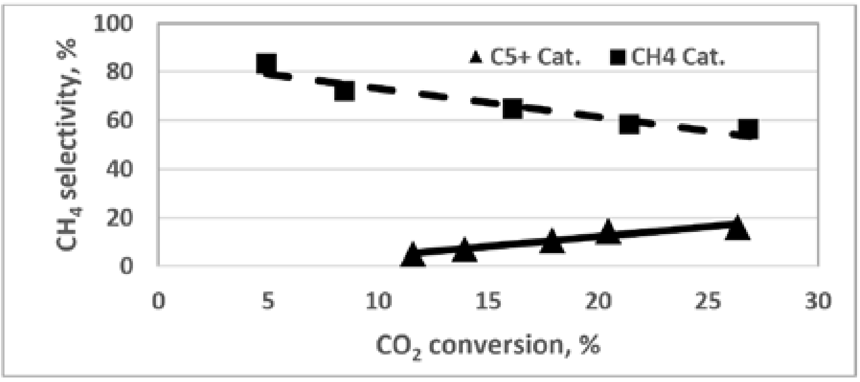

Figure 1. Dependence between CO_2 conversion and CH4 selectivity for catalysts, designed for C_{5+} hydrocarbons (C_{5+} Cat.) and CH_4 (CH_4 Cat) producing in CO_2 hydrogenation process

So it was shown, that the developed technique for catalyst preparation was flexible and can be used for catalysts, selective to different products.

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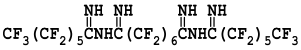
Acknowledgements
The work was carried out with the financialsupport of the RussianScienceFoundation No.24-29-20076.

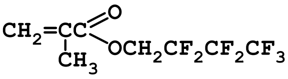
INVEST



$$CF_3(CF_2)_5\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}(CF_2)_6\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}(CF_2)_5CF_3$$

2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoro-N1,N8-bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-iminoheptyl)octanediimidamide

[1001651-40-6]



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}C({=}O)OCH_2CF_2CF_2CF_3$$

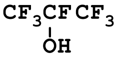
2,2,3,3,4,4,4-Heptafluorobutyl methacrylate

[13695-31-3]

$CF_2{=}CFCF_2OSO_2F$

Pentafluoroallyl fluorosulfate

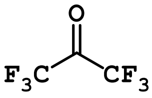
[67641-28-5]



$$CF_3\underset{OH}{\underset{|}{C}F}CF_3$$

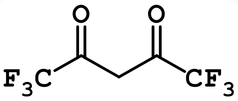
Hexafluoroisopropanol

[920-66-1]



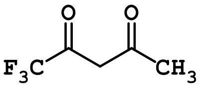
Hexafluoroacetone

[684-16-2]



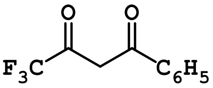
1,1,1,5,5,5-Hexafluoroacetylacetone

[1522-22-1]



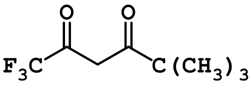
1,1,1-Trifluoroacetylacetone

[367-57-7]



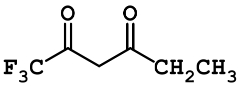
1-Phenyl-4,4,4-trifluorobutane-1,3-dione

[326-06-7]



1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione

[22767-90-4]



1,1,1-Trifluorohexan-2,4-dione

[400-54-4]

CF_3I

Iodotrifluoromethane

[2314-97-8]

CF_3CF_2I

Iodopentafluoroethane

[354-64-3]

$CF_3CF_2CF_2I$

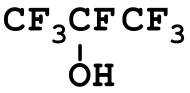
Heptafluoro-1-iodopropane

[754-34-7]

CF_3CFICF_3

Heptafluoro-2-iodopropane

[677-69-0]



$$CF_3\underset{OH}{\underset{|}{C}F}CF_3$$

Hexafluoroisopropanol

[920-66-1]

$CF_3CF_2CH_2CH_2CH_2OH$

4,4,5,5,5-Pentafluoropentan-1-ol

[148043-73-6]

$CF_3CF_2CH_2CH_2CH_2SH$

4,4,5,5,5-Pentafluoropentan-1-thiol

[148757-88-4]

$CF_3Si(CH_3)_3$

Trimethyl(trifluoromethyl)silane

[81290-20-2]

$HCF_2Si(CH_3)_3$

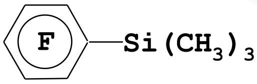
Trimethyl(difluoromethyl)silane

[65864-64-4]

$CF_2{=}CFOCF_2CF_2Br$

2-Bromotetrafluoroethyl trifluorovinyl ether

[85737-06-0]



Trimethyl(pentafluorophenyl)silane

[206-46-8]

$CF_2{=}CFOCF_2CF_2SO_2F$

Perfluoro(3-oxapent-4-ene)sulfonyl fluoride

[29514-94-1]

$BrCF_2Si(CH_3)_3$

Trimethyl(bromodifluoromethyl)silane

[115262-01-6]

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