NEW TRENDS
IN
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Yerevan, Armenia
September 24-28, 2023

NEW EMERGING TRENDS IN CHEMISTRY CONFERENCE
(NEWTRENDSCHEM-2023)

BOOK OF ABSTRACTS

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BOOK OF ABSTRACTS

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ENERGY OF CHEMICAL BONDS AS A DRIVING FORCE FOR ORGANIC REACTIONS: MOLECULAR SPRINGS, STEREOELECTRONIC FRUSTRATION, AND ELECTRON UPCONVERSION

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Molecules store energy and, as bonds are formed and broken, every chemical process can either store or release energy. This talk will discuss practical ways for incorporating this common knowledge into reaction design and in searching for new physical phenomena.

After outlining the interplay of kinetics with thermodynamics and the special role of weak bonds in catalysis, I will discuss how much energy can one store in common functional groups, introduce the familiar textbook functionalities that accumulate more energy than an excited state, and show how O-O bonds can rival C-C bonds as building block for creating complex polycyclic organic molecules.

I will show that the key to controlling the flow of energy in chemical reactions is in using unique stereoelectronic features of each functionality and in coupling unfavorable and favorable elementary steps in a chain of chemical transformations.

In the final part, I will introduce the phenomenon of electron upconversion, a counterintuitive way to transform weak reductants into strong reductants in a thermodynamically favorable fashion. Such processes enable electrocatalytic transformations where a single electron can drive multiple catalytic cycles.

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ARTIFICIAL INTELLIGENCE AND DIGITAL DESIGN IN CHEMISTRY: AT THE FRONTIER OF CHEMISTRY 2.0

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The rapid increase in the volume of accumulated experimental data, the complexity of correlating phenomena at the molecular and nanoscale levels, and the need for a qualitatively new leap in the development of new chemical technologies lead to the active introduction of artificial intelligence algorithms and digital design techniques in chemical research. Using specific chemical problems as examples, this report discusses current challenges focused on organic synthesis and dealing with the development of practical applications of AI algorithms for the creation of highly active catalysts [1,2], the analysis of spectral data [3], and digital optimization of experiments in organic synthesis [4] and catalysis [5].

Acknowledgment. This research was supported by the Russian Science Foundation, grant 22-13-00247.

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FATE OF A MOLECULE: FROM LABORATORY TO BEDSIDE

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Our research program has taken us from attempts to understand fundamental chemical reactivity to applying the insights we gained to biomedical research.

Our ability to construct new molecular architectures with desired properties depends on the efficient methods for controlled and selective formation of new chemical bonds in complex environments. Chemical transformations that reliably introduce and transform various functional groups are required for the synthesis of materials ranging from small molecule therapeutics to macromolecular multifunctional biomedical imaging and drug delivery systems. Catalytic reactions offer unprecedented potential for achieving these goals. Our studies of new reactivity, the insights into the mechanism and catalyst behavior, and the resulting applications to drug discovery, cellular and tissue imaging, and targeted therapeutics will be highlighted in the presentation.

DEVELOPMENT OF NOVEL C–H FUNCTIONALIZATION METHODOLOGIES

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We have developed a set of new transition metal-catalyzed C-H functionalization methodologies employing various tether strategies. These methods feature: (a) use of silyl group as a tether between a substrate and a reagent, thus transforming intermolecular reaction into an intramolecular reaction; (b) employment of a silicon-tethered directing group, which is traceless or easily convertible into valuable functionalities; (c) use of reactive silyl-tethered hydrosilane group; and (d) introduction of new N/Si-chelation concept that allows for a remote activation of aliphatic C-H bonds.

We uncovered new reactivity of hybrid Pd-radical species, generated at room temperature under visible light without use of exogenous photosensitizers. This led to the development of novel transformations, including new types of Heck reaction, aliphatic C–H functionalization methods, as well as new cascade transformations. A set of both directed and direct functionalization methods have been developed.

The scope of these transformations will be demonstrated and the mechanisms will be discussed.

CREATION OF GEOCHEMICAL BARRIER SYSTEMS AT HAZARDOUS AND RADIOACTIVE WASTE DISPOSAL SITES - WHAT GIVES CHEMISTRY?

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The most important practical task is the development of effective methods of toxic industrial and radioactive waste management, as well as rehabilitation of previously contaminated territories and decommissioning of objects of accumulated environmental damage. The solution of these tasks is impossible without creation of disposal facilities for such wastes and realization of the concept of on-site disposal during decommissioning of objects of accumulated environmental harm. In this regard, the important role in ensuring the long-term safety of such facilities with the use of special clay materials for the creation and restoration of engineering barriers has become obvious. To assess the ability of various clays to retain toxic components, information is needed on the mechanisms of chemical reactions at the mineral/water interface occurring in a wide range of geochemical conditions, the influence of crystalline structures of the clay mineral on filtration and migration properties and the speciation of toxic components. The complexity of studying such systems is caused, among other things, by the heterogeneity and complexity of the composition of both natural clays and aqueous solution. The paper considers the regularities of sorption of various metal cations (including radionuclides), characterized by high migration ability and toxicity, on promising materials of safety barriers - bentonite clays and kaolinite from industrial deposits of Russia and CIS, as well as their mixtures.

The main factors determining sorption such as structure of the main clay mineral (1:1 or 2:1), presence of impurity minerals (illite, iron oxides), solid:liquid ratio and solution composition on sorption were considered and summarized. An increase in the concentration of Ca^{2+}, Mg^{2+}, Al^{3+} cations in solution during interaction with clay samples was found to have a significant effect on the binding of metal cations.

It is shown that the behavior of ^{137}Cs(I) is significantly determined by the structure and charge distribution over the aluminosilicate layers of the sample and is strongly reduced in the presence of competing cations in solution. The sorption of ^{237}Np(V) is weakly dependent on the clay structure, but the presence of iron oxyhydroxide impurities is of great importance on the sorption. The sorption mechanism of Eu(III) is strongly dependent on the ionic strength of the solution, and at high ionic strength (above 0.1M) iron oxide impurities and clay mineral structure have a significant effect on the binding. In the case of U(VI) sorption, no significant difference was found between the studied samples, the composition and pH of the solution having a greater influence. Thermodynamic modeling of the sorption of Cs(I), Eu(III), Np(V), U(VI) on clays in a wide range of experimental conditions has been carried out. The proposed approach can be applied for predictive modeling of radionuclide migration in contaminated areas.

Necessary and sufficient characteristics of barrier clay materials (24 characteristics in total), which are required to be taken into account when designing geochemical barriers based on clays, were formulated. Based on this, a database of promising barrier materials was compiled.

ADVANCES AND APPLICATIONS OF INFRARED SPECTROSCOPIC IMAGING

Kazarian S.G.

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FTIR spectroscopy combined with the imaging capability of infrared array detectors provides a powerful tool to obtain both chemical and spatial information about the sample. The use of micro ATR approach to acquire FTIR spectra offers an increased numerical aperture due to the high refractive index of the ATR crystal. This leads to significantly improved spatial resolution being achieved with ATR-FTIR imaging compared to imaging in transmission or reflection modes. The improved spatial resolution allows one to obtain chemical images of many samples without recourse to a synchrotron source of infrared radiation.[1] This makes enhanced chemical imaging previously hampered by the inadequate spatial resolution, possible for many samples.[2] We have demonstrated applications of micro ATR-FTIR imaging to polymer blends, biomaterials, including biopsies, pharmaceuticals, hair and artwork.[3,4]

This talk will demonstrate new opportunities and applications of ATR-FTIR imaging with macro ATR approaches. For example, we developed ATR-FTIR imaging into a powerful analytical tool for analysis of materials and biomedical samples, and for studies of dynamic systems, such as tablet dissolution and drug release. Other new opportunities using this approach include imaging of medical and forensic samples, biomaterials, ionic liquids, high-throughput analysis, stone conservation.[5] It is particularly suited to studying microfluidics due to its high chemical specificity and ability to study dynamic systems. Microfluidics facilitate a high degree of control of chemical reactions with only small quantities of reagents. ATR-FTIR spectroscopic imaging was used to investigate secondary structure of model proteins under freeze thaw cycling stress conditions, which can lead to a substantial loss of product, and contributes to the high cost of antibody production. This research also aims to demonstrate the suitability of FTIR spectroscopic imaging for biopharmaceutical process monitoring.

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IMPROVING ORGANIC SYNTHESIS WITH PHOTOCHEMISTRY

König B.

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Light is an ideal reagent for organic synthesis. It provides energy to overcome activation barriers of reactions or even enable endothermic transformations. Photons can be used in large excess to drive a reaction to completion, but they will leave no trace. And visible or UV-A light is safe and non-toxic and easy generated with modern light sources, such as LEDs. The last two decades have seen the development of many synthetic methods that use sensitized or direct photochemistry to enable organic reactions at milder conditions, typically close to room temperature, but also open new reaction pathways which are impossible in thermal chemistry.[1] In this lecture we will focus on organic reactions that can only be performed photochemically, which produce products that are higher in energy than the starting materials or enable reaction with better predictability and overall efficiency.

The first class of reactions we discuss are redox-neutral reactions that need light energy input to proceed. The ideal atom economy of the reactions and excellent energy efficiency make such transformations ideal candidates for the preparation of chemicals on larger scale.[2] Dehydrogenative coupling reactions,[3] synthesis of alkenes from alkanes under dihydrogen evolution[4],[5] and the insertion of carbon dioxide into aliphatic [6] or aromatic [7] carbon-hydrogen bonds are examples of such reactions that will be presented.

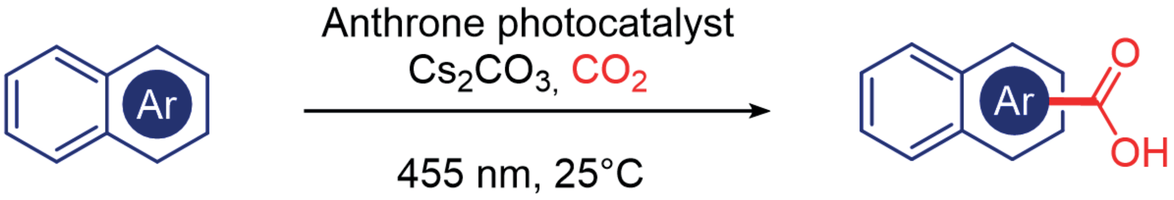

Figure 1. Redox-neutral C-H carboxylation [7].

A second class of reactions we will discuss are photochemical carbonyl Umpolung reactions, which enrich and extend the synthetic toolbox of carbonyl chemistry.[8], [9]

Cross-coupling reactions belong to the most important reactions in organic synthesis in industry and academia. We will discuss, how photochemistry can improve the performance of this reaction class. The new concept of adaptive dynamic homogenous catalysis (AD-HoC) uses light to control the redox state of catalytically active species, which allows the very fast and predictable cross-coupling of all classes of nucleophiles with halogenated arenes and heteroarenes.[10]

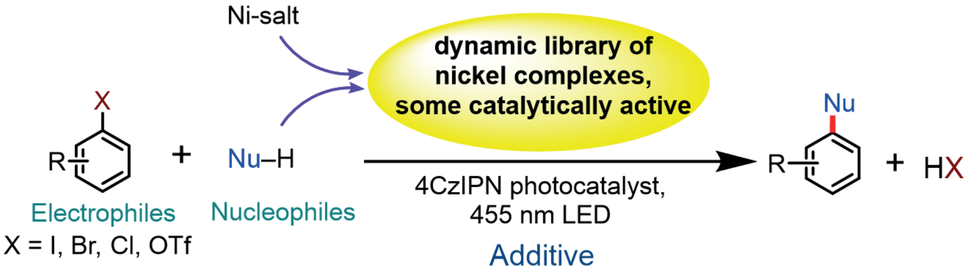

Figure 2. Concept of adaptive dynamic homogeneous catalysis (AD-HoC) in cross coupling. [10]

The examples illustrate the many opportunities that arise from combining catalysis with photochemistry. Current challenges are our limited mechanistic understanding of many processes, which calls for more detailed photophysical investigations.

The future for better catalysis is bright!

Acknowledgements

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ELECTROCHEMICAL SYNTHESIS: FROM HYDROCARBOXYLATION OF ALKENES TO COUPLING OF ARENES

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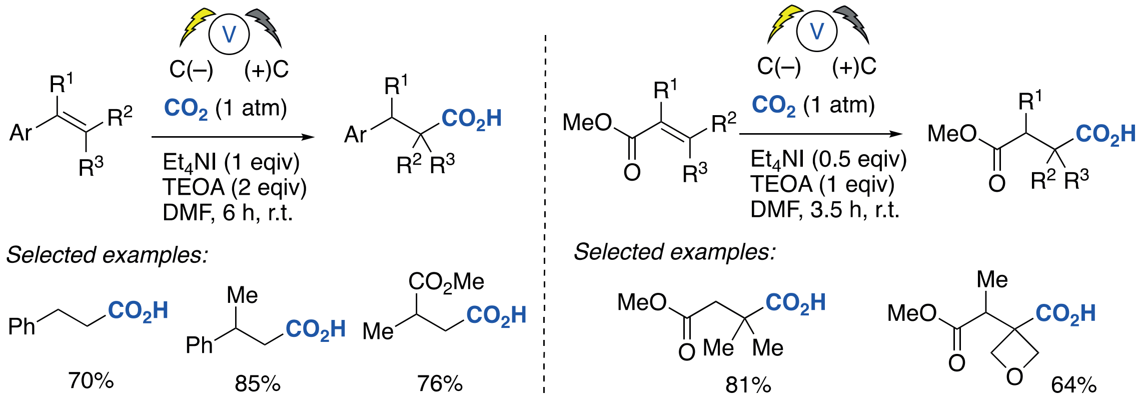
Electrosynthesis has been widely studied within the electrochemical community but represents an underused tool, with great potential for synthesis.[1] Currently, there are only a few processes at the industrial or pilot-plant scale for the electrosynthesis of organic molecules. Herein we report a new electrosynthetic approach to the selective hydrocarboxylation of alkenes,[2] dienes,[3] and esters.[4] The method allows direct access to carboxylic acids derived from terminal, *di-* and *tri-*substituted alkenes, as well as conjugated dienes and unsaturated esters, in a highly regioselective manner. A plausible reaction mechanism will be discussed.

A wider electrochemical methodology will be showcased by the asymmetric total synthesis of *N*-acetylcolchinol where all the redox processes, except for the asymmetric reduction, were carried out in the electrochemical cell.



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FLUORINATED NITROSTYRENES - SYNTHETIC ANALOGUES OF FLUOROACETYLENES

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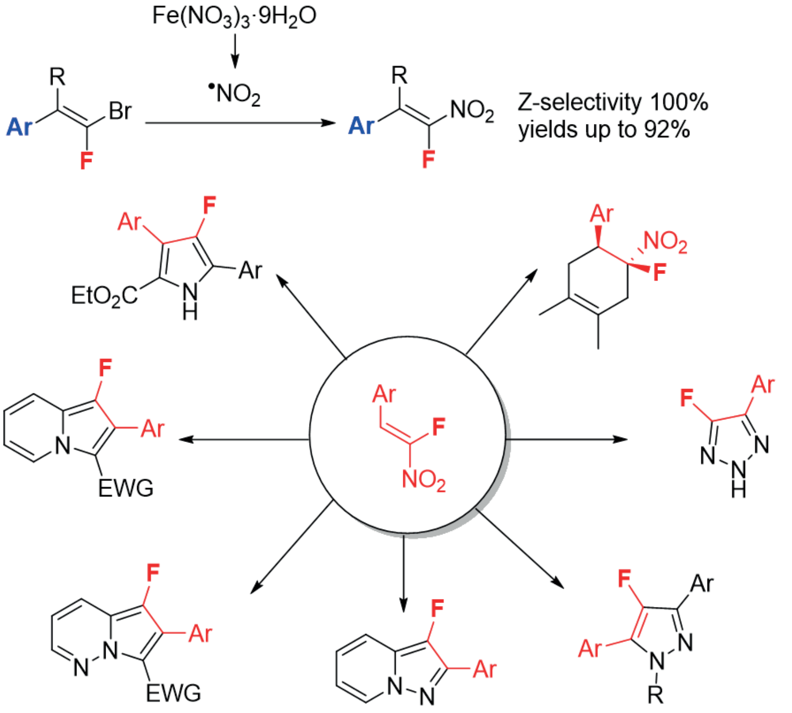
The use of fluorine-containing building blocks for the construction of fluorine-containing hetero- and carbocyclic systems is a very attractive approach. The introduction of fluorine at a late stage is often accompanied by the use of expensive fluorinating reagents, low yields and low selectivity. This report reveals the synthetic potential of fluorinated nitroolefins, which are analogues of unstable and explosive fluoroacetylenes. These compounds were obtained by radical nitration of 1-bromo-1-fluoroolefins [1] and were successfully used in the synthesis of a variety of fluorine-containing hetero- and carbocyclic compounds (Scheme 1). Special attention is paid to new possibilities for the efficient synthesis of previously unknown fluorinated compounds in the BODIPY backbone.



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PREDICTING AND RATIONALIZING NEW MATERIALS AND NEW PHENOMENA

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The breakthrough of crystal structure prediction has resulted in breakthroughs in related problems of compound prediction and prediction of stable molecules/clusters. I will discuss several chemically significant cases:

1. Discovery of anomalous compounds under pressure, such as Na_3Cl, NaC_{17} and highest-temperature superconductors known to date – H_3S, YH_6, CaH_6, ThH_{10}, LaH_{10}.
2. Discovery of counterintuitive phenomena at high pressure – formation of transparent insulating phase of sodium and chemical reactivity of helium.
3. Rationalization of these and other phenomena based on newly developed scales of electronegativity and chemical hardness.
4. Prediction of stable molecules – the formalism and its applications. In particular, I shall discuss the results on molecules and crystalline allotropes of sulfur, phosphorus and boron. Chemical diversity of hydrocarbons will be explained, as well as unusual molecules in the C-H-N-O system. I shall also discuss prediction of stable and catalytically active Cu-Au nanoparticles, and ultralow reaction barriers for oxidation of CO on some of these nanoparticles.

ADVANCING UNNATURAL *α*-AMINO ACIDS SYNTHESIS: STUDY OF CATALYTIC AND STOICHIOMETRIC SYNTHESIS METHODS

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The asymmetric synthesis of non-protein α-amino acids remains one of the most exciting and relevant topics in medical and organic chemistry. Constantly developing scientific groups offer new and promising approaches for the synthesis of enantiomerically enriched α-amino acids.

Among such methods, hydrogenation of olefins and imines, electrophilic amination of enolates, electrophilic alkylation of glycine derivatives and nucleophilic addition to α-imino esters, as well as other catalytic asymmetric approaches to the synthesis of unnatural α-amino acids, can be noted. These methods are widely used and remain the focus of researchers. However, despite progress in this area, each method has its drawbacks and limitations. In this regard, the development of effective and simple methods for the synthesis of enantiomerically enriched non-protein α-amino acids is still actually. This task is extremely important, as it opens up new perspectives and opportunities for synthesis and design, and also provides ample opportunities for innovative applications in medicine and other fields.

The discovery of these pathways not only expands our understanding of amino acid chemistry, but also contributes to the opening of new horizons for the development of technologies and approaches.

Our approaches to solving such challenges will be presented first focusing on the stoichiometric synthesis with using Ni (II) square-plane complexes as a synthon, and then catalytic asymmetric synthesis using salicylidene metal-complexes as catalysts.

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SYNTHESIS FOR BIOMIMESIS

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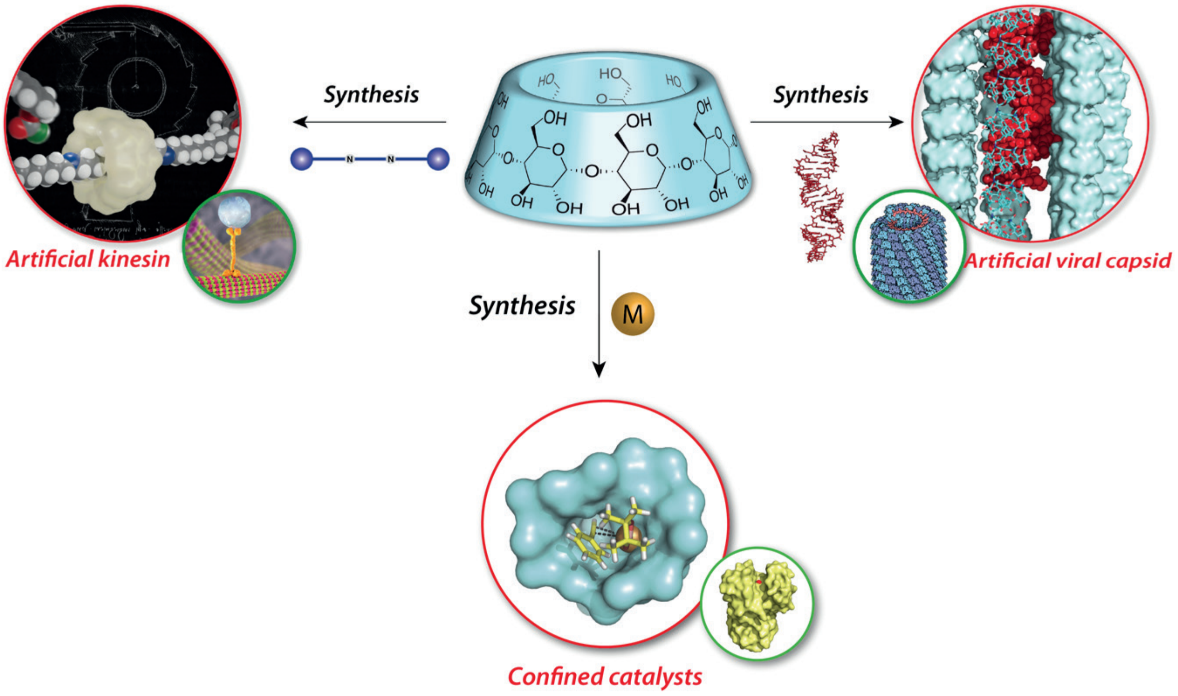
Biomimesis is a scientific and design approach that involves studying and emulating biological systems and processes to create new materials, products, or technologies that are more sustainable, efficient, and adaptable. In chemistry, it involves the design and synthesis of molecules, catalysts, and materials that mimic or are inspired by biological systems and processes, such as enzyme catalysis, photosynthesis, and molecular recognition.

Cyclodextrins are cyclic oligosaccharides possessing a cavity used in our daily life as deodorants, excipients or in chiral stationary phases. In these applications, they are unfunctionalized or randomly functionalized. The concept of "artificial enzyme" has been proposed by Breslow using these cavitand molecules [1] assimilating their cavity to the active site of an enzyme. However, a bottle-neck for their development was the lack of efficient functionalization. Over the years, we delineated several strategies to access poly-hetero-functionalized cyclodextrins.[2] The ability to place a function anywhere on a complex cavitand allowed us to mimic proteins. Hence we could add metallic reactive centers to imitate ***metallo-enzymes***.[3] We also conferred the ability to self-assemble around DNA as capsid proteins[4] and we designed a kinesin-like ***molecular motor***[5]...



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Value-BASED APPROACH TO SIMULATION AND ANALYSIS OF KINETIC MODELS OF CHEMICAL REACTION SYSTEMS. FROM H_2/O_2 MIXTURE EXPLOSION TO ANTIOXIDANT BEHAVIOR OF TOCOPHEROLS

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The report outlines the further application of the *value*-based analysis of the reaction mechanisms [1-3], to identify and analyze the critical states of reaction systems, as well as to reveal the antioxidant properties of tocopherols in lipid-containing media. The proposed *value* approach is based on the Hamiltonian systematization according to the objective functional of kinetic equations for the reaction species and rates of individual steps in the mechanism of a complex (multisteps) chemical reaction.The *value*-based approach allows:

- To determine and rank the *value*, the kinetic significance of individual steps and species of reaction mechanisms.
- To reduce excessive reaction mechanisms according to a definite criterion.
- To identify the critical states of reaction systems and the determination of their chemical content.
- To solve the problems of optimal control of a complex reaction based on the prevailing chemistry.

Using as example the reaction of hydrogen with oxygen, which is important for hydrogen energy, we show the effectiveness of the *value*-based approach in identifying and chemically understanding the critical conditions of reactions, delimiting the qualitatively and quantitatively different reaction modes. In the pressure-temperature coordinates, four critical limits are identified and chemically interpreted. In particular, the 4th limit inherent for high pressures is predicted for the first time.

The second part of the report presents a *value*-based study for a detailed, mechanistically strict prediction of antioxidant distinctive behavior of α-, β-, γ- and δ- tocopherols in the lipid peroxidation reaction. To this end, comprehensive, experimentally verified reaction kinetic mechanisms are constructed, using methyl linoleate as a model of an oxidizable lipid substrate.

One of the main conclusions of this detailed numerical examination is that the nonlinear, complex dependence of the induction period of the chain reaction of lipid peroxidation and the reverse order in the antioxidant potency of tocopherols with an increase in their initial concentrations has the same cause: an increase in the relative contribution of three key pro-oxidant reaction-steps. Simultaneously, the order of the pro-oxidant ability of tocopherols is opposite to that of the antiradical activity, so the reverse order in the antioxidant ability of tocopherols is recorded.

A further conclusion of this study is that these lection of isoform and optimal concentration of tocopherols from the point of view of medicine and nutrition is considered effective, based on the detailed chemical mechanisms of their antioxidant action on lipid peroxidation reactions and their kinetic analysis.

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INVITED LECTURES

SUPRAMOLECULAR AND DYNAMIC COVALENT CHEMISTRY OF METACYCLOPHANES: FROM RECOGNITION TO MOLECULAR DEVICES

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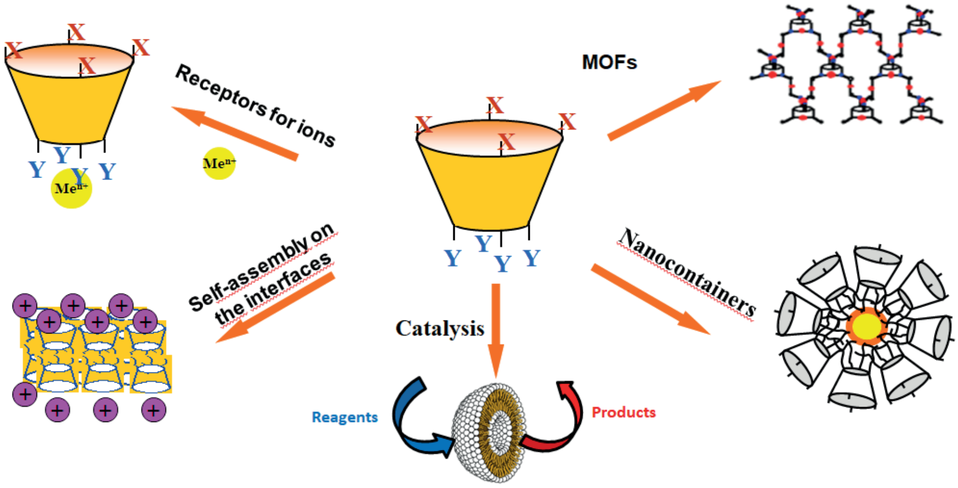
Metacyclophane derivatives in different conformations have many advantages to create a wide range of precursors for the design of very sophisticated supramolecular architectures. Dynamic covalent chemistry (DCvC) is a set of synthetic methods and techniques to design complex supramolecular structures from discrete molecular building blocks and is actively used in supramolecular chemistry, since it is based on the dynamic properties of molecular systems (self-assembly) and the ability to correct errors, which allows you to create large structures without defects.



Currently, DCvC is widely used to obtain complex organic molecules and aggregates, such as covalent organic frameworks (COF), molecular knots, new macrocycles of various sizes, polymers, as well as molecular devices and sensors. This report discusses the application of this synthetic strategy to the design of catalytic systems, molecular devices, and sensors for biomedical purposes.

The work was supported financially by the Russian Science Foundation (project no. 22-13-00304).

NOVEL ELECTRODE MATERIALS FOR METAL-ION BATTERIES

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Ninety percent of the energy produced today come from fossil fuels. Rapid consumption of these energy sources makes dramatically negative impact on our future due to ecological damage and climate change. In this sense the development of the environmentally benign renewable energy sources capable to replace fossil fuels and concurrently efficient large energy storage devices requires no justification. Li-ion batteries (LIBs) have been originally developed for portable electronic devices, but nowadays new application niches are envisaged in electric vehicles and stationary grid-scale energy storages. However, LIBs may be not fully adopted for these applications. The geographical scarcity and excessive demand for Li resources intensifies the development of alternative sustainable technologies based on vastly accessible materials, namely Na- and K- ion batteries.

The Na/K-based oxides and polyanion materials of transition metals are scrutinized as cathodes for these batteries aiming to enhance the specific energy, durability and rate capability. Whereas the layered oxides display greater volumetric energy density, the polyanion materials usually exhibit better cycling and thermal stability and higher C-rate capabilities due to covalently bonded structural frameworks. The polyanion compounds reveal an extra dimension in their crystal chemistry, which significantly extends the playground for designing materials with superior electrochemical performance. Further advantages are expected from the synergistic effect of combining different anions (such as $(XO_4)^{p-}$ and F^-) in the anion sublattice.

An overview of the research on novel phosphates and fluoride-phosphates as prospective electrode materials for the Na/K-ion batteries will be presented with a special emphasis on the interrelation between composition, synthesis conditions, crystal structure and electrochemical properties of the materials intended for practical applications.

Acknowledgement: This work was supported by the Russian Science Foundation, grant No. 17-73-30006.

UNCOVERING THE DYNAMICS OF INTRINSICALLY DISORDERED PROTEINS AND THEIR INTERACTIONS WITH NUCLEIC ACIDS

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A large fraction of human proteome (>40%) is often enriched in protein regions that do not form a well-defined tertiary structure under physiological conditions, and some are even entirely disordered. These intrinsically disordered proteins (IDPs) commonly interact with many different binding partners and can thus function as interaction hubs in cellular communication and regulation networks. Owing to their complexity, the investigation of IDPs often requires using integrative approaches, combining biochemical, biophysical and structural methods, as well as molecular simulations.

During my talk I will discuss our recent advances in characterization of dynamics of disordered translation initiation factors and their intra- and intermolecular protein - protein and protein -nucleic acid interactions. Combining single-molecule fluorescence spectroscopy (smFRET) and biomolecular nuclear magnetic resonance (NMR) we obtained a comprehensive picture of the conformational and interaction dynamics at a broad range of time (from nanoseconds to minutes) and molecular scales (from single monomers to dynamic complexes and large oligomers). These new insights are key for understanding the mechanism of function of such complex and highly biologically important proteins.

CONTROLLING BIOMEMBRANE ELASTICITY AND AMYLOID MORPHOLOGY VIA IONIC LIQUIDS

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Ionic liquids (ILs) are a vast class of organic electrolytes composed of an organic cation and either an organic or inorganic anion, whose melting temperature falls around room-temperature. In the last 20 years, several studies have shown a moderate-to-high toxicity towards cells and micro-organisms for a number of these compounds, breaking the dream of their absolute green character. Toxicity, however, is synonym with affinity, and this has stimulated a series of investigations focused on the mechanisms of action (MoAs) of ILs, which understanding can ease the development of IL-based approaches in drug delivery, bio-medicine, pharmacology and, more in general, bio-nanotechnology. After presenting an overview of the state-of-the-art of the MoAs of ILs [1], I will focus on some cases of study under investigation in my Lab [2-6]. First, I will discuss the absorption of ILs into lipid bilayers [2] (Fig. 1) and their effect on the bilayer elasticity and live cell migration [3,4]. I will then move into protein amyloidogenesis to show the effect of selected ILs on amyloid fibrils morphology [5]. I will conclude the invited talk by presenting some current work underway in my NanoBiophysics Lab [6]. The major approaches in use include atomic force microscopy and neutron scattering, which are complemented by computer simulations and a variety of biochemical tools.

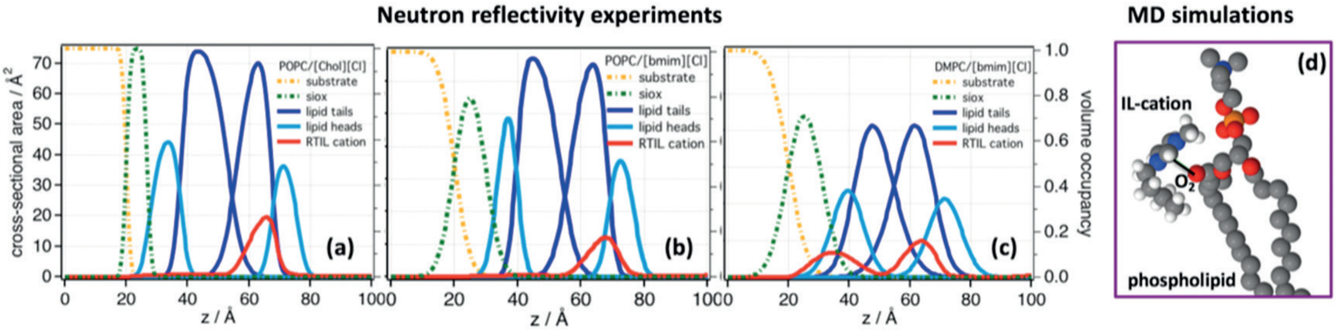

Fig. 1 – (a-c) Density distribution profiles of supported phospholipid bilayers doped with ionic liquids as a function of height *z* from the surface of the substrate obtained by fitting the neutron reflectivity data. Neutron reflectometry has allowed to model each single supported phospholipid bilayers with four different density distributions. Three cases are here reported. In (c), the diffusion of the cations into the inner leaflet is apparent, and this can imply diffusion into the cytoplasm through the cellular lipid membrane. In (d), a representative molecular dynamics simulations configuration of the [C_4mim] IL-cation in close contact with a POPC phospholipid molecule.

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REGIOSELECTIVITY OF NUCLEOPHIL ATTACK AS ONE OF THE FACTORS OF TRANSFORMATION OF PYRIMIDINE SYSTEMS

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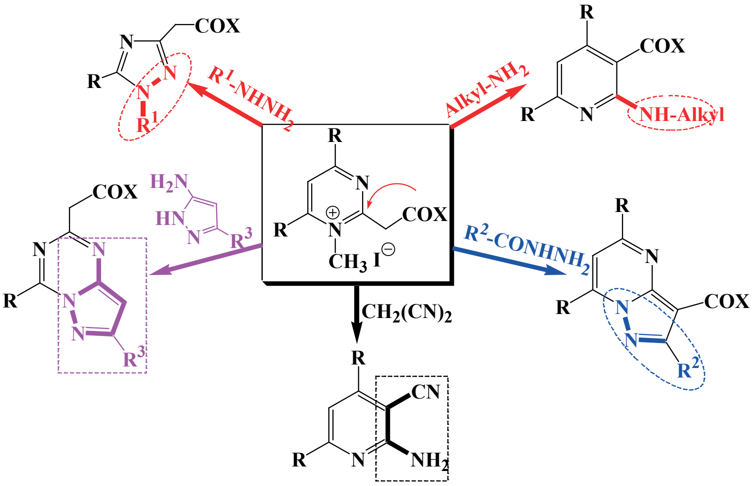
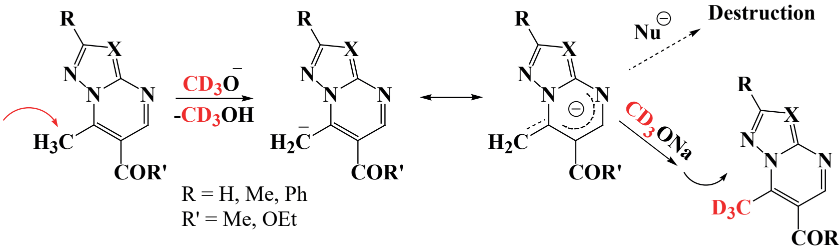
It is known that under the action of various nucleophiles on pyrimidinium salts, ring opening occurs, followed by recyclization. In this process, the reaction is often accompanied by the inclusion of a nucleophile fragment into a new ring. Such reactions lead to unusual transformations, which are often initially difficult to predict. Note that such transformations are also characteristic of condensed pyrimidine systems containing a bridging nitrogen atom.



All of the above recyclizations begin with the attack of the nucleophilic species on the carbon atom of the pyrimidine ring. However, in some cases, when nucleophilic reagents are involved, recyclizations do not occur and the reaction either does not proceed, or, after the opening of the pyrimidine ring, leads to the destruction of the molecule.

During the registration of ^{1}H NMR spectra of the initial pyrimidine systems (both pyrimidinium salts and pyrimidines with a bridging nitrogen atom) in CD_3ONa/CD_3OD solution, we observed an easy and fast H/D exchange of hydrogen atoms of methyl groups located in the pyrimidine ring. This indicates the attack of the nucleophilic particle (CD_3O^-) on the carbon atom of the methyl group, rather than the pyrimidine ring. The kinetics of the H/D exchange process has been studied on different systems, and the general nature of such transformations has been shown.



We believe that the discovered attack of the nucleophilic species on the carbon atom of alkyl groups can be a competitive process for the recyclization of pyrimidines. At the same time, the discovered process of H/D exchange, which proceeds easily and rapidly, and, most importantly, regioselectively, can become a method for the targeted introduction of deuterium atoms, and possibly also tritium, into drug molecules in order to study their activity, as well as the pharmacokinetics and mechanism of transformation.

ACTIVE METHYLENE THIOAMIDES AND SELENOAMIDES AS VERSATILE BUILDING BLOCKS IN HETEROCYCLIC CHEMISTRY

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Jassim N.A.T.[a], Dakhno P.G.[a], Frolov K.A.[c], Krivokolysko S.G.[c], Chigorina E.A.[d],
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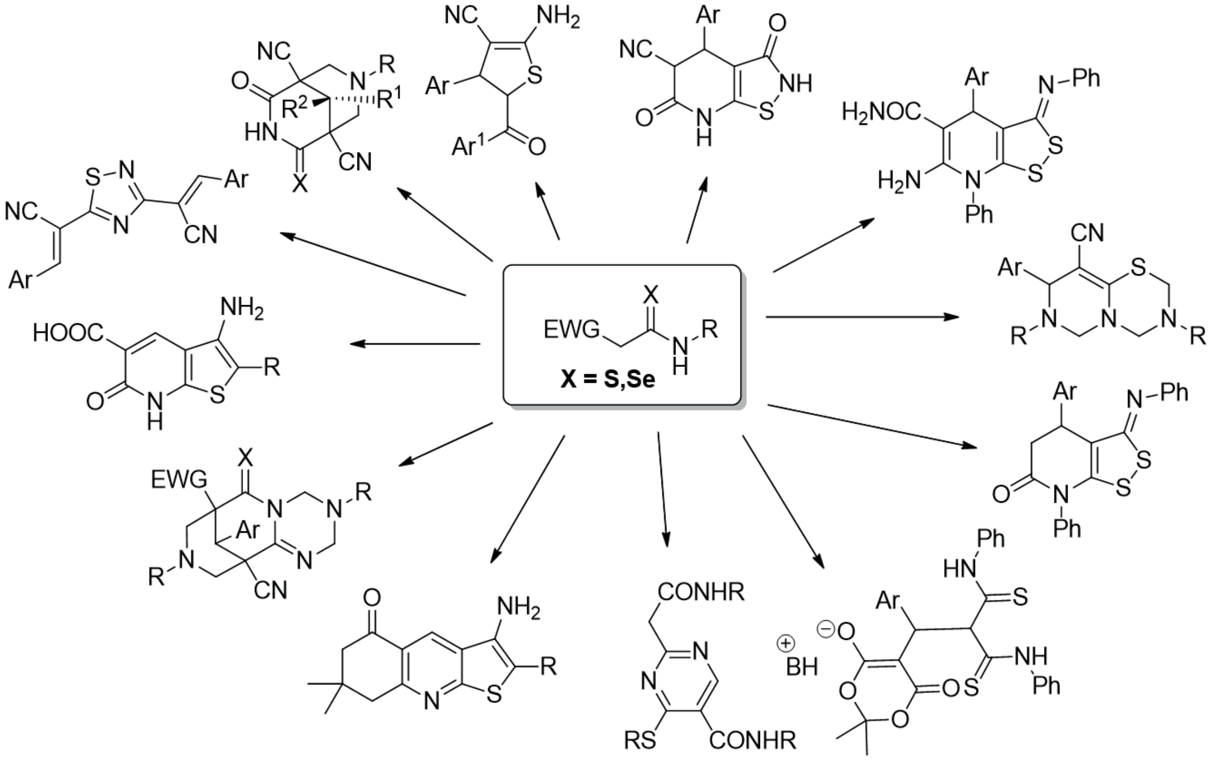
Active methylene thioamides and selenoamides are multifunctional reagents with several nucleophilic and electrophilic centers. They easily react with a wide range of electro- and nucleophilic agents to give a variety of N,S/Se-heterocycles. This lecture will focus on our studies of heterocyclization reactions involving active methylene thioamides and selenoamides. We have developed several new multicomponent/cascade reactions toward synthesis of 1,2,4-thia(selena)diazoles, dihydrothiophenes, pyrimidines, 1,3,5-thiadiazines, 1,3,5-selenadiazines, 3,7-diazabicyclo[3.3.1]nonanes, thieno[2,3-b]pyridines, and [1,2]dithiolo[3,4-b]pyridines. Some of the methods have been applied to a synthesis of libraries of small molecules for biological screening. The scope of these and some other transformations will be demostrated and the mechanisms will be discussed.



This research was funded by the Russian Science Foundation, grant number 22-23-00458, https://rscf.ru/en/project/22-23-00458/

IONIC LIQUIDS AS “GREENER” SOLVENTS FOR CHEMICAL REACTIONS: TRUTH OR MYTH?

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Never-ending revision of chemical processes from the viewpoint of toxicity of their participant substances is an integral part of modern chemistry. Still, in spite of active research on the topic, the common ideas about toxicity of even the most widespread chemical compounds often do not meet the reality. Among the recent examples of such contradictions are ionic liquids (ILs), which have been gaining popularity in various chemical and biological studies. Originally, ILs were considered low-toxic due to their nonflammability and nonvolatility and were though to become a safe alternative to traditional organic reagents and solvents. But gradually it has become evident that in truth many ILs possess moderate and even high toxicity.

Recently, we have carried out an analysis of toxicity of ILs as reaction media. For this purpose, we developed a principally new scheme of assessment of chemical reactions from the viewpoint of toxicity of their components. Until now, there have been no approaches for comparing several ways of synthesis of a particular product in various reaction systems. Our approach is suitable for all kinds of chemical processes, not only for those with ILs.

Up to now, numerous metrics for evaluation of environmental effects of chemical processes have been developed. However, the problem of a broad screening of various chemicals from the viewpoint of their influence on the environment, including humans, has not been solved yet. We propose using bio-Profiles and bio-Strips of chemical reactions for fast preliminary assessment of the impact of their participant compounds on living organisms [1,2]. bio-Profiles and bio-Strips are built on the basis of cytotoxicity of all the chemical compounds entering or leaving a given chemical reaction (Figure 1). These plots are supplemented with several metrics (bio-Factor and cytotoxicity potentials) reflecting the changes of the “overall cytotoxicity” during the reaction. In whole, bio-Profiles allow carrying out a direct comparison of various routes of synthesis of a particular product from the viewpoint of toxicity of their components. We used this approach for evaluating the contribution of a solvent into the “overall cytotoxicity” of chemical reactions by example of C-C cross-coupling processes.

The work was supported by the Russian Science Foundation (RSF Grant 21-13-00049).

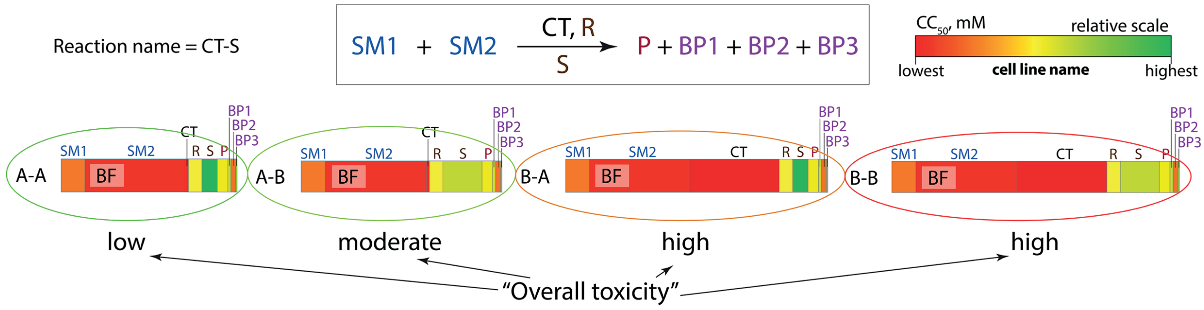

Figure 1. bio-Strips: fast preliminary evaluation of safety of chemical reactions. Reproduced with changes from [2].

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INSIGHTS INTO THE REGULATION OF LIGHT-INDUCED CYTOTOXICITY IN PHOTOACTIVE NANOMATERIALS

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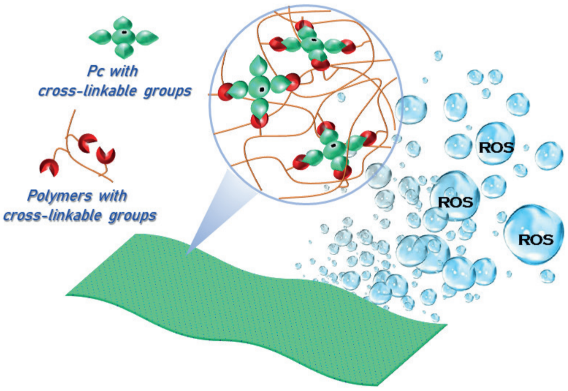
One of the greatest health challenges that society faces is the increasing incidence of pathogenic microorganisms that have developed resistance to multiple drugs. Therefore, the demand for antimicrobial (nano) materials that do not contribute to the development of resistance is rapidly increasing.[1] With tunable structures, remarkable photophysical properties, and the ability to produce reactive oxygen species (ROS) under red light irradiation, phthalocyanine derivatives have been investigated for many years as photosensitizers for antimicrobial PDT.[2] The combination of sunlight and a reusable photocatalytic material capable of generating ROS from dissolved molecular oxygen is a promising concept for the development of sustainable systems for the disinfection of wounds or decontamination of natural or industrial waters.



Schematic view of the generation of ROS in photofunctional nanomaterials upon irradiation.

Though there are many reports showing that such nanoporous surfaces exhibit very strong antibacterial and antiviral effects upon irradiation, major regulators of activity are still largely unverified and the requirements for effective antimicrobial action remain controversial. The design and synthesis of photoactive compounds that can be used as structural components of nanoscale materials and the structure-activity relationship of such systems will be presented.[3]

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SYNTHESIS, BIOLOGICAL PROPERTIES AND SAR INVESTIGATIONS OF NEW 2-ARYL- AND 2-PYRIMIDINYLPROLINES

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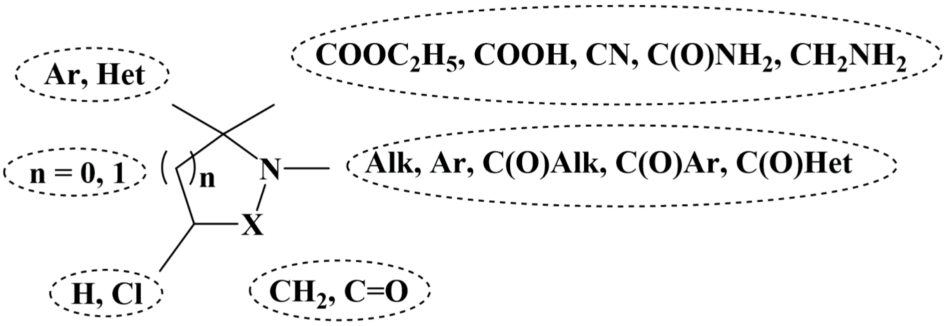
An available method for synthesis of 2-arylprolines and 2-arylazetidines has been developed, which includes the synthesis of corresponding arylglycine derivatives and intramolecular cyclization under the phase transfer catalysis conditions.

By the reaction of 2-arylpyrrolidinecarbonitriles with conc. H_2SO_4 the corresponding acetamide derivatives were synthesized. Substituted 2-arylpyrrolidinecarbonitriles were reduced to corresponding aminomethylpyrrolidines, using $CoCl_2$: PEG-300 : $NaBH_4$ system.

By condensation of 6-aminopyrimidines with pyrrolidones or pyroglutamic acid methyl ester in the presence of PCl_3, pyrimidin-2,4(1*H*,3*H*)-diones, containing substituents in pyrimidine and pyrrolidine rings, have been synthesized. Other derivatives of these compounds were synthesized as a result of the reaction of 6-aminopyrimidines and different 5-hydroxypyrrolidin-2-ones in glacial acetic acid medium.



The study of antibacterial, antitumor and anti-HIV properties of 2-aryl-, 2-pyrimidinylprolines allowed revealing highly active compounds and finding a number of patterns of relationship between structure and biological activity.

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A SCALABLE ONTOLOGY-BASED APPROACH FOR STRUCTURING AND AUTO-INDEXING ADVANCED AND NANOMATERIALS RESEARCH DATA: MAKING RESEARCH DATA STRUCTURED, VISIBLE, SEARCHABLE AND AI-READY

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In the new era of LLMs many areas were disrupted in a positive way leading to substantial amplification of our capabilities to analyze large amounts of data and extract new knowledge out of it. Separately from this, the research data on chemical and materials sciences disciplines still stays very fragmented and spread through multiple databases, hosted by different universities' servers. It is not yet FAIR, looking from the point of view of this term's recent interpretation - Fully AI-Ready.

The amount of research data produced by experimental chemistry and material science is growing exponentially. This presents an enormous challenge to efficient search, structure, index, and what is most important - analyze it. Currently a large amount of research data is hidden behind paywalls, mostly – in non-indexed pages of supporting materials to the article. Moreover, during their experiments, experimental scientists generate large amounts of precise data. But not all of this data got eventually published, because most of it doesn't fit the articles' main philosophy. As a result, it is discarded or stored on personal and institutional drives and becomes invisible and unavailable both for humans and for machines. But this information has a huge value if scientists and ML/AI-powered machines have controlled access to it.

As an important step towards the FAIR-ification of chemistry and material science research data we developed an advanced ontology for structuring, labeling and organizing experimental data for advanced and nanomaterials, which could be easily used by both humans and machines to mine and extract new knowledge. We plan to open-source this comprehensive ontology for a wider community of chemists and material scientists in order to enrich it with a community›s wisdom and cover a broader number of disciplines and subdisciplines.

FROM IDEA TO PRODUCT: THE 4th PARADIGM OF DATA-DRIVEN PRODUCT DEVELOPMENT IN MATERIAL SCIENCE

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Functional Materials Lab, Institute of Chemical Physics after A.B. Nalbandyan, NAS RA

Abstract: The development of new materials is essential for addressing the energy needs of a growing global population. In the transition from oil-based energy resources to renewables, such as solar energy, the need for new materials that can efficiently harvest and store energy has become increasingly important.

The application of data-driven product development, or the 4th paradigm, has revolutionized the way we approach material science research and development. In this presentation, we will discuss the use of artificial intelligence (AI) and particularly machine learning (ML) in the development of new materials, specifically perovskite solar cells.

Our work highlights the importance of data-driven development in material science and its potential to revolutionize the field. We hope that our findings will inspire future research initiatives and contribute to the development of new materials that can help to meet the energy needs of our society.

Additionally, we will discuss the differences between academic and industrial projects and the unique challenges and opportunities that each present.

PREPARATION AND EXPLORATION OF HEAVIER PNICTOGEN SPECIES

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Owing to their roles as versatile reagents and pivotal intermediates in numerous chemical processes, the properties and reactivity of carbenes (R-$\ddot{C}$-R) and nitrenes (R-$\ddot{N}$:) have been extensively studied, despite their high reactivity.[1-2] However, there are still many families of reactive intermediates that have eluded isolation and spectroscopic identification. Among these are arsinidenes (R-$\ddot{As}$:), the neutral monovalent arsenic congeners of nitrenes, and phosphinidenes (R-$\ddot{P}$:)[3-5] with six electrons in their valence shell. Multiple attempts have been made to prepare free arsinidenes, but the detection and identification of these species have been hampered by their instability and fleeting existence.[6] All other evidence for the existence of arsinidenes has been derived from trapping and complexation experiments. The talk reports the first synthesis, IR, and UV/Vis spectroscopic characterization of parent phenylarsinidene (1) and its reactions with small molecules (O_2, CO, NO) leading to several novel species that have not been reported (2-5) (Figure 1A).[7] We illustrate that the chemical transformations involved are distinctly different from those observed with triplet nitrenes[8] and phosphinidenes,[4-5] the lighter congeners of 1.

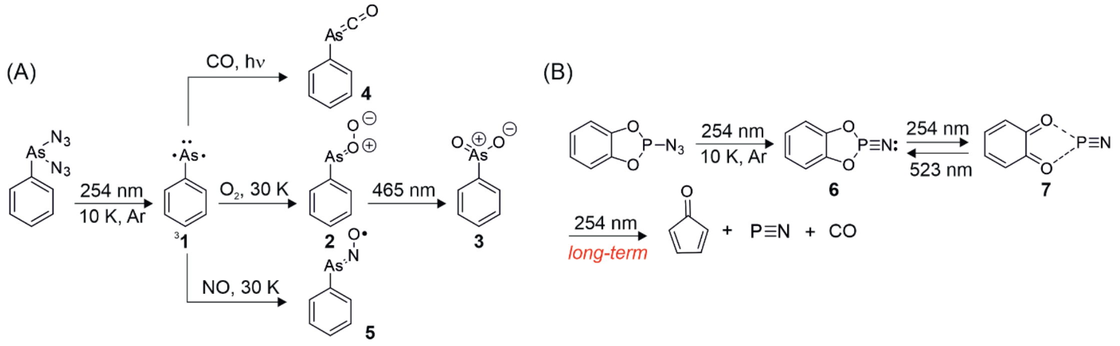

Figure 1. (A) Phenylarsinidene (**1**) and products of its reactions with O_2, CO, and NO.
(B) Photochemical generation of 6 and 7 and subsequent reactivity.

The quest for molecular precursors that can release the extremely reactive heavier homologs of dinitrogen N_2, such as P_2, As_2, PN, is a fascinating area of research within the realm of group 15 element chemistry.[9-10] However, the high reactivity of PN and the absence of a suitable molecular precursor for its release have prompted scientists to synthesize molecules that contain embedded phosphorus monitride units.[10] Here we report the first PN-bearing van der Waals complex (7) that was generated in cryogenic matrices utilizing UV light irradiation of the corresponding azide precursor. Besides IR and UV spectroscopic characterization, its recombination to covalently bonded (o-phenyldioxyl)-λ^5-phosphinonitrile (6) was triggered by subsequent 523 nm irradiation through a concerted mechanism, which reveals the first observed reactivity of PN towards organic molecules (Figure 1B).[11]

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C-H BOND ACTIVATION AND CROSS-COUPLING ON Al(I) AND Ga(I) COMPOUNDS

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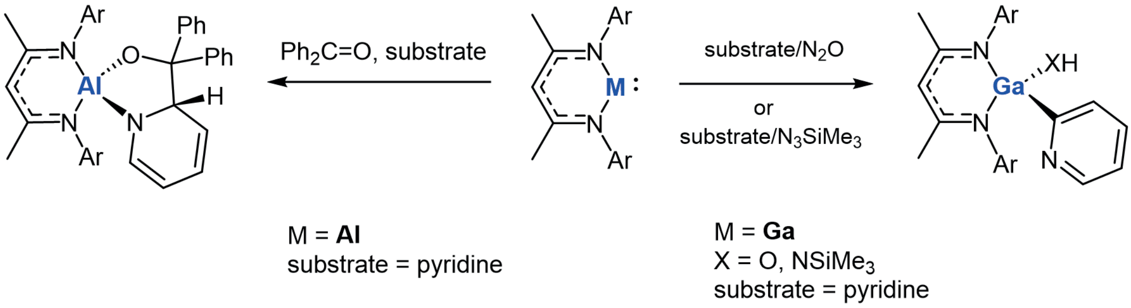
Activation of small molecules by low-valent main group compounds is a hot topic,[1] of which the bond cleavage by carbenoids, electronic analogues of carbene, is the most common.[2] The NacNac-supported Al(I) and Ga(I) compounds NacNacM have been in the focus of several groups, including ours. In this talk we shall review the results of the past decade of research[3] and highlight the increasing complication of reactivity, progressing from bond activation to multicomponent reactions and coupling.[4]



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MECHANISTIC NMR STUDY OF REACTIVITY OF KETONES AND ACETYLENE IN IONIC LIQUIDS AND SUPERBASIC CONDITIONS

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Deuterium exchange reactions of alkyl and phenyl ketones were studied in ionic liquids (ILs). The catalytic properties of certain imidazolium based ILs were compared, and it was revealed that the nature of anion in ILs plays important role in catalysis of H/D exchange reactions of ketones. The consecutive deuteration of CH, CH_2, and CH_3 groups in a series of ketones was monitored by NMR spectroscopy, and the dependences on various experimental factors, such as the nature of IL and deuterated solvent, their concentration and temperature were estimated. Different approaches to obtain maximal deuteration degree in short amount of time were tested, and the experimental conditions for effective deuteration are suggested.

Reactivity of acetylene was studied in superbasic conditions by NMR monitoring of $^1J_{CH}$ hydrogen-carbon one bond spin-spin coupling constant in ^{13}C NMR spectra. The coalescence (collapse of splittings) of $^1J_{CH}$ was revealed and attributed to chemical exchange processes. The dependence of coalescence on temperature, addition of water, acid and various bases was studied. Several possible mechanisms of chemical exchange processes were suggested based on quantum chemical calculations. The deeper understanding of observed phenomenon will be an important step in understanding of functionalization chemistry in liquid phase.

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PEROVSKITE SOLAR CELLS: RECENT ADVANCES AND CHALLENGING TASKS

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Perovskite solar cells (PSCs) draw great attention due to their outstanding performance and facile solution processing. However, commercialization of PSC is hindered by the relatively low stability of hybrid perovskites upon various atmospheric factors as well as low operational sustainability of the device components. A wide spectrum of different approaches is proposed to enhance the intrinsic stability of the applied materials and their interfaces, including perovskite active layer compositional engineering, passivation techniques, and modification of charge-transport layers.

These methods significantly pushed the stability of the PSCs up however, under real operational conditions, device encapsulation is mandatory since it serves not only as a barrier to ‘‘external” degradation factors such as moisture and oxygen but also provides mechanical protection and prevents lead leakage from the cells to the environment.

Recently we introduce a simple and universal scalable encapsulation strategy for perovskite solar cells based on thermal vacuum evaporation of MgF_2 or MoO_{3-x} capping layer followed by sealing the device with glass and UV-curable polymer. The proposed encapsulation method is beneficial to most of the other known encapsulation approaches being fully harmless to perovskite and transporting layers and processible at room temperature. Vacuum deposition of the capping layer promotes efficient removal of water, oxygen and organic solvent residuals from the device prior to sealing and could be easily performed using standard equipment for metal electrode deposition. The proposed strategy is transferrable to any lab-scale perovskite solar cell prototypes regardless of their geometry and architecture and results in excellent stability of the devices in ambient air and long operating conditions. Upon the 1000 hours stability test at ambient air (30%–60% RH), the cells preserved 92.9% of their initial efficiency on average under 1 Sun illumination at constant maximum power point tracking (MPPT, ISOS-L-1) and over 96% under storage in the dark (ISOS-D-1), thus evidencing for the high effectiveness of the proposed encapsulation approach.

HOW TO CREATE A NEW ANTISEPTIC?

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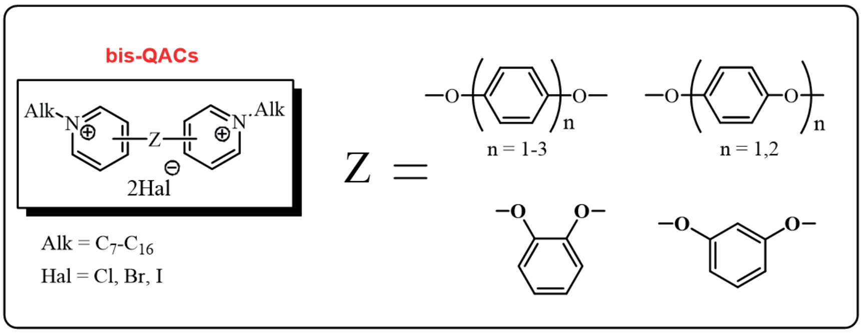
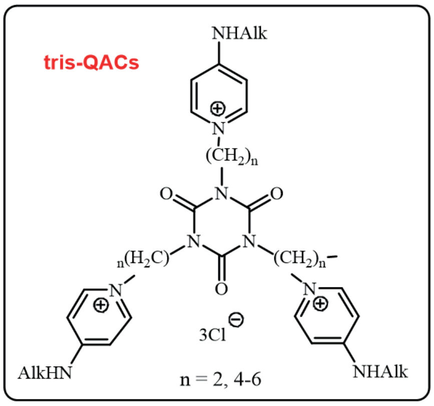
Currently, on the Russian market of medical devices, a significant part of antiseptics is made on the basis of quaternary ammonium compounds (QACs). The most famous and effective antiseptics based on mono-QAC are benzalkonium chloride, cetylpyridinium chloride, miramistin, based on bis-QAC – chlorhexidine, alexidine, octenisept, mestamidin. Various strains of bacteria, including pathogens, are known to develop resistance to antimicrobial drugs over time [1,2].

In this work, we propose an original approach to the synthesis of several new types of QACs based on pyridinium salts [3]. By varying the linker between pyridinium nuclei, bis- and tris-QACs [4] were obtained, which have antibacterial and antifungal activity against a wide range of highly resistant pathogenic bacteria (both gram-positive and gram-negative) and fungi, surpassing the activity of known antiseptics. Of particular note, the new QACs have been successfully tested against highly resistant clinical strains isolated from clinical specimens during the investigation of infections in 2016-2018.





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ORAL PRESENTATIONS

DESIGN OF NOVEL CHEMICAL TRANSFORMATIONS UTILIZING NITROOLEFINS, AND THEIR APPLICATION TO ACCESS BIOLOGICALLY ACTIVE MATERIALS

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Development of synthetic approaches towards alkaloid analogs containing indolyl fragment is one of the central topics of modern synthetic and medicinal chemistry. We have recently reported on investigations of assuring antitumor properties for 2-aryl-2-(3-indolyl)acetohydroxamic acids, which demonstrated significant cytotoxicity against glioma, melanoma, esophagus cancer and many other cancer cell lines inherently resistant to induction of apoptosis and poorly responding to the treatment with proapoptotic medicines. Expanding the search, we stumbled upon the need for elaboration of novel approaches towards analogous structures non-accessible by standard methods. To this end, during the first stage of the project, an efficient method for activation of 3-(2-nitroethyl)-1H-indoles towards spirocyclization and subsequent rearrangement into 2-(1*H*-indol-2-yl)acetonitriles was developed. These compounds serve as key precursors for the entire project.

It was proposed that the mechanism of this activation involves stabilization of reactive tautomeric nitronate species in a form of phosphorylated mixed anhydride, formed upon interaction of poorly reactive nitroalkane with phosphoryl chloride in the presence of a base.

Biological activity of these novel 2-(1H-indol-2-yl)acetonitriles was investigated. It was found, that a number of these compounds showed micromolar activity (about 10 μм) against seven cancer cell lines: A549, A549, U373n, HS683, HeLa, HS683, and B16F10.

Reactivity of 2-(1H-indol-2-yl)acetonitriles and their immediate precursors 4’H-spiro[indole-3,5’-isoxazoles] in the presence of various nucleophiles under various conditions was investigated. Preparation of alkaloid-like structures employing this approach should be specially mentioned.

Funding: This work was supported by grants from the Russian Science Foundation (Grant number 21-73-20051). https://rscf.ru/en/project/21-73-20051/

CHEMISTRY OF 3-CYANOKETONES: OUTSTANDING PERSPECTIVES

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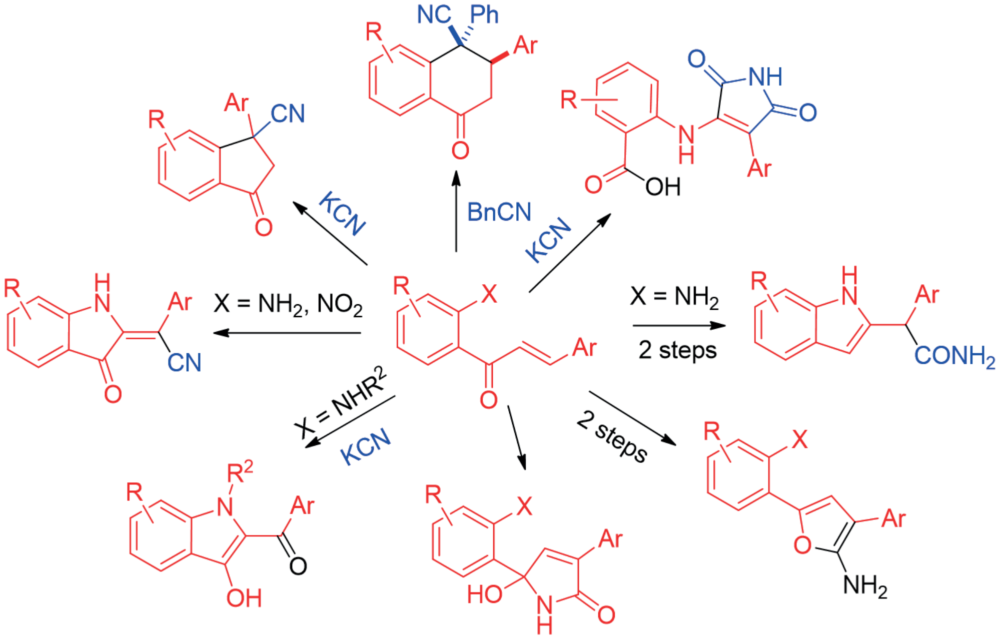
The last time presented to mankind quite a few new problems. Efficient and environmentally friendly synthesis methods, characterized with high yields, a small number of stages, and the use of available reagents, began to take the first place. Cascade transformations allow is able to solve all of the above problems at once, excluding the intermediate isolation of reaction products, reducing the process time, which is reflected in lower resource consumption and less influence of the human factor.

Our new direction devoted to the chemistry of 3-cyanoketones. These derivatives contain a high density of functional groups, which allows implement a bunch of unexpected transformations with the formation of previously unknown and difficult to obtain compounds with promising properties, including with diastereosective methods, shown by us recently.



Funding: The study was supported by the Russian Science Foundation (grant № 21-73-10029, https://rscf.ru/project/21-73-10029/)

FUNCTIONALIZED PHOSPHONIUM SALTS: CHEMICAL PHYSICAL AND ANTIMICROBIAL PROPERTIES AND APPLICATION

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The organic salts (ionic liquids) field has expanded in the last decade to include an ever-wider range of application areas [1]. Functionalization of organic salts brings in advanced properties and offers new opportunities for development within and beyond chemistry.

In the present study, a number of novel quaternary phosphonium salts with oxygen-containing substituent was synthesized. The crystal packing appeared to be depending on cation structure. In the first series of experiments, we utilized functionalized phosphonium salts for microcrystalline cellulose dissolution applying DMSO as a co-solvent. Using differ combination of the functional group in cation structure and the nature of anion we found structural features that were responsible for effective cellulose dissolution. The selected phosphonium salts dissolve up to 5 mass% of cellulose which is comparable with known N-containing analogous [2]. A recent research showed that compounds under study are safe to non-pathogenic microorganisms which could serve as fermenting ones at the following step of biomass treatment.

The scope of the functionalized phosphonium salts was extended with chiral compounds containing *L*- and *D*-menthol moieties. Antimicrobial properties of the chiral salts were evaluated.

This research was supported by the Russian Science Foundation (RSF grant N° 22-23-20161).

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HYDROSILYLATION – KEY CATALYTIC APPROACH TO Si–C-BONDS FORMATION

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Hydrosilylation, i.e., the addition of hydrosilanes to unsaturated hydrocarbons, mainly alkenes, is a key method for creating Si–C-bond (Figure 1). This reaction is used on a large scale and presents the most successful example of homogeneous catalysis in industrial application. Moreover, hydrosilylation opens a way to a wide variety of organosilicon products, which are widely used in the main areas of industry from aviation and space to agriculture and medicine.[1]

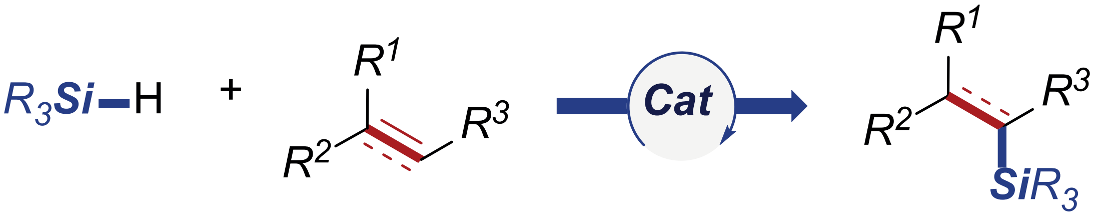

Figure 1

Industrial hydrosilylation catalysts are Pt^0-complexes – Speier's and Karstedt's catalysts, which have been employed since the middle of XX^th^ century. However, intensive studies of this reaction and development of the new catalysts continue until today. On the one hand, it is related to high platinum cost and its irretrievable “scattering”, products contamination by colloid platinum, etc. On the other hand, it is because of low activity to sterically hindered compounds, low selectivity in functionalized alkenes/alkynes hydrosilylation, etc.

There are several approaches in modern chemistry, aimed to solve these economical, ecological, chemical and technological problems:[2] (1) development of [M]-free hydrosilylation; development of new homogeneous [M]-catalysts based on (2) cheaper and more accessible earth-abundant transition metals and (3) platinum series metals,[3] in particular, single-atom catalysts; and transition to reusable and recyclable heterogeneous and heterophase[4] catalytic systems. Our scientific group results in these directions will be discussed in this presentation.

Acknowledgements
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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF HIGH ENTROPY MAX PHASES

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In the quest of novel materials for functional applications a concept of entropy stabilized multicomponent systems was expanded to high entropy MAX phases aimed at utilizing the spare potential of high entropy materials (HEMs) and MAX compounds [1,2]. HEMs with numerous principal elements open up an almost endless field for designing a new class of materials with unexpected physicomechanical, catalytic and chemical features. High entropy MAX phases have already demonstrated enhanced potential to outperform the structural and functional properties of both high entropy materials and MAX phases. However, the synthesis and reaction mechanism of high entropy MAX phases is in its nascent stage of exploration. The existing research mainly focuses on few compositions prepared by long-lasting milling of commercial elemental powders or respective MAX phases followed by calcination, annealing or hot pressing [3]. It is assumed that a lower contribution of configurational entropy can lead to the formation of a multiphase system (undesired phases) in the absence of postannealing treatment due to the nature of competing phases. Hence, detailed parametric studies and formation pathways are required to understand the trends in facile synthesizability of pure high-entropy MAX phases. The self-propagating high-temperature synthesis (SHS) already demonstrated to be a prospective approach for the production of single-phase binary carbides, high entropy materials and MAX phases in a single and short (up to min) cycle. For the preparation of target high entropy MAX phase, the respective metals and carbon black were used as precursors. The configurational entropy of the system was estimated satisfying the necessary and sufficient conditions for the formation of substitutional single-phase solid solutions (1.38R). To promote self-sustaining reaction between metals and carbon in the combustion mode organic polymer was introduced to the initial mixture. At that, combustion temperature of 1400°C was achieved leading to the formation of target high entropy $M_4A_1X_3$ phase (413 HEMAX) in the postcombustion zone (Fig. 1a), which was regulated via sample diameter, apparent density, external pressure and polymer amount. The influence of the heating rate and dwelling time on the composition of the final product was unraveled. Based on the XRD pattern, the lattice parameters and lattice strain were calculated (Fig. 1b). Lamellar grains characteristic to high entropy MAX phases were obtained (Fig. 1c).

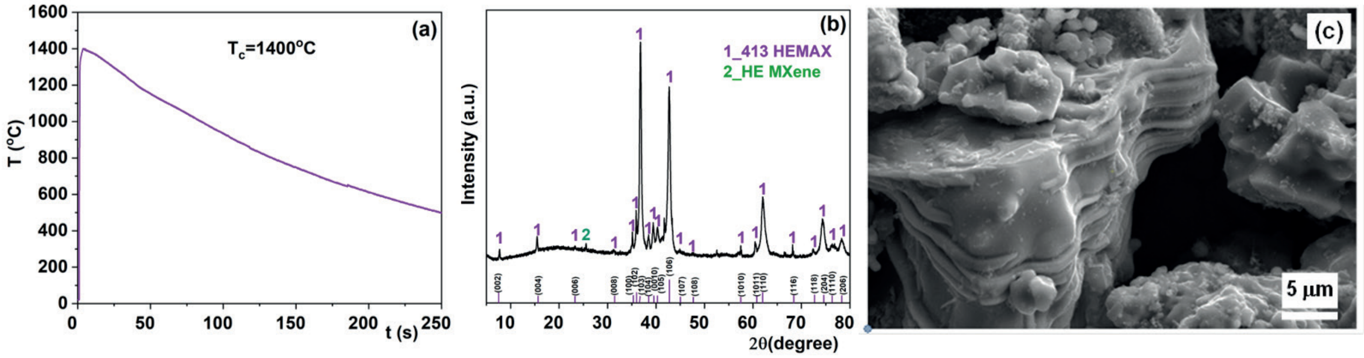

Fig. 1. Combustion thermogram (a), XRD pattern (b) and SEM image (c) of 413 high entropy MAX phase

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THE REACTION OF IODINE WITH SUBSTITUTED ALKYNES IN THE PRESENCE OF CADMIUM(II) ACETATE

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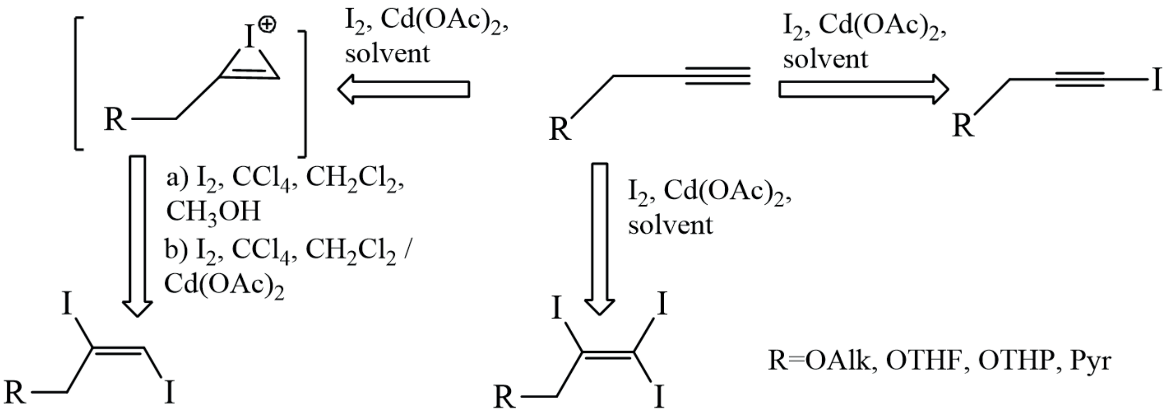
Organoiodine compounds represent one of the important class of compounds due to their unique chemical, physical and biological properties, and their widespread applications in life sciences and materials science. As chemical reactivity of the iodinenated compounds usually differs from many other organic compounds, various synthetic methodologies have been developed to introduce iodinenated substituents [1]. It should be noted that there are no data in the literature on the interaction of terminal alkynes with iodine in the presence of cadmium (II) acetate, however, it is known that the treatment of alkenes with iodine and cadmium (II) acetate in acetic acid gives high yields double bond additions.

In this work the features of the interaction of propargyl compounds with iodine in the presence of cadmium (II) acetate has been revealed. Ways of addition of iodine to the triple bond and substitution of the CH-acidic hydrogen atom are shown, and the role of solvents in iodination is optimized.



Based on the foregoing, it can be concluded that the chemoselectivity of mono-, di-, and triiodination of some acetylenic systems in the presence of cadmium (II) acetate is sufficiently affected by: the nature of the solvent, the reaction temperature, the ratio of the amounts of alkyl propargyl ether to iodine, and the methods of final processing reaction mixture. As can be seen from the obtained experimental data, the nature of the solvent significantly affects the course of the reaction in the presence of cadmium (II) acetate both in bipolar aprotic (DMSO) and polar protic solvents (methanol, ethanol), leading to the formation of iodolkines and triiodide. The highest yields of iodolkines were recorded using DMSO as the solvent. An excess of the propargyl substrate unambiguously leads to iodolkines. By varying the reaction conditions (using a twofold excess of iodine in DMSO (or methanol)) it is possible to achieve individual (one-pot) preparation of triiodides, the highest yields of which have been noted during the reactions in DMSO.

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MECHANISTIC DIVERSITY IN (DE)HYDROGENATION REACTIONS CATALYZED BY BIFUNCTIONAL TRANSITION METAL SYSTEMS

**Osipova E.S., Sedlova D.V., Nekrasov R.I., Peganova T.A., Gutsul E.I.,
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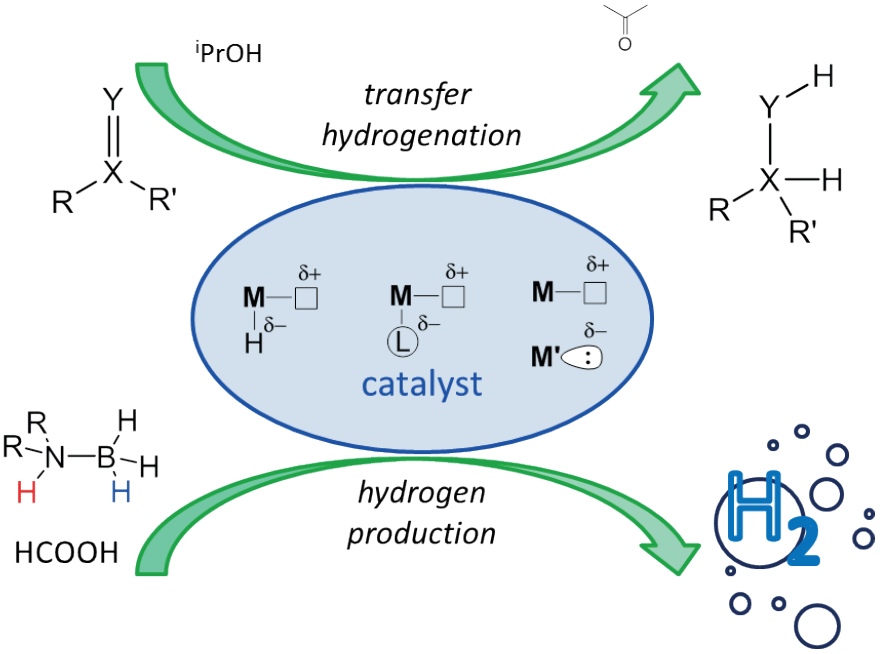
Bifunctional transition metal complexes in which core metal atom and a ligand fragment possess Lewis acid and base properties are nowadays under active investigation as potential catalysts for various transformations, e.g. (de)hydrogenation, dehydrogenative coupling, alkene isomerization, etc. In many of these reactions hydride species are active intermediates involved in substrate activation, activation or formation of molecular hydrogen and so on. In this talk we will discuss the mechanistic peculiarities and the role of noncovalent interactions in liquid organic hydrogen carriers dehydrogenation catalyzed by mono- or bimetallic systems [1-4], and transfer hydrogenation of ketones catalyzed by ruthenium and rhodium iminophosphonamide complexes [5-6].



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HEXANUCLEAR CLUSTER COMPLEXES OF MOLYBDENUM AND RHENIUM: ON THE WAY FROM THE SYNTHESIS TO POSSIBLE APPLICATIONS

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Octahedral cluster complexes described by the general $[\{Mo_6X_8\}L_6]^n$ и $[\{Re_6Q_8\}L_6]^m$ (X = Cl, Br or I; Q = S or Se; L = apical inorganic or organic ligands) harmoniously combine promising for various applications chemical and physical properties. In particular, such complexes exhibit high chemical and photostability of the $\{Mo_6X_8\}^{4+}$ and $\{Re_6Q_8\}^{2+}$ cluster cores, which are responsible for the high X-ray contrast and are responsible for the triplet excited state of luminescence. Compounds based on these clusters are characterized by broad luminescence spectra extending into the red/near infrared region (from ~550 to more than 950 nm) with impressive emission quantum yields. Various research groups have confirmed the biocompatibility and low toxicity of various octahedral metal cluster complexes. Together, these properties make the octahedral cluster complexes of molybdenum and rhenium attractive objects for creating various luminescent materials, photocatalysts and for biomedical applications.

Some details about the synthesis, structure and properties of various octahedral cluster complexes of molybdenum and rhenium as well as materials based on them will be presented at the conference.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation.

STUDY OF PHOTOCHEMICAL THREE-COMPONENT REACTIONS USING ELECTROSPRAY IONIZATION MASS SPECTROMETRY

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Photochemical reaction mechanisms investigation is a field of interest for chemists from different research groups [1]. Among the various analytical methods electrospray ionization mass-spectrometry (ESI-MS) proves to be one of the most sensitive, fast and accurate approach. One of the chellanges for photochemical mechanistic studies is a detection of short-lived species [2]. For this purpose, the different custom–made setups need to be designed [3].

In our laboratory we realized in practice approach for investigation of photochemical transformations and studying the reaction mechanisms by ESI-MS. We carried out the step-by-step online monitoring of photochemical transformations by merging of light source and mass spectrometer.

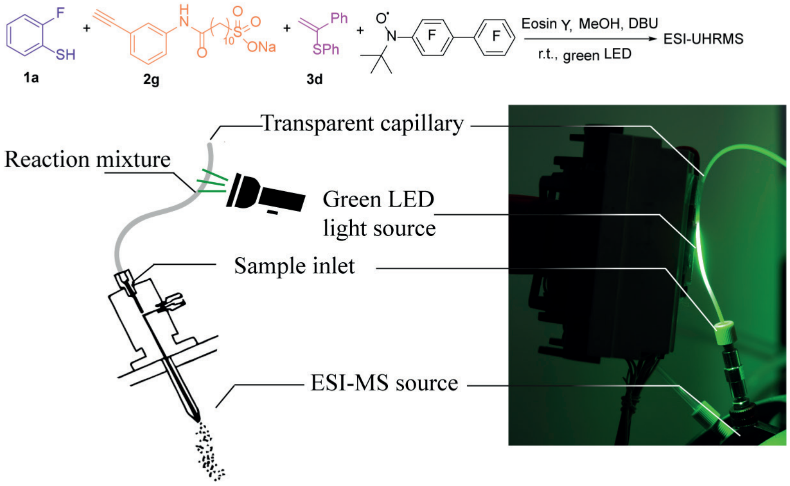

Figure 1. Photo-Chem-ESI device and its application for thiol-yne-ene reaction mechanism investigation [4].

We performed the thiol-yne-ene reaction with the trapping reagent inside a transparent capillary in the immediate vicinity of the ionization chamber of the mass spectrometer [4]. Under green light the signals corresponding to the ions of the products, by-products and trapped intermediates appeared immediately in mass spectrum. When the light was switched off the intensity of signals was dropped. These experiments proved the key role of the light in thiol-yne-ene transformation.

This work was supported by the Russian Science Foundation (grant № 21-13-00193).

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PUSHING THE LIMITS OF NON-TRANSITION ELEMENTS: THE POWER OF DPP-BIAN BISAMIDE LIGAND

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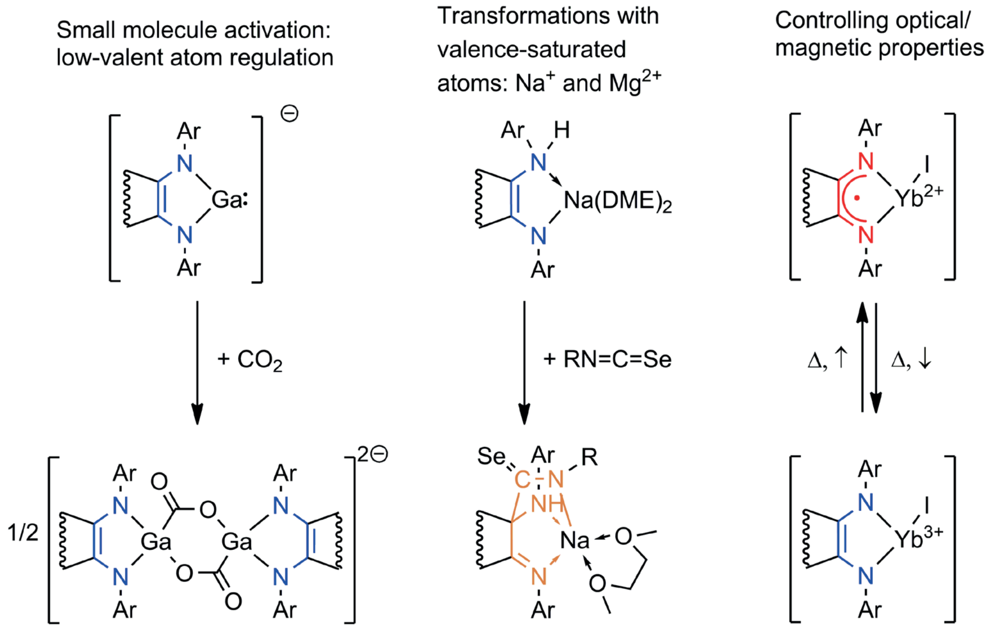
The transition elements are crucial in chemical processes, both on an industrial and laboratory scale, as highlighted by Nobel Prizes in 2001, 2005, and 2010. Non-transition elements are limited in their usefulness due to factors such as difficulty changing oxidation state, the inability to form multiple metal-metal bonds, and limited electron donor/acceptor capabilities. However, the discovery of low-valence chemistry techniques has allowed for the development of new transformations that were previously inaccessible to higher valency elements. One such technique is the use of cooperative ligands, which can participate in chemical transformations alongside the coordination center.

This report discusses the application of the dpp-bian (1,2-bis[(2,6-di-iso-propylphenyl)imino]acenaphthene) cooperative bisamide ligand in three areas:

(i) regulating the activity of low-valent atoms to activate small molecules and element-carbon bonds; (ii) carrying out chemical transformations involving valence-saturated atoms such as Na^+ and Mg^{2+}; (iii) controlling the optical and magnetic properties of a substance.



This work was supported by Russian Science Foundation (Grant No. 21-73-20153)

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THE ROLE OF PROTON AND HYDRIDE TRANSFER IN THE TRANSITION METAL COMPLEXES TRANSFORMATIONS

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Many chemical and biochemical (stoichiometric or catalytic) processes involve hydrogen transfer reactions where formation of noncovlent bonded intermediates is a key step.[1] In case of transition metal hydrides the formation of M-H$^{\delta-}\cdots$Acid or M-H$^{\delta+}\cdots$Base adduct entails an additional polarization (repolarization) of an M-H bond and, thus, activate the M—H bonds involved and stimulate further transformations. At that, the nature of the orbital interactions in the complex determines the reaction pathway: proton transfer to hydride ligand in the case of $\sigma_{MH}\rightarrow\sigma^*_{XH}$ donation, metal atom protonation in the case of $n_M\rightarrow\sigma^*_{XH}$, metal hydride deprotonation in the case of $n_N\rightarrow\sigma^*_{MH}$, and hydride transfer to Lewis acid in the case of $\sigma_{MH}\rightarrow n^*_B$. [2] The M—H bond polarization change character depends only from the partner type (acid or base) and not depend from its nature (Broensted or Lewis).[3] If noncovalent adduct contains both protic and hydridic hydrogens (dihydrogen bonded (DHB) complex MH$^{\delta-}\cdots{}^{\delta+}$HX) whole process should be considered as a concerted proton-hydride transfer, where extent of certain bond polarization determines the resulting mechanism (Figure 1).

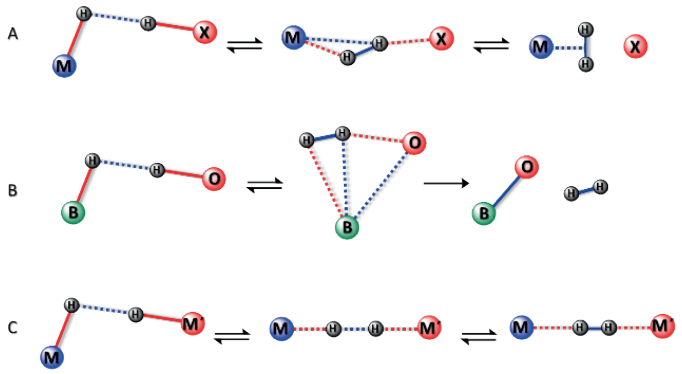

Figure 1. Representation of different processes involving DHB complexes.

The role of this processes in the stochiometric and catalytic reactions of different transition metal complexes will be discussed.[4-7]

Acknowledgements: *This work was financially supported by the Russian Science Foundation (project No. 19-13-00459)*

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PLATINUM AND RUTHENIUM COMPLEXES PROSPECTIVE FOR PHOTO-ACTIVATED CHEMOTHERAPY: FUNDAMENTALS OF PHOTOCHEMISTRY

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Photo-activated chemotherapy (PACT) is a prospective medical technology of anti-tumor treatment based on phototransformations of platinum metals complexes. Under the action of light the prodrugs are transformed into their active forms, which can effectively bind with the DNA preventing transcription and replication (cisplatine-like mechanism). In comparison with traditional photodynamic therapy based on triplet sensitizers, photochemotherapy does not need dissolved oxygen. It is important because many tumors are hypoxic. In spite of practical importance, photochemistry of potential anti-cancer complexes typically is not known in detail. Combining steady-state and time-resolved methods of photochemistry, we try to establish the mechanisms of photolysis, which can help in understanding the nature of therapeutic action.

We will consider photophysics and photochemistry of several platinum and rithenium complexes in the time range from hundreds of femtoseconds to minutes. The systems under discussion are:

(1) Mixed-ligand diazido complexes of Pt(IV), namely *cis,trans,cis*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$, *trans,trans,trans*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$ [1] and *trans,trans,trans*-$[Pt^{IV}(N_3)_2(py)_2(OH)_2]$ [2]. The feature of their photochemistry is the chain character of the first stage of photolysis (photoaquation). The therapeutic action of these complexes is caused by the combination of cisplatine-like binding of Pt(II) photoproducts to DNA and reactions of $N_3^{\bullet}$ radical.

(2) Simple Ru(II)-dmso complexes *trans*-$[RuCl_2(DMSO)_4]$ and *cis*-$[RuCl_2(DMSO)_4]$, which cisplatin-like light-induced cytotoxicity is based on ultrafast (characteristic times are tens of picoseconds) reactions of photochemical aquation / rearrangement [3, 4].

(3) Ru(II) bipyridine complex $[Ru(bpy)_2(NH_3)_2]^{2+}$, which is photochemically transformed to the cytotoxic DNA-binding form $[Ru(bpy)_2(H_2O)_2]^{2+}$. The photoaquation occurs in the microsecond time domain starting from the lowest electronic-excited (triplet) state of the initial complex.

In all the cases, quantitative information on the photophysics and photochemistry including quantum yields and rate constants of the reactions of short-live intermediates is provided.

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OPTIMIZED, COST EFFECTIVE, ROBUST AND REPRODUCIBLE PROCESS FOR THE SYNTHESIS OF DRONABINOL

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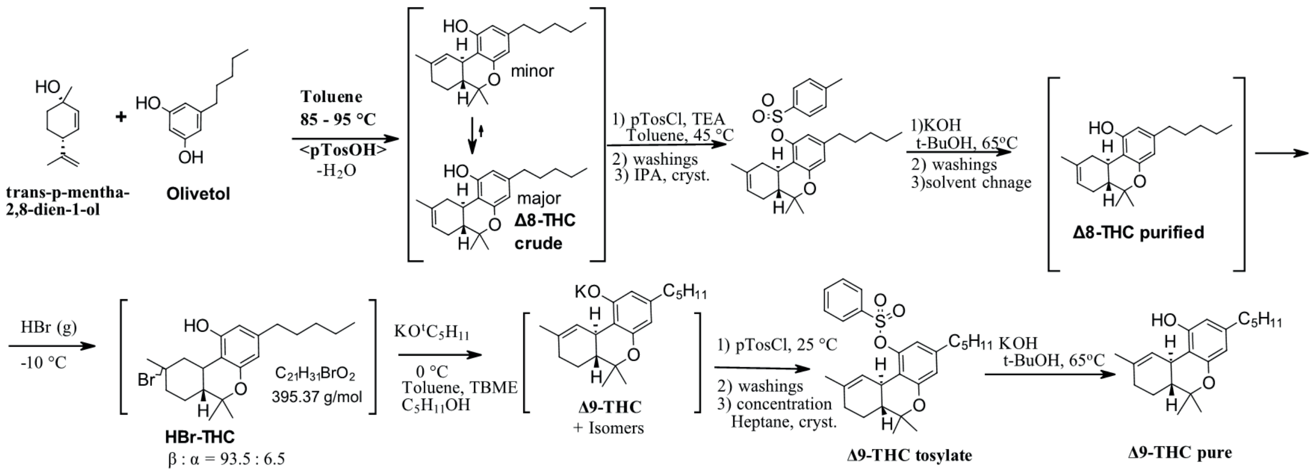
Dronabinol is a generic name for the molecule of Δ⁹-tetrahydrocannabinol (Δ⁹-THC). It has indications as an appetite stimulant, antiemetic, and sleep apnea reliever[1]. It is approved by the FDA, as safe and effective, for HIV/AIDS induced anorexia and chemotherapy induced nausea and vomiting only[2][3]. The latter increases pharmaceutical interest and triggers development of more efficient synthetic approaches of this cannabinoid compound.

The main challenge for a large-scale manufacturing process of Δ⁹-THC lies with the properties of the compound, being an oily substance sensitive to isomerization and air oxidation. Isolation of the pure compound is thus troublesome and often entails the use of multiple chromatographic separations and purifications.

Conversion of the Δ⁹/ Δ8-THC(s) to crystalline derivatives for purification purposes, by making use of the phenolic OH-moiety as esters of carboxylic-, carbamic- or sulfonic acids, has been reported [4].

Goal of the work was to provide robust and reproducible process for the large-scale manufacturing of Δ⁹-THC by using tosylate derivatives for the purification purposes.



It was found that the content of desired β-Hal THC in isomeric mixture can be significantly increased by using HBr instead of HCl in the hydrohalogenation step. Eventually, the best conditions for the elimination step providing 98-99% conversion of β-Br-THC to Δ⁹-THC and non-conversion of α-Br-THC, have been developed.

With the provided procedure after cleavage of Δ⁹-THC tosylate the content of THC isomers is stable and the product meets all specifications of the API.

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SYNTHESIS AND FURTHER TRANSFORMATIONS OF NEW DERIVATIVES OF BUTENOLIDES

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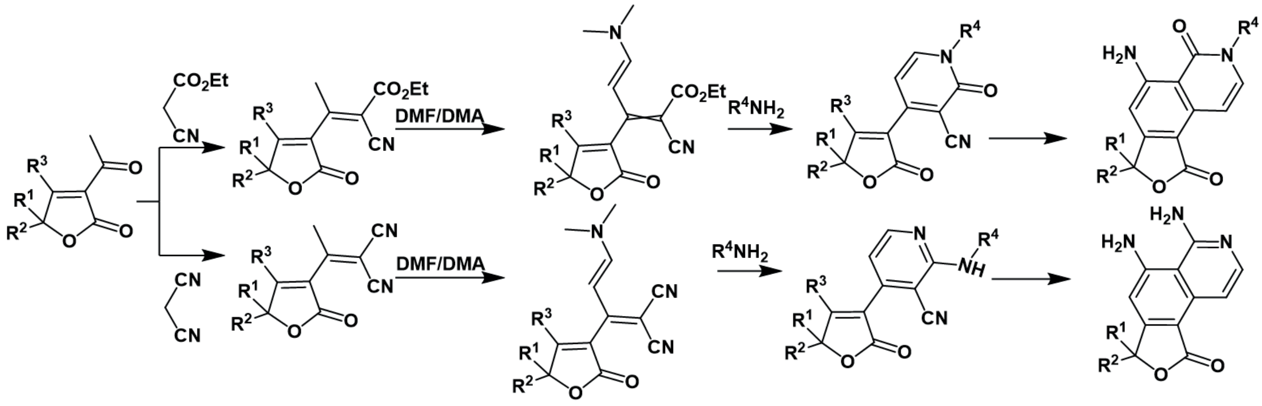
3,4-Disubstituted furan-2(5H)-one fragment is present in many natural, biologically active compounds. In particular, furan-2(5H)-one derivative containing nonidentical aromatic substituents in positions 3 and 4 of the furan ring exhibit various biological activities [1]. An example is the anti-inflammatory drug Rofecoxib [4-(4-methanesulfonylphenyl)-3-phenylfuran-2(5H)-one]. Eutypoid A isolated from the marine mangrove fungus Eutypa sp. (# 424)[2] and gymnoascolides[3] isolated from the Australian soil ascomycetes Gimnoascus reessii and Malbranchea filamentosa IFM41300 are natural 3,4-disubstituted furan-2(5H)-ones.

We started with 3-acetyl lactones as primary compounds and using Knoevenagel reaction obtained corresponding compounds, which further reacted with dimethylformamide dimethyl acetal (DMF/DMA). In the final stage the reactions with primary amines lead to disubstituted furan-2(5H)-ones.[4-7]



Further intramolecular cyclization if possible between R^3 =Me and cyano group of pyridines or pyridone derivatives. Depending on the derivative the results of the reactions are two different skeletons of final compounds.

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MULTISCALE ELECTRON MICROSCOPY STUDIES IN PURSUIT OF CATALYTIC SPECIES IN LIQUID REACTION MEDIA

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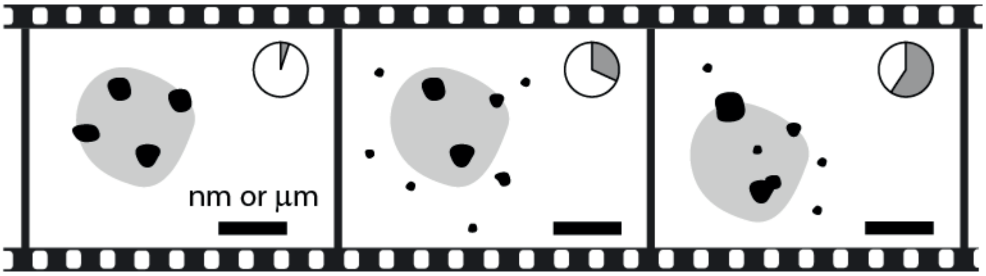
The current level of understanding of the mechanisms of liquid-phase catalytic processes used in fine organic synthesis emphasizes the important place of nano- and microscale phenomena in the general picture of the evolution of catalytically active species during the reaction [1]. The transition from the level of individual molecules with clearly defined chemical structures to more complex spatially heterogeneous systems operating at different levels of matter organization requires the use of new physicochemical analytical methods that allow the simplest and most efficient extraction of structural information [2]. Modern techniques based on electron microscopy in liquid phase allow direct observation of chemical processes in real time with high spatial resolution. To date, a number of approaches have been developed to study liquid-phase organic and organometallic systems under high vacuum conditions of an electron microscope chamber and the destructive effect of an electron beam. Among them: cryogenic electron microscopy of frozen samples, in situ observations in non-volatile ionic liquids, as well as electron microscopy analysis of the samples inside vacuum-tight microcells, which preserve the liquid reaction medium in its native state [3].



Using liquid-phase electron microscopy and a number of related techniques, the transformations of the catalytically active phase for the palladium-, nickel- and copper-mediated carbon-carbon and carbon-sulfur bond formation reactions were studied at the nano- and microscale levels. Application of the electron microscopy method made it possible to directly observe the formation of “cocktail”-type catalytic systems based on zero-valent metal nanoparticles in the case of C-C bond formation reactions [4] as well as on micro and sub-microparticles of sulfur-containing coordination polymers in the case of C-S coupling and heterofunctionalization processes [5-7].

This work was supported by the Russian Science Foundation (RSF grant No 22-13-00286).

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SYNTHESIS OF PRECURSORS FOR OBTAINING TARGETED RADIOPHARMACEUTICALS BASED ON SHORT PEPTIDES, ANALOGS OF THE HORMONE SOMATOSTATIN

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The development of radiolabeled peptides with high affinity and specificity for over expressed receptors for certain types of cancer is a rapidly growing area of nuclear medicine.

Octreotide, a synthetic, more stable analogue of somatostatin, is widely used in radiopharmaceuticals (RP) for the diagnosis and treatment of neuroendocrine tumors. However, it has a number of disadvantages for clinical use, namely a relatively short half-life and immunogenicity. To solve these problems, radiopharmaceuticals based on shorter peptides have been proposed.

Methods have been developed for obtaining a number of conjugates with an ethylenediamine linker [1], and conjugates with protected peptides, to increase their resistance to proteolysis in the body. A fundamentally new bifunctional chelator that binds to peptides through the formation of a phenylhydrazone linker has been proposed, and a number of its conjugates with various peptides have been obtained.

In the development of these works, we synthesized new precursors with various linkers for the design of targeted RPs based on the pharmacophore fragment of the somatostatin hormone tetrapeptide H-Phe-D-Trp-Lys-Thr-OH [2]. Linkers based on hydrazine, ethylenediamine, and aminocaproic acid were used. Additionally, this tetrapeptide has been modified by adding 1,3-thiazolidinecarboxylic acid (Thz) and L-proline (Pro) to it to improve cytotoxic properties. Synthesis routes have been developed and conjugates of peptides with chelators have been obtained.

Research was done using equipment of «Research Chemical and Analytical Center NRC «Kurchatov Institute» Shared Research Facilities under project's financial support by the Russian Federation, represented by The Ministry of Science and Higher Education of the Russian Federation, Agreement No. 075-15-2023-370 dd. 22.02.2023.

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NOVEL TYPE OF NEUTRAL MIXED-VALENCE SYSTEMS: THE AMINYL RADICAL-CATIONS WITH THE CHARGE CANCELED

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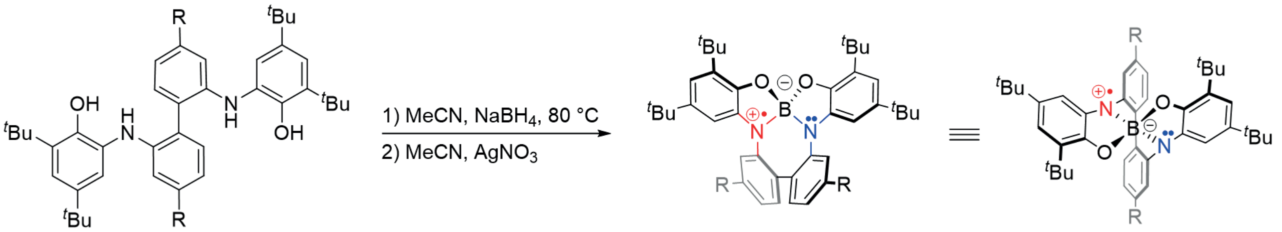
Compounds containing atoms in unusual valence states often exhibit interesting properties. Thus, mixed-valence (MV) systems are of interest as hole-transporting materials in organic electronic devices; they provide valuable insight into intramolecular electron and charge transfer phenomena in biophysical processes, etc. The overwhelming majority of pure organic mixed-valence compounds known to date are radical-ions; neutral mixed-valence radical systems are extremely rare.

Novel type of stable MV aminyl radicals that has no analogs was designed and synthesized in almost quantitative yield using the facile one-pot procedure that can be easily gram-scaled. Two “halves” of the molecule are connected via the spiro boron center and the biphenyl bridge; all three linkers are almost orthogonal to each other. Due to orthogonality, all parts of the molecule are largely independent, but, being combined into a single whole, they can exert a pronounced stabilizing effect on the redox centers, which are in unusual valence states. The biphenyl bridge does not directly participate in the spin delocalization, but it provides stability of the aminyl radicals and influences the rate of electron transfer between the redox centers in the different valence states. Variation of the electronic properties of the biphenyl bridge significantly influences the reorganization energy of the MV system and alters the energy barrier separating two spiro-conjugated redox centers.

The experimental and quantum-chemical in-depth study of new radicals revealed a number of important features, which make them promising for practical applications. Their “panchromatic” properties (strong absorbance in a broad spectral range, including the near IR region) make them of potential interest as solar-cell materials. Stable themselves, the radicals can form stable cations and anions under one-electron oxidation and reduction, thus showing ambipolar redox behavior. All radicals demonstrate the SOMO-HOMO inversion (SHI) that may contribute to the enhanced stability of new open-shell molecules. The “depth” of the inversion is dependent on the substituent in the biphenyl bridge. Importantly, the SHI phenomenon was supported experimentally, using spectroelectrochemical UV-Vis and ESR study: formation of the triplet biradicals was directly detected using the ESR method.

Synthesis, the peculiarities of the electronic structure of the novel MV radicals and prospects of their practical use will be discussed in the presentation.



R	H	^{t}Bu	F	OMe	NMe$_2$	CF$_3$
Yield	95 %	91 %	94 %	79 %	84 %	84 %

Acknowledgement: *The work was supported by Russian Science Foundation (Project N 22-13-00093)*

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GENERATION OF NO FROM NITRITE AND NITRATE BY METALLOPORPHYRIN-CATALYZED METABOLISM WITH H_2S/THIOL

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Nitrite (NO_2^-) has been shown in the past decade to be an important species in mammalian physiology and a source of nitric oxide (NO) that acts as vasodilator and intrinsic signaling molecule [1]. It has been shown that biological thiols (cysteine and gluthathione) reduce the water-soluble iron porphyrin nitrite through an oxygen atom transfer mechanism (OAT) that leads to the formation of iron porphyrin nitrosyl and the corresponding sulfenic acid [2]. Another detailed studies demonstrated that the reaction of a similar porphyrin nitrite with hydrogen sulfide (H_2S) , which is now accepted as a third signaling molecule along with CO and NO, also leads to the formation of porphyrin nitrosyl species [3].

In contrast to nitrite, biological nitrate (NO_3^-) is generally considered as relatively unreactive end-product of nitrogen metabolism in mammalian systems. However, we have showed earlier, that nitric oxide is able to activate iron porphyrin nitrate through OAT to produce the reduced species [4]. At the same time, until now the H_2S has not yet been considered as a possible mediator of this reaction.

Here we present the low-temperature FT-IR and Uv-Vis spectroscopic results of the reaction H_2S and EtSH with sublimed layers containing the CoTTP(NO_2) nitro, MnTTP(ONO) nitrito and FeTTP(ONO_2) nitrato porphyrin complexes (TTP - meso-tetra-p-tolylporphyrin dianion $^{2-}$). The eventual products of this reaction in all cases are the respective nitrosyl complexes CoTTP(NO), Mn(TTP)(NO), FeTTP(NO) and respective disulfides. The mechanism of the reactions that accounts for all spectroscopic observations with the use ^{15}N and ^{18}O labeled and natural abundance NO_x is proposed to proceed through the O-atom transfer reaction from coordinated NO_x^- to H_2S and EtSH. The transient intermediates detected upon monitoring the reaction from 77K to room temperature and final products, analyzed by mass spectrometry are discussed.

Acknowledgements: The financial support from SCS of the Republic of Armenia (Project 21AG-1D040) is gratefully acknowledged.

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MECHANISTIC INSIGHT INTO THE LOW-TEMPERATURE BOOSTING OF ZIF-67 ELECTROACTIVITY IN OXYGEN EVOLUTION REACTION

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An efficient electrocatalyst is crucial for sustainable hydrogen-fuel production, where cobalt oxyhydroxide is one of the most active catalysts for alkaline water splitting. Here, we designed a series of Co-based catalysts fabricated by direct low-temperature calcination of ZIF-67 for electrocatalytic oxygen evolution reaction (OER). Interestingly, the treatment of the pristine ZIF-67 by the temperature of only 200 degrees C was found to induce the most electroactive composition with a high electrochemically active surface of 373.5 cm(2) and turnover frequency of 129.7 s(-1), while a high specific surface area (1745 m(2).g(-1)) is preserved. It resulted in a robust catalyst with a low overpotential of 317.8 mV at 10 mA.cm(-2) and accelerated charge transfer, leading to improved performances in electrochemical energy conversion from water. Moreover, using in situ spectroscopy, XRD and microscopic techniques the active intermediates, for example, M-O, M-OH, and M-OOH were revealed and thus the exact mechanism of the reaction was proposed. Due to the formation of active species a lattice oxygen mechanism (LOM) was revealed [1]

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NAMED REACTIONS IN ACTION: A STRATEGIC APPROACH FOR OBTAINING ENANTIOMERICALLY ENRICHED UNNATURAL α-AMINO ACIDS

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The search for new biologically active substances has always remained an urgent task. Among the known compounds, amino acids occupy a special place. As a part of natural products, such as antibiotics, peptides, they played a significant role from the very first days of their discovery. Due to the presence of two functional groups that differ from each other in all physicochemical properties, amino acids are easily modifiable having become indispensable components of modern medical chemistry and prove to be increasingly important in the composition of new drugs. These "unusual" amino acids have a wide range of properties and irreplaceable in modern medical chemistry. The use of unnatural amino acids as inhibitors of enzymes – targets of drugs is one of the important areas of pharmacology.

In this work, we present an interesting approach that involves the using of named reactions, including Glaser and Mannich, on the amino acid moiety of square-planar Ni(II) complexes. Through this method, we successfully synthesized a range of novel enantiomerically enriched non-protein amino acids.

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FORMATION OF HYDROGEN-INDUCED MAX PHASES BASED ON NONSTOICHIOMETRIC CARBOHYDRIDES OF IV-V GROUP METALS AND ALUMINUM IN THE HYDRIDE CYCLE AND STUDY OF THEIR PHYSICAL AND CHEMICAL PROPERTIES

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MAX Phases combine the advantages of both ceramic and metallic materials and in some publications, they are referred as “metal ceramics”. They are multilayer chemical compounds. Current methods of their synthesis are unsuitable for their mass production. The creation and development of new methods and technologies for their producing are urgent tasks of materials science. At IChPh of NAS RA, new, highly efficient “hydride cycle” (HC) method has been developed for synthesis of refractory metal alloys. The gist of the method is the use of transition metal hydrides as starting materials. In the present work, for the first time HC was used in the synthesis of Ti_2AlC, Ti_3AlC_2, $Ti_{0.9}Nb_{0.1}C_{0.5}Al_{0.5}$, $Ti_{0.8}Nb_{0.2}C_{0.5}Al_{0.5}$, $Ti_{0.7}Nb_{0.3}C_{0.5}Al_{0.5}$ etc. MAX phases. Three reactions were studied: $TiC_{0.45\div0.55}H_{0.22\div1.17+0.5}Al \rightarrow Ti_2AlC + H_2\uparrow$, $TiC_{0.67}H_{0.31\div0.39}+0.33Al \rightarrow Ti_3AlC_2 + H_2\uparrow$ and $Ti_{0.9\div0.7}Nb_{0.1\div0.3}C_{0.4\div0.5}H_{0.61\div1.1} + 0.5Al \rightarrow (Ti_{0.9\div0.7}Nb_{0.1\div0.3})_2AlC + H_2\uparrow$. Preliminarily, HCP $TiC_{0.45}H_{0.22\div1.17}$, FCC $TiC_{0.67}H_{0.31\div0.39}$ and $Ti_{0.9\div0.7}Nb_{0.1\div0.3}C_{0.4\div0.5}H_{0.61\div1.1}$ carbohydrides were synthesized in combustion mode (SHS). The influences of the titanium carbohydride/aluminum ratio, grain sizes of titanium carbohydrides (micro and nano sizes), pressure of charge compaction, dehydrogenation/sintering modes (heating temperature and rate) on the characteristics of the HC-synthesized phases were studied. For certification of the obtained phases, the chemical, differential thermal, X-ray phase, SEM analyses were used. The XRD and DTA analyses of the intermediate and final products permitted to follow the path of the MAX-phases formation: MAX-phases in HC formed in solid phase reaction, by diffusion mechanism, in one technological stage. A number advantages of HC method relative to the traditional ones in the synthesis of the MAX-phases were demonstrated.

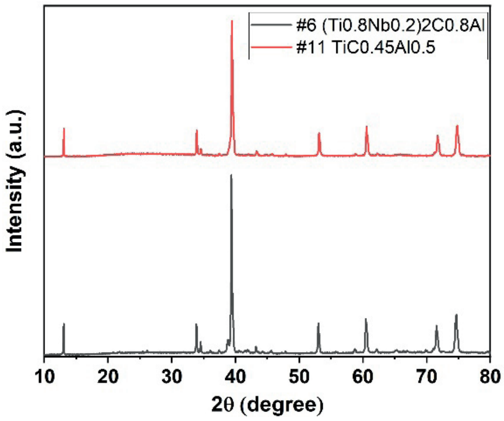

Fig. 1. Diffraction patterns of TiC0.45Al0.5 and (Ti0.8Nb0.2)2AlC0.8 MAX phases, received in HC upon heating at 1000°C for ~ 1 hour.

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IS IT REASONABLE TO REPLACE NOBLE METALS WITH EARTH-ABUNDANT METALS IN CATALYSIS? THE UNEXPECTED RESULTS OF COST ANALYSIS.

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One of the clear general trends in academic research of catalytic reactions in the 21st century is the intention to replace noble metal catalysts with their 3d metal analogs. Apart from other reasons, the need for such a replacement is commonly justified by the high cost of the noble metals. We carried out a cost analysis of the syntheses of isoquinolone heterocycles by various C-H activation methods and demonstrated that many organic substrates and reagents are, in fact, more expensive than catalytic amounts of the noble metals. Therefore, in contrast to popular opinion, the use of 3d metals in catalysis may have no economic benefits. This is especially true for the small-scale, late-stage functionalization reactions, which are popular among academic researchers.

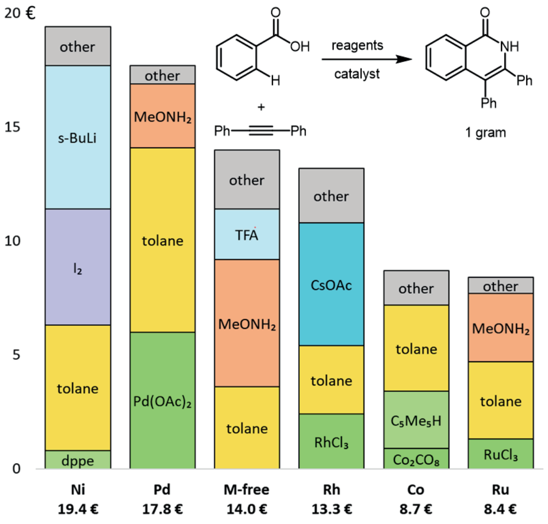

Figure 1. Price diphenyl-isoquinolone (in € per gram) obtained from benzoic acid and tolane by six methods, involving Ni, Pd, Rh, Co, and Ru-based catalysts, or via metal-free synthesis.

Acknowledgements

This work was supported by the Russian Science Foundation (grant # 17-73-30036).

DEUTERIUM AND ^{13}C-LABEL INCORPORATION IN BIS(PHOSPHINEOXIDE)ETHANES USING CALCIUM CARBIDE

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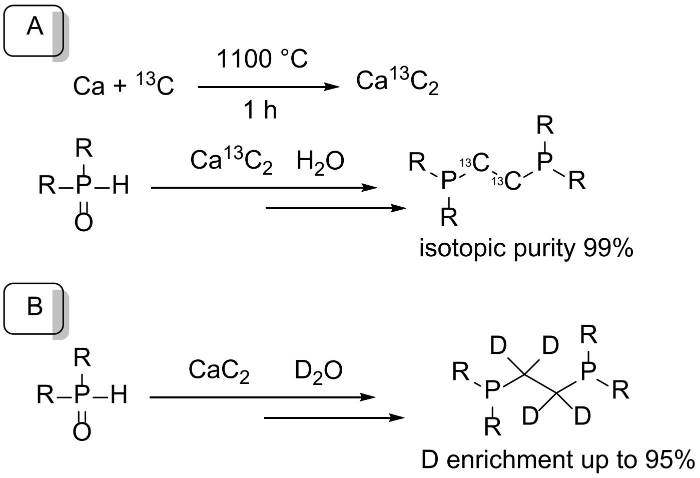
Incorporation of stable labels into organic molecules is a valuable opportunity to investigate mechanisms of reactions and to define structure of complex molecules. Non-radioactive deuterium and ^{13}carbon labels plays crucial role in these tasks. Deuterium incorporation provides particular information about structural combination of labeled molecules, and ^{13}C label sufficiently increases concentration limits of analyzed substrates using NMR spectroscopy. Although the labeled compounds are in high demand, there is still lack of the approaches to introduce labels. Many compounds were synthesized in labeled and non-labeled forms; however, the scope of starting components (label carrier) is very limited.

In this work, calcium carbide was considered as an efficient carrier of ^{13}C label (Scheme 1, A); and hydrolysis of carbide with D2O was developed as an approach to incorporate D-label is a series of organic substrates (Scheme 1, B).



Scheme 1. Calcium carbide as an initial compound in labelling:
A) ^{13}C label incorporation; B) D-label incorporation

As a result, a series of labeled phosphineoxides was synthesized with good yields and high D and ^{13}C enrichment.[1] Isolated compounds were stable and ready for further transformations. The structure and label insertion were confirmed by NMR, XRD and single X-ray analysis. The synthesized phosphineoxides were successfully hydrogenated to the corresponding phosphines according to standard $HSiCl_3$-based protocol.

^{13}C-labeled calcium carbide was synthesized from calcium metal and commercially available ^{13}carbon by heating a mixture in an oven for 1h according to the previously described procedure.[2] Deuteration was also developed previously using O,S,N-vinyl derivatives.[3] Labeling of P-containing compounds described here is completely new.

The work was supported by RSF (№21-73-20003).

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PERICYCLIC DANCES WITHIN SEVEN-MEMBERED SYSTEMS: TOWARDS SUPERIOR FLUOROPHORES

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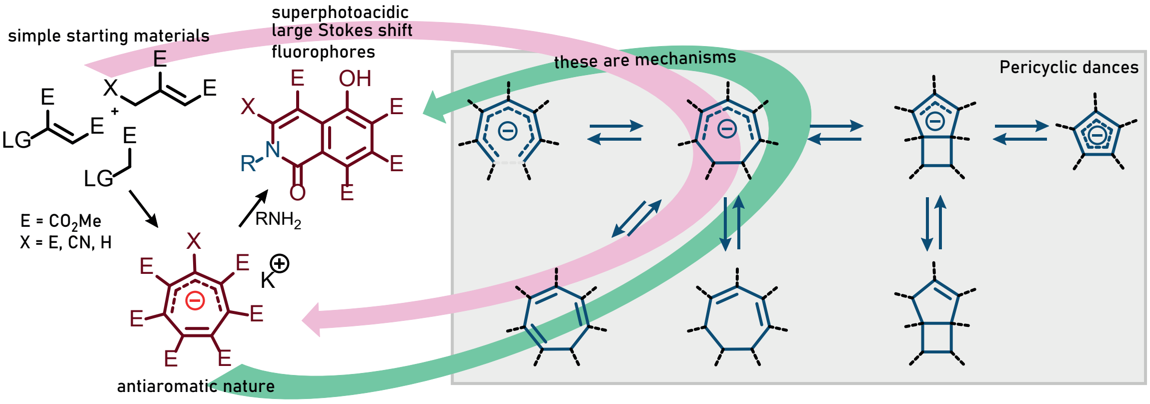
Pericyclic reactions are a powerful method to create and modify carbo- and heterocyclic compounds. Using reaction cascades including electrocyclic transformations at some stages we have developed approaches to the synthesis of heptasubstituted electron-deficient cycloheptatrienes and their corresponding anions [1-2]. We investigated the interconversions between various seven-membered systems as well as five-membered cyclopentadienes via the "pericyclic dances" and harnessed them to lead the dance in nearly any direction [2-4].



Cycloheptatrienes and their salts we used in the synthesis of a new class of fluorescent dyes via again the pericyclic dance cascade. The fluorophores possess a noticeable quantum yield and a large Stokes shift which is brought about by their superphotoacidity. In the ground state 5-hydroxyisoquinolones demonstrate pKa of 3.4 while the excited molecules are strong acids with pKa values down to -6.0 and thus they ionize in aqueous media. Therefore, even in a strong acidic medium we observe absorption of a neutral form and fluorescence of anions [5].

The work was supported by the Russian science foundation (grant #23-23-00624).

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NOVEL APPROACHES TO TRANSITION-METAL CATALYSED C-H FUNCTIONALIZATION OF FURAN CORE IN FURAN PLATFORM CHEMICALS

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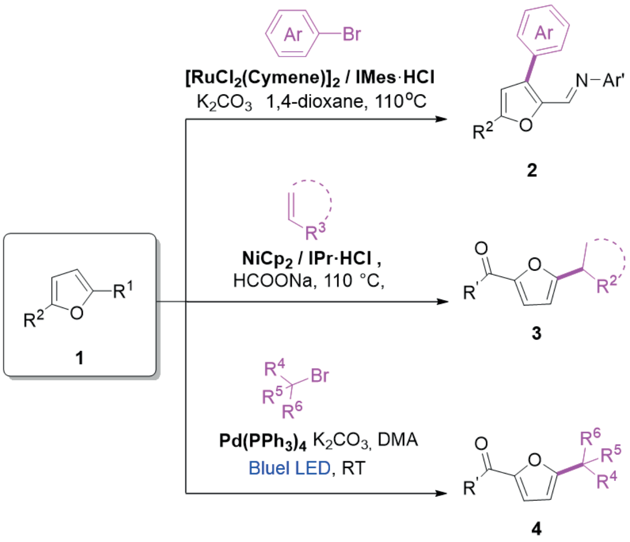
Plant biomass is considered as the most important renewable feedstock for the chemical industry and energy. One of the most important ways of processing plant biomass is the hydrolysis and dehydration of polysaccharides into furan platform chemicals, such as furfural, 5-hydroxymethylfurfural (HMF) and acids, esters, amides, etc. [1]. New routes of furan platform molecules functionalization relied on C-H bond activation reactions attracted much attention in recent years. The C-H activation approach can significantly extend possibilities of using biomass-derived furan platform compounds as renewable feedstock in chemical industry.

In this study, we developed new catalytic systems for selective C(5)-H and C(3)-H bonds functionalization of bio-based furans. The developed systems are relied on the use of Pd [2], Ni [3], and Ru complexes and salts in combination with different types of ligands such as NHC or phosphines (Scheme 1).



Scheme 1: Developed catalytic system

We also demonstrated using of visible light to activate the palladium-catalyzed C-H alkylation of furan core [2]. Versatile substrates including derivatives of furoic acid and aldehydes were employed. Developed approaches allow to obtain 5- or 3- functionalized furans (aryl or alkyl derivatives) with good to excellent yields from readily available furan platform compounds and provide new opportunities for deep processing of plant biomass.

The work has been supported by the Russian Science Foundation (RSF grant 23-73-00088).

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STRATEGY OF C-H FUNCTIONALIZATION IN THE DESIGN OF PHARMACOLOGICALLY ACTIVE COMPOUNDS AND FUNCTIONAL MATERIALS

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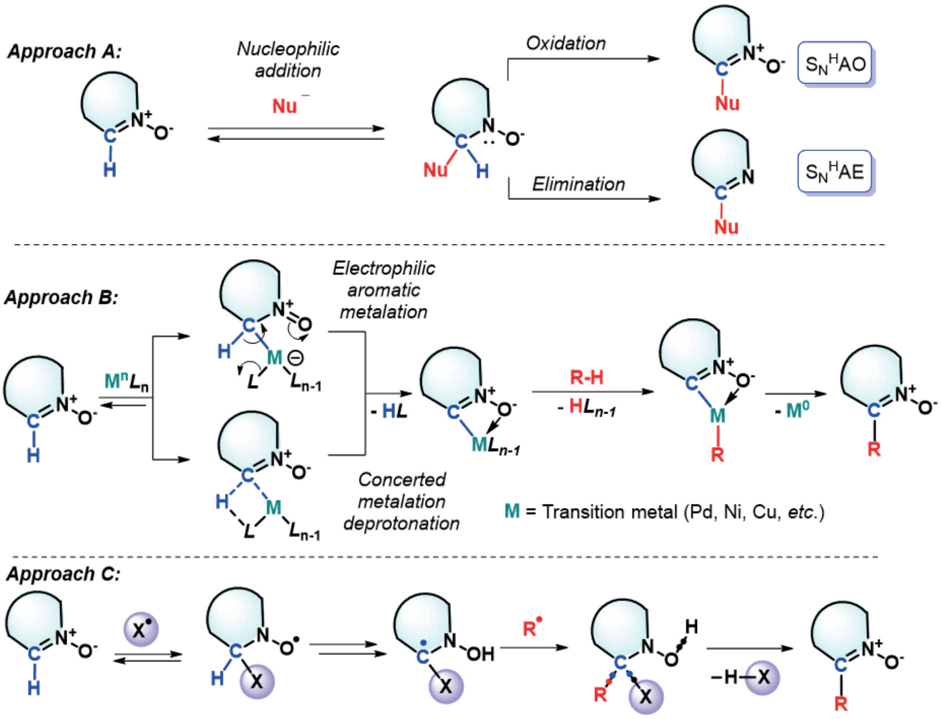
The methodology of C-H functionalization is well established as a convenient synthetic tool in the chemistry of azaheterocyclic compounds. In particular, this strategy provides efficient approaches to design target organic molecules of various architectures for medicinal chemistry and materials science. Particularly, these synthetic schemes have successfully been applied by our group to modify both aromatic and *non*-aromatic azaheterocycles by means of creating novel C-C and C-N bonds using by metal-free nucleophilic substitution of hydrogen S_N^H (*Approach A*), transition metal-mediated cross-dehydrogenative coupling (CDC) reactions (*Approach B*), as well as radical-mediated cross-dehydrogenative coupling (CDC) reactions (*Approach C*) [1, 2].



A: Nucleophilic substitution of hydrogen reactions according to «Addition-Oxidation» S_N^H(AO) and «Addition-Elimination» S_N^H(AE) protocols
B: Transition metal-mediated cross-dehydrogenative coupling (CDC) reactions
C: Metal-free radical-mediated cross-dehydrogenative coupling (CDC) reactions

The research was supported by the Russian Science Foundation (Project No. 23-63-10011).

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SUPRAMOLECULAR INTERACTONS IN THE CHEMISTRY OF BISPIDINES: FROM BIOLOGICAL TO CATALYTIC ACTIVITY

Medved'ko A.V., Dalinger A.I., Zakirov A.M., Mirakbarov M.H., Chistyakov G.D., Troshin I.I., Vatsadze S.Z.*

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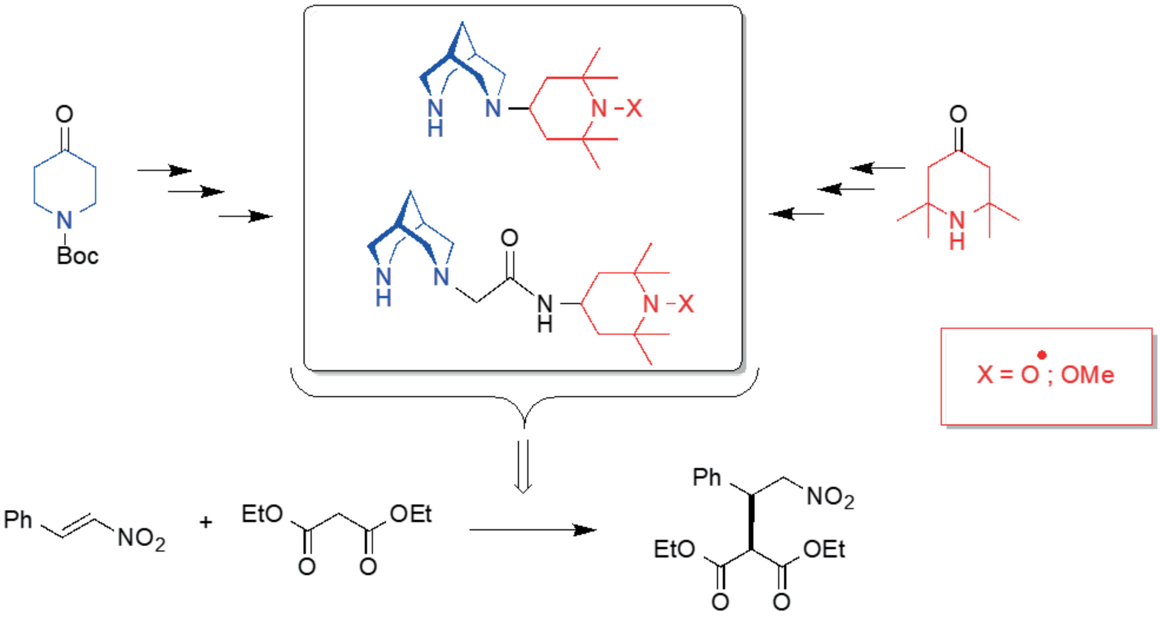
Currently, bispidines are being studied in the following areas: catalysis (organocatalysis and metal complex catalysis), biologically active molecules, components of organic materials. Their supramolecular chemistry is recently reviewed in [1] and the anti-viral activity is reported in [2].

The possibility of functionalization of both nitrogen atoms of the bispidine core with different substituents (see, for example [3]) allows one to design the catalitycally active molecule equipped with various groups possessing the additional properties (spectral, chiroptical, magnetic etc.).



The report will describe the achievements in the *operando* study of catalytic processes involving bispidines using *reporter groups* specially introduced into the catalyst structure (examplified by organocatalytic addition of diethyl malonate to nitrostyrene).

This work was supported by the Russian Science Foundation (project no. 23-73-00122).

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ELECTROCHEMICALLY MEDIATED OXIDATIVE C-C AND C-HET COUPLING

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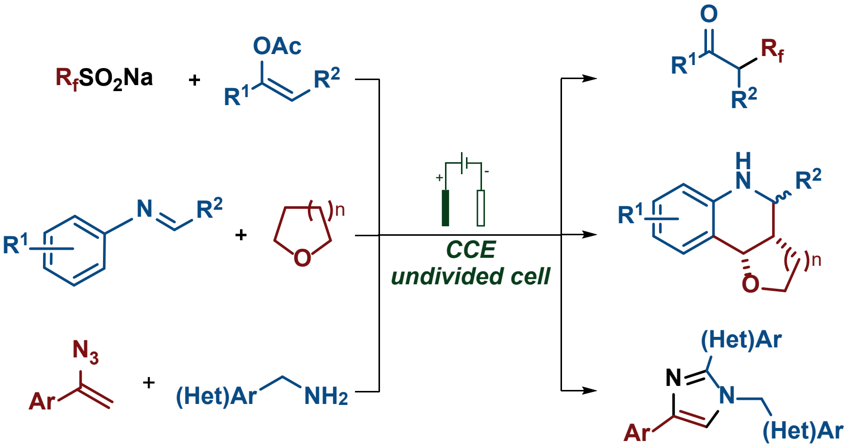
Nowadays, electroorganic synthesis is considered as one of the most actively developing areas of modern organic chemistry. This study develops state-of-the-art synthetic organic electrochemistry – methods for C-C and C-Het bonds formation.

The electrochemical synthesis of fluorinated ketones from enol acetates and R_fSO_2Na in an undivided cell under constant current conditions was developed.[1] The electrosynthesis proceeded *via* perfluoroalkyl radical generation from sodium perfluoroalkyl sulfinate followed by addition to the enol acetate and transformation of the resulting C radical to a fluorinated ketone. The method is applicable to a wide range of enol acetates and results in the desired products in yields of 20 to 85%.



We disclosed the electrochemical synthesis of cyclic ether-annulated tetrahydroquinolines from imines and cyclic ethers.[2] The electrosynthesis proceeds *via* the enol ether formation from ethers following the aza-Diels-Alder [4+2] cycloaddition. The non-obviousness of the discovered process is due to the fact that cyclic ethers, common solvents for electrochemistry, are oxidized into enol ethers while the electrochemically labile imines must wait for the formation of a partner for cycloaddition while remaining unconsumed. Synthesized cyclic ether-annulated tetrahydroquinolines exhibit high antifungal activity, which is superior to the commercial fungicide Triadimefon.

Also, an electrochemically induced synthesis of imidazoles from vinyl azides and benzyl amines was reported.[3] The discovered transformation is a multistep process whose main steps include the generation of electrophilic iodine species, 2*H*-azirine formation from the vinyl azide, followed by its reactions with benzyl amine and with imine generated from benzyl amine. The cyclization and aromatization of the obtained intermediate lead to the target imidazole. Despite possible cathodic reduction of various unsaturated intermediates with C=N bonds, the efficient electrochemically induced synthesis of imidazoles was carried out.

This work was supported by the Russian Science Foundation (project 21-13-00205).

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DOMINO REACTIONS FOR THE SYNTHESIS AND FUNCTIONALIZATION OF INDOLE DERIVATIVES

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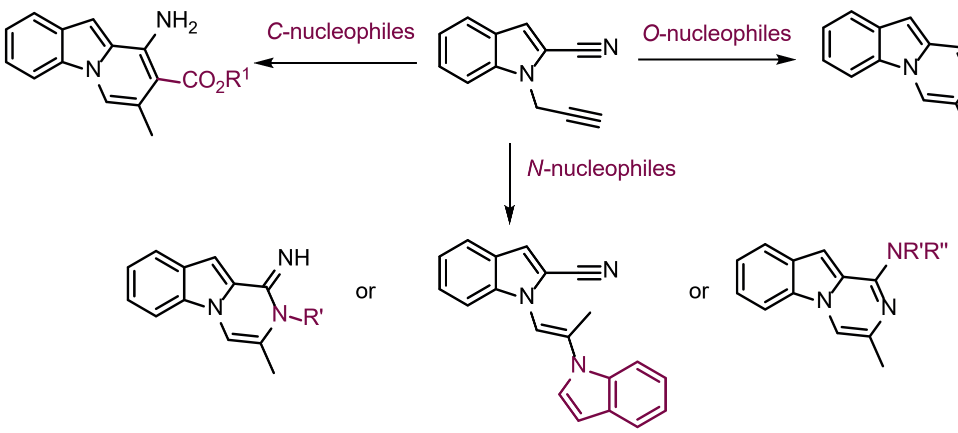
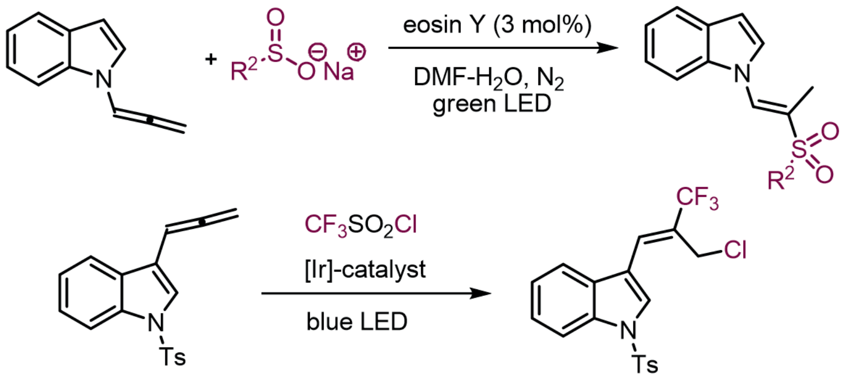
Indole derivatives are crucial heterocyclic motifs for drug discovery, agrochemistry, and materials sciences. The search for new effective syntheses and modifications of indoles is ongoing. A series of domino transformations of 1-(propargyl)indol-2-carbonitriles has been developed for the synthesis of annulated indoles under the action of C- [1], O- [2] or N-nucleophiles [3]. In general, the domino processes proceed through an alkyne–allene rearrangement, nucleophilic addition, and nucleophilic cyclization reaction sequence.



Photocatalyzed reactions of (allenyl)indoles are useful for the synthesis of valuable indole derivatives. We have developed an effective photocatalyzed hydrosulfonylation of *N*-(allenyl)indoles [4], and chlorotrifluoromethylation of 3-(allenyl)indoles [5].



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SOLUTION COMBUSTION SYNTHESIS OF THE Ni_3CuN ANTIPEROVSKITE BATTERY MATERIAL

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Perovskites exhibit numerous fascinating properties and support the operations of many modern technologies. Their counterparts, known as antiperovskites, are electronically inverted perovskite derivatives with the general formula X_3BA where X is a cation, A and B are different-sized anions [1]. Nanoscale antiperovskite materials are a rising star family of functional materials with potential applications in energy conversion and storage devices, nano-electronics, and advanced thermal management technologies. Among antiperovskite materials, complex nitrides, such as Ni_3CuN attracted significant attention due to interesting catalytic and magnetic properties [2]. There are several methods to synthesize antiperovskite nitrides. These approaches contain time- and energy intensive multiple high-temperature steps, but other than these, the structural homogeneity, such as the distribution of nitrogen in materials, is not always high.

To overcame such challenges, we used the solution combustion synthesis (SCS) method for the preparation of Ni_3CuN antiperovskite material as an affordable and alternative method. SCS is a low cost, simple, fast and energy efficient method to produce powders with desired morphology where the primary source of heat comes from combustion reaction between metal nitrate and organic fuel [3]. Rapid heating leads to evaporation of the solvent and formation of a viscous gel, as well as initiation of a high-temperature self-sustaining reaction in the gel leading to the formation of uniform nanostructured materials.

We developed an approach according to which a homogeneous aqueous solution made from nickel and copper nitrates ($Cu(NO_3)_2$, $Ni(NO_3)_2$)) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$), as a fuel, has heated under the inert gas flow which inhibited the entry of air into the reaction zone, at the same time ensuring the production of pure antiperovskite without oxide mixture. Also, it was shown that the formation of Ni_3CuN antiperovskite is due to the nitrogen present in the fuel, but not the N_2 which in several runs serve as a reaction medium.

The reaction in $3Ni(NO_3)_2+Cu(NO_3)_2+5C_6H_{12}N_4$ solution yields pure target material, which is characterized by the particle size of ~100-200 nm. EDS analysis results testify that the sample has a fairly homogeneous distribution of both the metals and nitrogen. The results indicate the formation of a compound with a 3:1 molar ratio of nickel and copper.

SCS prepared antiperovskite was subjected to TEM analysis. The results showed that in addition to crystalline centers, amorphous areas are also present in the final product which probably can be a product of the fuel decomposition, which has not yet managed to formulate a crystal structure. This is also evidenced by the EDS analyses carried out for the amorphous areas, according to which they are rich of C, N elements. The comparison of d-spacings of XRD and SEAD analysis indicate that the crystalline areas in the product are responsible for Ni_3CuN antiperovskite material.

The prepared antiperovskite was subjected to thermal stability tests by using thermogravimetric analysis (TGA). The studies showed that the material is stable up to 800 K.

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RESPONSIVE NANOCARRIERS BASED ON RESORCINARENES

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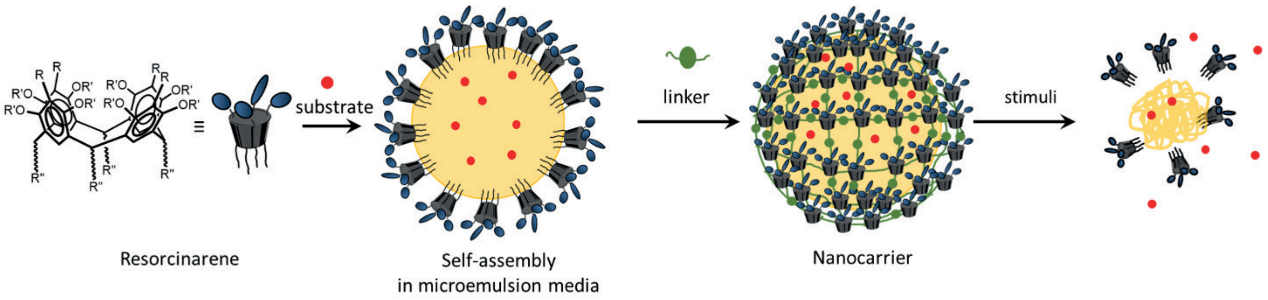
One of the fastest-growing fields of science is the development of nanocarriers for binding and release of substrates [1]. Nanocarriers are required in medical for imaging and targeted drug delivery, in agriculture to increase pesticide efficiency or delivery antidots in case of poising, and in industry to develop new kinds of catalytic systems [2].

We have created a novel method for producing nanocarriers. The method is based on the self-assembly and polymerization of amphiphilic resorcinarenes derivatives - macrocyclic molecules and calixarenes analogs. Resorcinarenes come in a bowl-shaped form that is hydrophobic and only soluble in organic solvents, but the addition of hydrophilic moieties on the upper rim provides it amphiphilic qualities that allow it to function as an emulsifier. They organize at the oil/water interface in a microemulsion, directing the lower rim's tails into the oil dispersed phase while the hydrophilic moieties of the resorcinarenes face water (Figure 1). In order to create stimuli-responsive polymer nanocarriers that can be used for controlled substrate release, the tails are cross-linked using reversible covalent connections.

Compared to traditional carriers like liposomes, micelles, and so on, nanocarriers based on resorcinarenes have a number of benefits. The majority of the time, resorcinarenes are not hazardous and are created using non-toxic reagents. Stronger than linear polymeric or supramolecular nonpolymeric carriers, a polymeric spherical network created during the polymerization process retains the substrates. Resorcinarene derivatives are formed as the nanocarriers decompose, which should make it much easier for the body to eliminate them. Previously, we have created new catalytic systems and targeted drug delivery utilizing this method to create nanocarriers for controlled binding of substrates.



Scheme 1. Nanocarrier development strategy by microemulsion polymerization of resorcinarene derivatives for stimuli-responsive substrate delivery.

Acknowledgements *We are grateful for the financial support of the Russian Science Foundation (Grant 23-23-00381).*

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF NEW DERIVATIVES OF DITERPENE ACIDS

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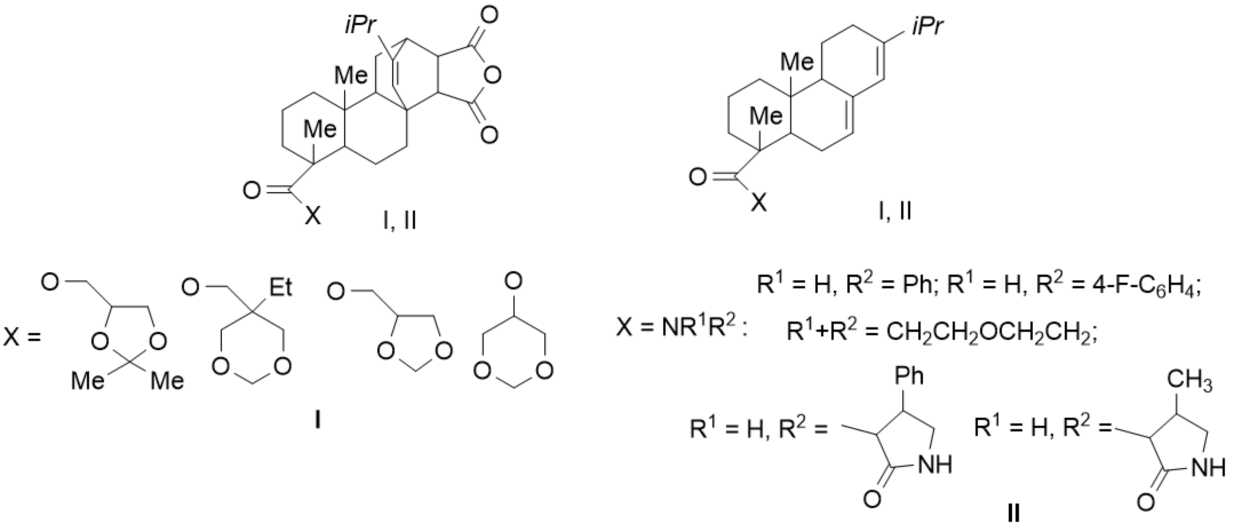
Diterpenic acids, in particular, abietic and levopimaric, are available components of pine resin *Pinus sylvestris L.*, common in Russia, and are used as a basis for the production of a number of biologically active compounds [1]. On the basis of abienic acid (AA) and maleopimaric acid (MPA), we synthesized a series of new heterocyclic amides and esters of types **I** and **II** containing a diterpene moiety (Fig. 1). Conditions have been found that make it possible to obtain these compounds with high outputs.

Pic 1.



The anticoagulation and antiaggregation activity of AA and MPA amides was studied. The effect of these compounds on the plasma component of the hemostasis system to varying degrees was found. Among the substances obtained, leading compounds have been identified. The report discusses the structure-activity relationship in the series of reactants obtained.

The work was financially supported by the state task of the Ministry of Education and Science of the Russian Federation "Development and creation of low-tonnage products and reagents (corrosion and scale inhibitors, antioxidants, biocides, additives, etc.) for petrochemical processes and purification of aqueous media from pollution, replacing imported substances and materials. Theoretical and experimental approaches (FEUR-2023-0006).

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AMINOBENZOIC ACIDS AS KEY BUILDING BLOCKS FOR THE SYNTHESIS OF ISOCOUMARIN-SUBSTITUTED ISOQUINOLINIUM SALTS, INDENONE IMINES OR INDENYL AMINES

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Recently, we have shown that isocoumarins can be used for creating OLED devices due to their high stability and the presence of aggregation-induced emission (AIE)[1]. One of the most efficient methods for the synthesis of isocoumarins is based on the C-H annulation of readily available benzoic acids with alkynes.[2] In this work, we modified this approach for the synthesis of various isocoumarin-substituted heterocyclic compounds using aminobenzoic acids accompanied by benzaldehydes instead of benzoic acids (Figure 1). It was found that the reaction pathway strongly depends on the donor-acceptor properties of substituents in benzaldehydes. For example, the reaction with electron-rich benzaldehydes selectively gives isocoumarin-substituted isoquinolinium salts, while in the case of electron-withdrawing substituents, indenone imines or indenyl amines are the predominant products.

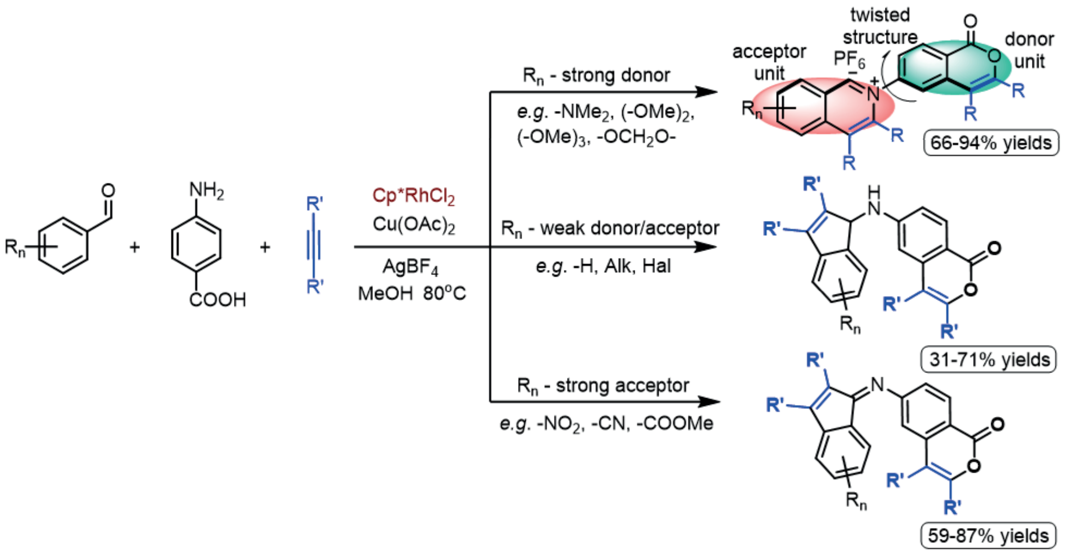

Figure 1. Tandem C-H annulations of benzaldehydes and aminobenzoic acids with acetylenes

The heterocyclic frameworks in the isocoumarin-substituted isoquinolinium cations are orthogonal, which prevents direct conjugation between the donor and acceptor units and leads to the decrease of energy gap between the first triplet and singlet excited states ΔE_{ST}. It is important to note that isocoumarins act as a donor group, while the positively charged isoquinoline derivatives act as an acceptor unit. These structural and electronic features make these compounds potential candidates for the construction of high-performance OLEDs with a TADF effect.

Acknowledgements
This work was supported by the Russian Science Foundation (Grant No. 17-73-30036-П).

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STUDY OF SYNTHESIS AND PROPERTIES OF NEW TYPES OF SILICONE ELASTOMERS CONTAINING DIFFERENT DRUGS

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Silicone polymers (polysiloxanes) are used in medicine as implants, drug delivery vehicles, and transdermal patches. Polysiloxane elastomers are synthesized from hydroxyl-terminated polydimethylsiloxane (PDMSOH), tetraethoxysilane as four-functional crosslinking agent (TEOS) and a curing catalyst. This synthesis option allows one to vary the properties of the cross-linked matrix by changing the molecular weight (MW) of PDMSOH, the type of catalyst, the ratio of PDMSOH and TEOS, etc [1]. TEOS is the most used crosslinker, and though silicon glycerate (Si GL) and propylene glycolate (Si PGL) are known compounds but up to now they were not used in such reactions. We carried out a comparative study of the use of tetra-alkoxysilanes in crosslinking reactions with PDMSOH of various viscosities and MW, and their effect on the properties and parameters of the crosslinked polymer composites.

It has been shown that the speed of crosslinking reaction significantly increases in the series: Si-PGL>-Si-GLY>TEOS. TG-MS investigations show that the studied composites can be used as “containers” for the storage of nicotine and glycols containing up to 50% by weight of the composites. They can be used for therapeutic purposes (for smoking cessation) in the form of skin (transdermal) nicotine-containing films, and for use in aerosol-generating systems at high temperatures, for example, in electronic smoking devices containing nicotine and glycol (glycerin, 1,2-propylene glycol).

Based on the data obtained from the studies of the synthesized composites, these systems were used in the synthesis of transdermal films containing Diclofenac sodium and Furazolidone. The effects of these drugs, as well as the type of cross-linking agents on the duration of film formation (crosslinking-curing), the kinetics of the drug release in *in vitro* experiments, and the swelling of samples (in 0.9% NaCl solution) were studied.

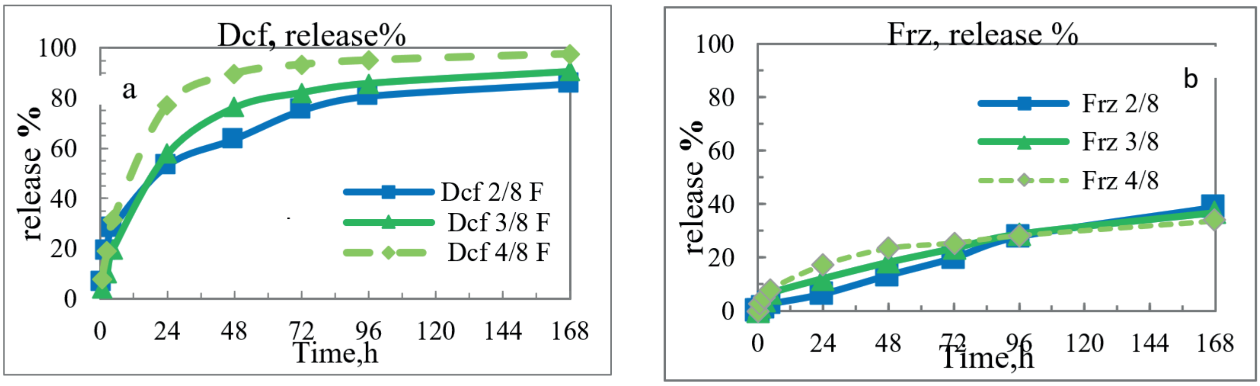

Fig. Cumulative percentage of desorption of Dcf (a) and Frz (b) from films with glycerol (44%)

It was found that the chemical structure of the drug and the type of the cross-linking agent play a significant role in the formation of composites, having an influence both on their morphology and on the amount of the drug release.

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SYNTHESIS OF {Zn_2Ln_2} HETEROANIONIC COMPLEXES WITH ANIONS OF BENZOIC AND PENTAFLUOROBENZOIC ACID

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Coordination compounds of lanthanides, especially of Eu^{3+} and Tb^{3+}, attract much attention among researchers with their huge variety of potential applications due to their bright metal-centered luminescence. Such compounds may be applied as sensors, diodes, and lasers or in catalysis and biomedical imaging. Nowadays increasing the luminescent quantum yields of these compounds is one of the most vital tasks. It is known that the use of aromatic ligands makes it possible to obtain compounds with bright luminescence due to the additional antenna effect [1]. Moreover, the introduction of the d-block, which consist of d10 metal ions and monocarboxylic acid anions, in turn, may also affect the photoluminescent properties of compounds positively. In this regard, aromatic carboxylic acids are widely used as organic ligands. Using two types of anions of different nature in the synthesis of compounds leads to the occurrence of strong non-covalent interactions. This may additionally stabilize the crystal structure of the compounds [2]. A prime example may be the simultaneous coordination of pentafluorobenzoate and benzoate anions to a metal ion, which leads to the formation of supramolecular chains, stabilized with π … π, C-H…F, C-F… π and other intra- and intermolecular interactions, which may positively affect their photoluminescence properties.

In this work two heterometallic heteroanionic benzoate-pentafluorbenzoate {Zn_2Ln_2} complexes [$Zn_2Ln_2(bz)_4(pfbn)_6(phen)_2$] were obtained (Ln = Eu(**IEu**), Tb(**ITb**); bz – benzoate anione; pfbz – pentafluorbenzoate anion; phen – 1,10-phenantroline). The conclusion about the stability of the obtained compounds may be made based on the facts that they were obtained with different yields and ratios of reactants $Zn(pfbz)_2$:$Ln(bz)_3$ = 2:1 and 1:1. Varying the initial salts (using $Zn(bz)_2$ and $Eu(pfbz)_3$ or $Zn(pfbnz)_2$ and $Ln(bz)_3$) also entails preservation of the anion ratio of the final product. A homoanionic complex $Zn_2Eu_2(bz)_{10}(phen)_2$ (**II**) was obtained to trace the influence of anions inclusion in the case of heteroanionic complexes. The obtained compounds **I** and **II** were characterized by XRD, CHN analysis and IR spectroscopy. Photoluminescent properties were studied for compounds I and II. It has been shown that the inclusion of two types of anions into the structure of the complexes leads to an increase in the luminescence quantum yield of heteroanionic complexes (69%) and a decrease in the intensity of nonradiative transitions, reflected in the high lifetimes of the luminescence excited state. These values almost do not change with the rising of temperature from 77K to 300K (1,83 ms at 77K and 1,71 ms at 300K).

The work was carried out with the financial support of the Russian Science Foundation, grant № 22-73-10192

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QUINOLINE AND ISOQUINOLINE NITRO DERIVATIVES IN OXIDATIVE $S_N{}^H$-AMIDATION REACTIONS

<u>Borovleva A.A.</u>, Avakyan E.K., Pobedinskaya D.Yu., Ermolenko A.P., Larin A.N., Borovlev I.V., Demidov O.P.

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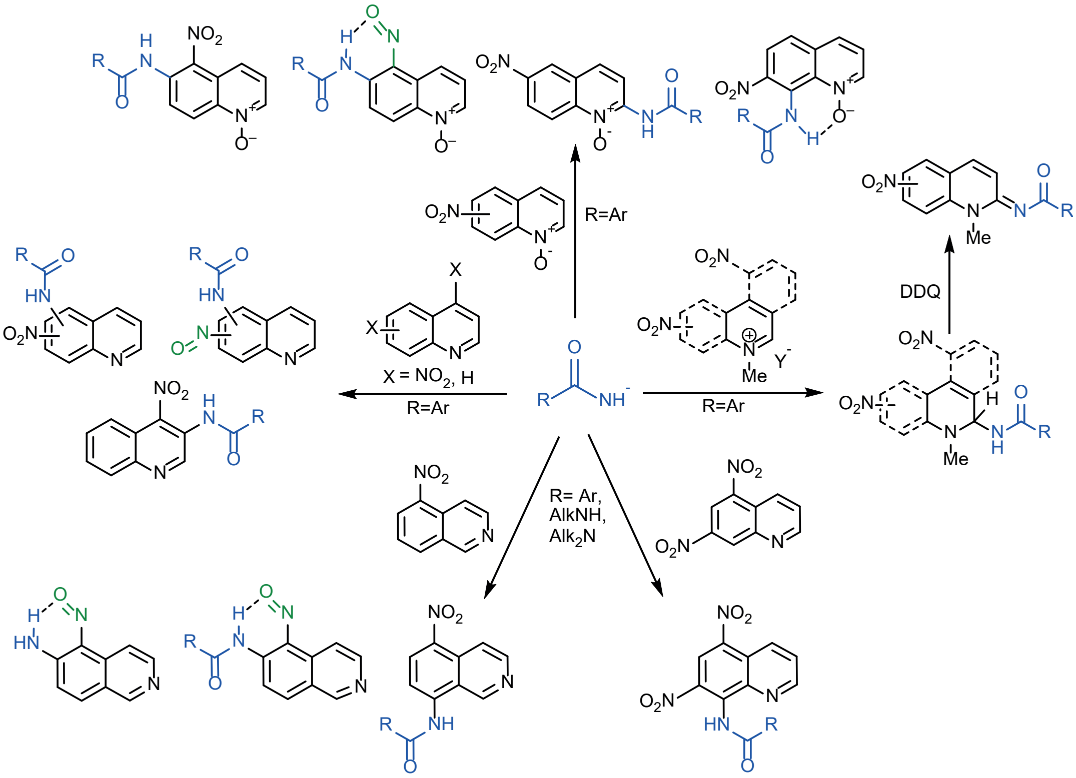
The structures of quinoline and isoquinoline are important molecular scaffolds in various natural and synthetic compounds that are widely used in pharmacology, medicine, and materials science; therefore, the search for new methods for the functionalization of these heterocycles is still of great interest.

Direct C-H functionalization of aromatic compounds by the action of nucleophilic reagents largely meets the requirements of modern organic synthesis, which assume the economy of all transformation parameters, which corresponds to the so-called PASE concept (Pot-, Atom-, and Step-Economic), as well as the principles of “green” chemistry. An important variation of these processes is the oxidative nucleophilic substitution of hydrogen ($S_N{}^H$), which does not require the use of halides and transition metal catalysis. This methodology is applicable to electron-deficient substrates such as azines and nitroarenes.

The report discusses the results of studies carried out by our laboratory on the possibility of oxidative $S_N{}^H$-amidation and carbamoylamination of nitro derivatives of quinoline and isoquinoline, as well as the regioselectivity and chemoselectivity of these reactions.



The authors express their gratitude to the North Caucasian Federal University for financial support in the framework of the project to support the projects of scientific groups and individual scientists.

EXPERIMENTAL AND COMPUTATIONAL INVESTIGATION OF THE CAGE EFFECT'S INFLUENCE ON PHOTOINDUCED MIGRATION OF CYMANTREN

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Bochenkova A.V.,[d] **Medvedev M.G.,**[a, c] **Telegina L.N.**[c]

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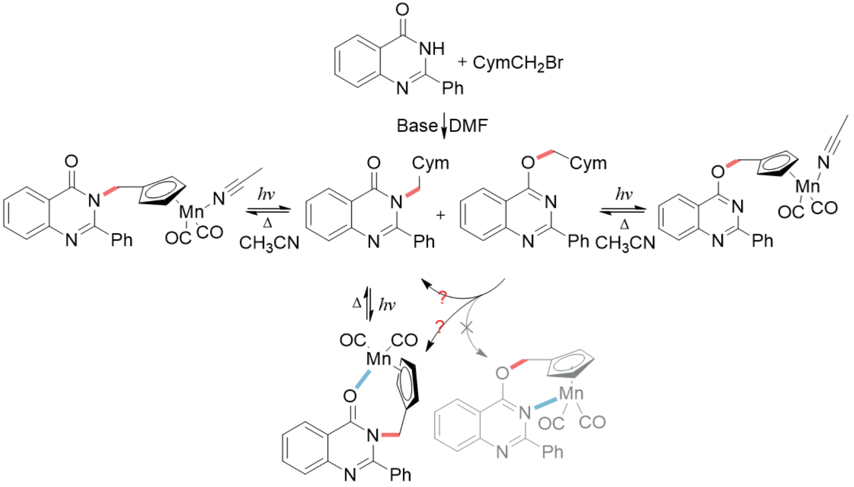
Cyclopentadienylmanganese tricarbonyl (Cymantrene) *modus operandi* upon excitation consists in releasing one carbonyl with the formation of a 16-electron Mn complex and then filling the emerged Mn valence with whatever is present nearby before proceeding to the thermodynamic sink [1] We present [2] the first example of photochemical transfer of the cymantrenyl moiety where cymantrene does not release one of its carbonyls upon photoexcitation, which is proven by various spectral methods. A tandem experimental and computational investigation based on the DFT (density functional theory), allows us to explain this unexpected behavior: the rearrangement, indeed, begins with the dissociation of a single ligand, but the cage effect [3] traps CO molecule in the solvent cell allowing it to reattach after intramolecular rearrangement. We proved our hypothesis by quantum chemical modeling of the rearrangement mechanism and conducting an experiment in an ultrasonic bath. Ultrasonic irradiation breaks solvent cages, freeing CO and forcing reaction to stop at the dicarbonyl complex.



This work was supported by the Russian Science Foundation (#22-73-10124)

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DESIGN AND SYNTHESIS OF COORDINATION POLYMERS BASED ON TRANSITION METALS WITH PHOTOSENSITIVE AND PHOTOINERT LIGANDS

Chistyakov A.S.[a], **Zorina-Tikhonova E.N.**[a], **Shmelev M.A.**[a], **Vologzhanina A.V.**[b], **Kiskin M.A.**[a], **Sidorov A.A.**[a], **Eremenko I.L.**[a]

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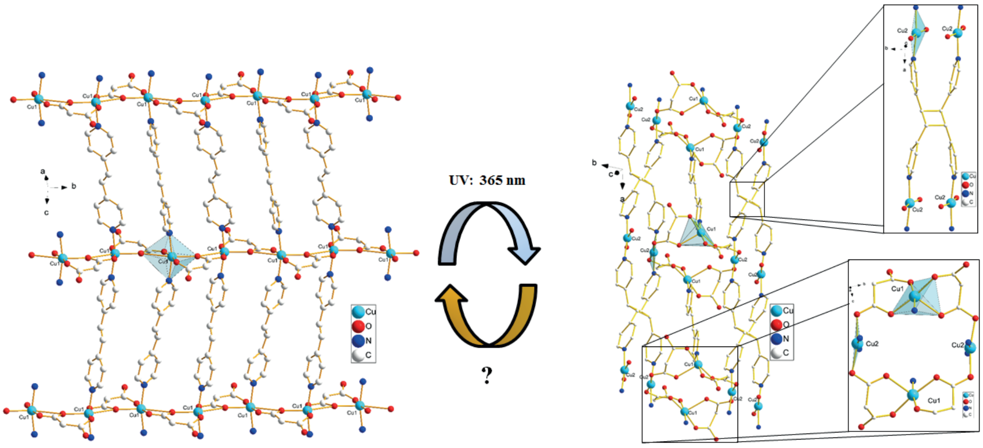
Nowadays, the synthesis of coordination polymers is one of the rapidly evolving parts of coordination chemistry, because of their potential applications in many areas including heterogeneous catalysis, separation and storage of gases, magnetism, and many others [1,2]. The use of photosensitive ligands allows the preparation of polymers that can participate in the reactions of [2+2]-cyclophotoaddition. The study of the cyclophotoaddition reactions is important from the point of view of studying such natural phenomena as photosynthesis and phototaxis, and, in addition, it makes it possible to obtain materials for optical recording and information storage systems [3].



$\{[Cu(Mal)(bpe)]\cdot 2MeCN\}_n$ $\{[Cu_4(Mal)_4(bpe)(tpcb)]\cdot 6H_2O\}_n$

In this research, the extensive series of coordination polymers (Mn^{II}, Cu^{II}, Zn^{II}) with various substituted malonic acid anions and bridged N-donor ligands were synthesized. The single-crystal-to-single-crystal [2+2]-photoaddition reaction was performed for those compounds that fulfil its conditions [4]. As a result, new coordination polymers with different conversion degrees were obtained. The approach of using photoactive ligands may be useful for obtaining composite materials. Thus, while using 4-allyl-2,3,5,6-tetrafluorobenzoic acid as a ligand, containing a photoactive allyl group, new compounds of *3d* elements ($[M(4\text{-}Al\text{-}tfb)_2(1,10\text{-}phen)(H_2O)]$), where M = Mn^{II}, Cu^{II}, Zn^{II}, Cd^{II}) or heteroleptic complexes of *4f* elements, for example$[Dy_2(4\text{-}Al\text{-}tfb)_4(Bnz)_2(1,10\text{-}phen)_2]$, have been synthesized.

This study has been supported by the Russian Science Foundation (22-73-10192).

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ELECTRONIC AND GEOMETRY STRUCTURE AND OF TETRABENZOPORPHYRIN METAL COMPLEXES BY QUANTUM CHEMICAL CALCULATIONS

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The geometries and electronic structure of the sequence of tetrabenzoporphyrin metal complexes (MTBP, where M=Zn, Cd, Al(Cl), Ga(Cl), In(Cl), Fe, V(O), Ti(O); Fig. 1) were investigated by means of quantum chemical calculations. Density functional theory (PBE0 functional combined with triple-zeta def2-TZVP basis set [1] with Grimme dispersion correction D3 [2]) was used for the structure optimization followed by the computation of the harmonic vibrations and NBO-analysis of electron density distribution.

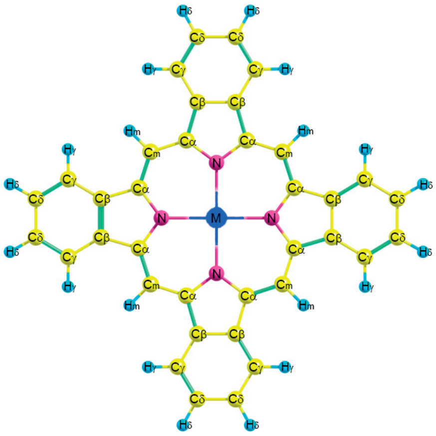

Figure 1. Molecular model of tetrabenzoporphyrin metal complexes.

It was found that the nature of the metal atom slightly affects on the core structure, while the dimensions of the coordination cavity of the macrocycle increased in accordance with the ionic radii of metals. The complexes with Zn, Cd, Fe are planar with D_{4h} symmetry while the complexes with axial ligand (MTBP, where M=Al(Cl), Ga(Cl), In(Cl), V(O), Ti(O)) are doming distorted (C_{4v}). NBO analysis revealed the strong interactions of the types LP(N) → ns(M) and LP(N) → np(M), where n is a principal quantum number. The Wyberg bond indices showed the ionic character of M-N bonds with a noticeable covalent contribution.

The electronic absorption spectra were simulated with the use of time-dependent (TD) DFT for Zn, Cd, Al, Ga and In complexes and simplified TDDFT for other complexes. We should note a minor influence of the metal nature on the Q-band position. The most intensive bands of the UV-Vis spectra observed in the Soret near-UV region.

The electronic structure of FeTBP in ground and low-lying excited electronic states was determined by CASSCF method, followed by MCQDPT2 approach utilization. It was established that the singlet electronic state possess a complex composition while the wave functions of ground triplet state $^3A_{2g}$ and low-lying high-spin $^5A_{1g}$ electronic states have a form of single determinant.

This work was supported by the Russian Science Foundation grant 21-73-10126.

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CARBONYL-CONTAINING FURAN-3-CARBOXYLATES IN THE SYNTHESIS OF ORIGINAL MONO- AND BIHETEROCYCLIC STRUCTURES

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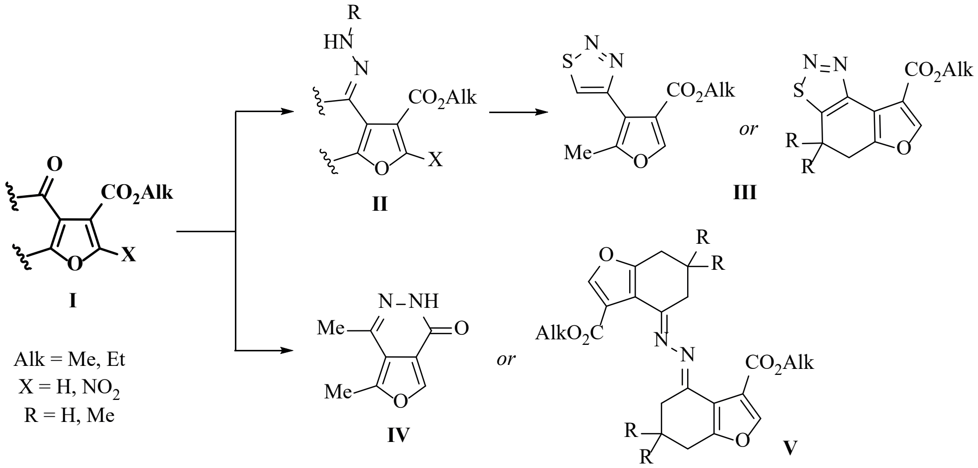
Furan-3-carboxylate representatives are known as substances with a number of practically significant properties, including inhibition of insulin secretion [1] and antiparasitic activity [2].

Carbonyl-containing furan-3-carboxylates **I** that were synthesized in the interaction of alkyl-3-bromo-3-nitroacrylates with aliphatic [3] or carbocyclic [4] CH-acids are promising substrates for further functionalization in the reaction with nitrogenous nucleophiles and new heterocycles construction based on the resulting products [5].



It was shown, that the reaction of furan-3-carboxylates **I** with phenyl(4-nitrophenyl, 2,4-dinitrophenyl) hydrazine, hydrazinecarboxamide and *N*-phenylhydrazinecarboxamide leads to the corresponding hydrazones **II** formation in the *E*-configuration.

Some of the hydrazones **II** – furan-3-carboxylates semicarbazones are converted under Hard-Mori reaction conditions into the thiadiazole furancarboxylates **III**.

However, reactions of hydrazine with monocyclic furan-3-carboxylates **I** lead to the formation of 4,5-dimethylfuro[3,4-*d*]pyridazin-1(2*H*)-one **IV**, and with benzofurancarboxylates **I** – to *bis*-hydrazones **V**. All products structures were characterized by complex of physicochemical methods, including X-ray diffraction analysis.

The research was supported by an internal grant of the Herzen State Pedagogical University of Russia (project № 3VG).

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[M]-/ORGANO-CATALYZED AEROBIC OXIDATION AS THE GREEN WAY FOR THE PREPARATION OF FUNCTIONALIZED ORGANOSILICON COMPOUNDS

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Organosilicon derivatives are widespread organoelement compounds produced industrially. However, to date, only limited range of functionalized organosilicon products are commercially available. In this regard, their potential is not yet fully recognized. This is partially due to the limitations during their synthesis derived from poor stability of Si–C, Si–O- and Si–Cl-bonds in harsh conditions, non-neutral media and in the presence of strong oxidants.

On the other hand, aerobic oxidation utilizing oxygen from air is one of the most attractive functionalization techniques. A great improvement in this field gained in the past decades allowed wide range of functional groups to be introduced into organic molecules. However, aerobic oxidation is still understudied for the functionalization of organosilicon compounds.

In this research, we proposed tandem [M]-/organo-catalytic system for mild liquid-phase oxidation of organosilicon using molecular oxygen. This approach showed to be viable for the synthesis of silanols[1,2] and carboxyphenylsilanes,[3] containing organo-, siloxy- and alkoxy-groups (figure 1), showing the high selectivity of the suggested catalytic system.

Applicability of the synthesized silanols in further synthesis of dumbbell-shaped and graft siloxane polymers was also studied.[4] Polyfunctional carboxyphenylsiloxanes were used in synthesis of siloxane-containing esters and amides,[5] as well as were used as building blocks for hybrid porous (HOF, MOF) polymers.

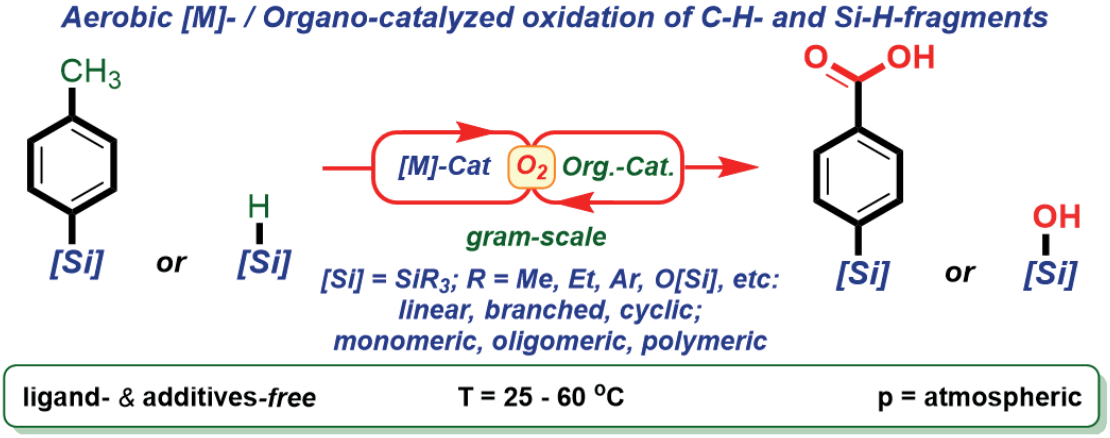

Figure 1.

Acknowledgements

This work was supported by a grant of the Russian Science Foundation (RSF grant 19-73-10172-П)

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THE ANTIOXIDANT EFFECT OF OXALIC ACID DIAMIDE DERIVATIVES IN THE LIVER AND BRAIN OF WHITE RATS

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Scientific and Technological Center of Organic and Pharmaceutical Center

The term “antioxidant” has become widespread since the 90s of the 20th centuries, when scientists put forward a hypothesis about the role of free radicals in the early stages of atherosclerosis, as well as the importance of oxidation in chronic diseases, vision loss. As a result of metabolic processes in a living organism, free radicals are formed in the cells of the human body, which can also have a harmful effect, but antioxidants produced in cells neutralize free radicals. When the balance between free radicals and antioxidants in the body is disrupted, it can lead to oxidative stress. Oxidation is the only and necessary process for the human body. However, when there is an imbalance between activities, oxidative stress occurs. When there are more free radicals, they damage adipose tissue, DNA, and proteins. Proteins, lipids and DNA make up a significant part of the human body, so their damage over time can lead to serious diseases such as diabetes, atherosclerosis, hypertension, neurodegenerative diseases, and oncology. Without antioxidants, free radicals cause serious damage very quickly, which can eventually lead to death.

The studies were carried out on 48 outbred white male rats weighing 180-200 g, kept on a normal diet. Animals were euthanized under Nembutal anesthesia administered intraperitoneally at a dose of 40 mg/kg. At the final stage, the slaughtered animals were cremated. The work is carried out in accordance with the Directive of the European Council (2010163IEU) on the care and use of experimental animals.

Statistical processing of the obtained data was carried out using programs (Statistic for Windows) that output Student’s t-test. Differences were considered significant at $P<0.05$. Thus, on the basis of the studies carried out, it can be concluded that the compounds of a number of oxalic acids diamides have an antioxidant activity on the process of free radical lipid oxidation in the brain and liver. According to the data obtained, it can be concluded that this group of compounds is promising in terms of the search for new antioxidant compounds.

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SYNTHESIS AND PROPERTIES OF FRAMEWORK STRUCTURES BASED ON D-METALS COMPLEXES

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Metal–organic frameworks (MOFs) are crystalline, organic–inorganic hybrid compounds in which metal ions and organic multidentate ligands are linked together by coordinate bonds. Transition metals, alkaline earth metals, actinides and even mix metals are used for the synthesis of MOFs. N-containing aromatics or multivalent aromatic carboxylic acids are commonly used organic linkers in MOFs [1].

Zeolitic imidazolate frameworks (ZIFs), as a subclass of metal organic frameworks (MOFs), are high porous crystals with zeolite-type structure built by metal ions and imidazolate ligands [2]. ZIFs possess the properties of high crystallinity, large specific surface area, chemical and functional tunability. Nowadays, ZIF-materials can be synthesized using a variety of methods which in general can be divided into two groups: solvent-based and solvent free. Solvothermal synthesis has been widely employed owing to its simplicity and especially high throughput [3]. Comparatively higher yield, precise control over the shape distribution, size, and crystallinity of material prepared are the major advantage of this method.

In this work a variation of the synthesis parameters of a metal–organic frameworks at solvothermal method conditions was carried out [4]. For constructing structural units, transition metal salts ($CoCl_2$, $Co(NO_3)_2$ and $FeCl_3$) and organic linkers (2-ethylimidazole and terephthalic acid (BDC)) were used. NaOH and triethylamine were used as catalysts for terephthalic acid deprotonation. It was shown that triethanolamine did improve MOF structural properties.

Using infrared spectroscopy, a qualitative composition of the samples was determined. The FT-IR spectra of the obtaining frameworks have characteristic bands that are consistent with a number of published data and they are almost completely identical, pointing to the reproducibility of the synthesis method under the chosen conditions.

The morphology of the obtained powders was studied by scanning electron microscopy. It is shown that the presence of further structuring agents causes the aggregation of the formed framework particles and crystal enlargement. It was found that the addition of triethylamine leads to the preparation of high dispersed powders due to the ligand deprotonation and the reagent hydrolysis before complexation.

Nitrogen adsorption isotherms in the pores of MIL-88B, MOF-51 and Co-ZIF were obtained, by processing of which the parameters of the porous structure of the synthesized samples were found. The terephthalic acid reaction with NaOH gives a DMF-insoluble Na_2BDC salt. This procedure is likely to cause blockage of the porous structure and large crystal formation. Alternatively, when triethylamine is used as a catalyst, it generates a DMF-soluble carboxylic form that can easily be complexed with metal ions and rapidly form MOFs with a highly porous structure.

The work was carried out with the financial support of the Russian Science Foundation (project No. 22-73-10158).

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SYNTHESIS AND SPECTRAL-LUMINESCENT PROPERTIES OF PHTHALOCYANINE METAL COMPLEXES CONTAINING AZOCHROMOPHORES WITH CUMYLPHENOXY GROUPS ON THE PERIPHERY

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Complexes of phthalocyanines with metals are knows as a compounds with promising properties such as high chemical and thermal stability, as well as unique optical and electrical ones. The nature of the central metal ion and substituents are a tool for fine-tuning the physicochemical characteristics of compounds. The introduction of azo groups makes it possible to expand the range of light absorption of these compounds, and the presence of halogen atoms on the periphery leads to a decrease in aggregation, which makes it possible to expand the scope of phthalocyanine complexes.

In this regard, this work is devoted to the synthesis and study of spectroscopic properties of metal complexes with zinc, magnesium and aluminum phthalocyanines containing azochromophore at the periphery.

At the first stage of the work, diazotization of aniline or dibromoaniline was carried out in order to obtain diazonium salts, which were used in the azo coupling reaction with 4-(2-phenylpropan-2-yl)phenol. Further, the resulting dye was used as a nucleophile in interaction with 3/4-nitrophthalonitrile.

Metal complexes synthesis were carried out by template fusion of substituted nitriles with appropriate Zinc and magnesium acetate at 180-190 ^{o}C.

All synthesized compounds were isolated and purified using column chromatography.

The identity of all the compounds obtained characterized by 1H NMR, IR spectroscopy and elemental analysis.

The luminescent and spectral properties of phthalocyanine metal complexes in various solvent processes have been studied.

Due to the good solubility of the synthesized complexes in organic solvents, their spectral properties were studied. The effect of the nature of the metal, the location in the substituent and solvent on the position of the main band and the behaviour of the spectral curves is shown. It has been established that the position of the Q-band for peripherally substituted complexes is hypsochromically shifted relative to the corresponding non-peripherally substituted phthalocyanines.

The work was carried out with the financial support of the Russian Science Foundation, agreement 22-23-00831 using the resources of the Center for the Collective Use of Scientific Equipment of IHTU (with the support of the Ministry of Education and Science of Russia, agreement No 075-15-2021-671).

TETRAHYDROFLUORENYL SKELETON AS A PROMISING PLATFORM FOR CATALYST DESIGN

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Since their discovery in 1965, indenyl rhodium complexes have attracted much attention, due to their high efficiency in many catalytic processes. The indenyl effect, which is expressed in the facilitation of auxiliary ligand substitution as a result of η^5–η^3 isomerization of indenyl ligand, allows to formation of an addition vacant coordination site. However, this flexibility leads to a weakening of the metal–indenyl bond, which limits the catalytic applications of indenyl complexes [1,2]. The problem of weak binding could be solved by functionalization of indenes, but this usually requires multi-step procedures.

In the present work, we report a simple approach to stabilized indenyl rhodium complexes based on readily available 1,2,3,4-tetrahydrofluorene. Their high catalytic activity was demonstrated in the synthesis of amines and various heterocyclic compounds [3]. The subsequent one-step modification of tetrahydrofluorene made it possible to develop a family of rhodium catalysts with a trisubstituted indenyl ligand. We also elaborated a convenient method for the synthesis of chiral tetrahydrofluorenyl rhodium complexes, which showed high catalytic activity with moderate enantioselectivity in several reactions (Figure 1).

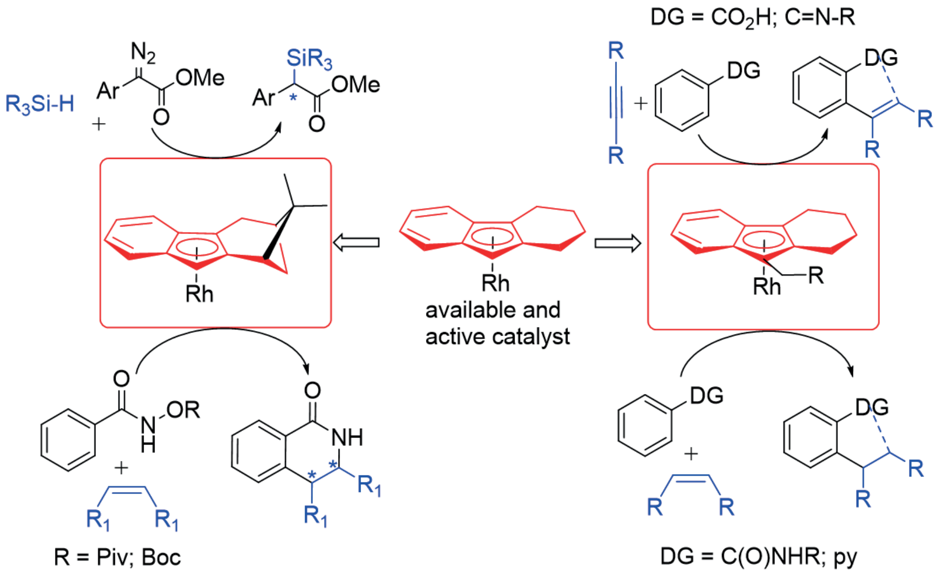

Figure 1. Rhodium catalysts based on tetrahydrofluorenyl skeleton

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SYNTHESIS AND SPECTRAL PROPERTIES OF A FLUORESCENT SENSOR BASED ON THE 4-HYDROXY-3-METHOXY-BENZALDEHYDE-SUBSTITUTED BODIPY COMPLEX

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Boron-dipyrrine based dyes (BODIPY) are a promising class of compounds with a wide range of applications. BODIPYs are used for labeling protein structures, for the production of OLED devices, as PDT agents. BODIPY can be a sensor for pH environment, its polarity and viscosity. Moreover, BODIPYs are remarkable for the variety of structural modifications, high fluorescence quantum yields, narrow absorption and emission bands, excellent thermal and photochemical stability.

In this work the investigation of meso-substituted boron-dipyrrine complex based on 4-hydroxy-3-methoxybenzaldehyde (vanillin) is described. The synthesis was carried out in solution under an inert atmosphere and purified by column chromatography at each stage. The structure of the resulting complex was confirmed by various analytical techniques such as mass spectrometry, NMR and IR spectroscopy.

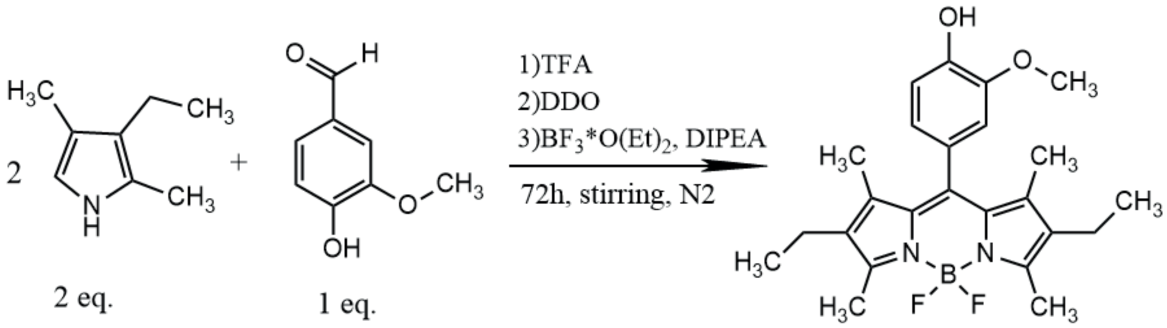

Figure 1. Scheme of the synthesis of the 8-substituted described BODIPY

To further study the properties of the synthesized structure, electronic absorption and fluorescence spectra were obtained at different media parameters. A number of 15 solvents were selected according to Catalan and Camlet-Taft scales. From the evaluation of the data obtained, a significant hypochromic shift was observed. The obtained complex was not a sensor to environmental polarity.

The pH-probes were investigated with various aqueous-ethanol mixtures of HCl and NaOH. The fluorescence of the described complex decreases significantly at pH=9, indicating the potential for this BODIPY as a pH-sensor.

The complex without alkyl substituents in its backbone is currently being synthesized to investigate its rotor properties and to compare related structures.

HYBRID MAGNETIC HYDROGELS FROM NATURAL AND SYNTHETIC POLYANIONS

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Hydrophilic magnetically sensitive hydrogels are promising systems for biomedical applications as containers for targeted delivery of biologically active substances. Magnetically controlled hydrophilic nanocomposites have proven to be an effective anti-tumor tool. With an external magnetic field, the composites loaded with drugs can be delivered to a specific area of the body, thus providing a targeted therapeutic effect. However, the introduction of magnetic nanoparticles into hydrogel particles is accompanied by a decrease in the solubility and loading capacity of nanocontainers, which necessitates additional functionalization of hydrogels. To solve this problem, the modification of magnetic hydrogel based on sodium hyaluronate with linear sodium polyacrylates (PA) was carried out.

A sample of a magnetic hydrogel (MHG) based on sodium hyaluronate as a matrix stabilizing maghemite magnetic nanoparticles was synthesized. The content of iron in the MHG, determined via dissolution of the hydrogel in water followed by spectrophotometric titration with sulfosalicylic acid, was of 12.5 wt%. Aqueous solutions of linear PA with molecular weights ranging from 2.1 to 15 kDa were added to the resulting hydrogel.

The obtained systems were studied with dynamic light scattering, laser microelectrophoresis, IR spectroscopy, turbidimetric titration, XRD, scanning and transmission electron microscopy and magnetometry. It was established that all added PA's have been incorporated into samples of initial MHG resulting hybrid MHG's. The carboxylate groups quantity on the surface of particles of each sample was determined. It was shown that the incorporation of PA into the MHG leads to a significant additional functionalization of MHG particles. It was established that the effective size of magnetic nanoparticles in the modified systems also increases in comparison with the initial hydrogel, indicating the clustering of maghemite nanoparticles due to their interaction with PA. It was found that the magnetic characteristics change significantly when the MHG is modified with PA. The features of hybrid MHG enzymatic decomposition under the action of hyaluronidase were demonstrated. It was found that the addition of PA to the MHG leads to increase in the rate of enzymatic decomposition of the resulting hybrid MHG particles. The effect of molecular weight of added PA on the time of enzymatic decomposition of MGHs was shown. It was established that the increase of PA molecular weight leads to decrease in time of enzymatic decomposition of the modified MHG's.

The work was supported by Russian Science Foundation (project no. 23-12-00125). The STEM studies were performed using the equipment of the Joint Research Centre for Physical Methods of Research, Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

INTERRUPTED NEF REACTION OF CYCLIC NITRONATES: DIASTEREOSELECTIVE ACCESS TO DENSELY SUBSTITUTED A-CHLORONITROSO COMPOUNDS

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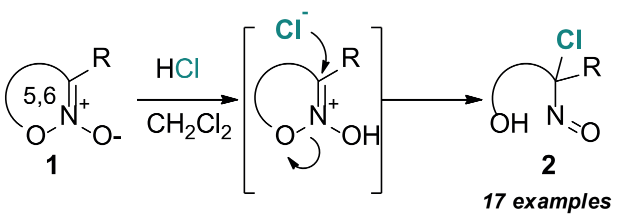
Interrupted reaction occurs when a chemical process is redirected to obtain new end product. This new process may take place with significant selectivity and conversion, therefore be applicable not only in mechanistic investigations of parent reaction but also as a reliable tool in organic synthesis.

Classical Nef reaction (nitro to carbonyl conversion) was discovered in 1894 by Swiss chemist J. U. Nef. The mechanism of this transformation involves deprotonation of primary or secondary nitroalkane to form a nitronate anione, which undergoes O-protonation, followed by a nucleophilic addition of water to the C=N bond. Elimination of HNO from the resulting intermediate leads to the carbonyl compound. In this work, we report an interrupted variant of Nef reaction, namely a reaction of cyclic esters of nitronic acid **1** with hydrochloric acid leading to α-halonitroso compounds **2**. The nature of this transformation resides in a nucleophilic addition of the chloride anion to the C=N double bond with simultaneous heterolytic cleavage of the N-O bond.



- *Conformation-driven further functionalization*
- *Switchable diastereoselectivity*
- *Yields up to 99%*
- *Interception of Nef's intermediate*

α-Halonitroso compounds possess a unique bifunctional moiety, which grants them unusual ambiphilic character and high reactivity towards nucleophilic, electrophilic and radical species. In particularly, these compounds are involved in nitroso Diels–Alder, nitroso ene, nitrosoaldol and photochemical reactions. On the other hand, reliable synthetic procedures allowing access to α-halonitroso compounds are almost exclusively limited to electrophilic chlorination of oximes, which does not tolerate oxidation-labile groups. The reported transformation allows to alleviate this disadvantages, offering a mild non-oxidative approach to the diastereoselective synthesis of α-halonitroso compounds bearing a free hydroxyl group. Which could be exploited for further conformation-driven tandem transformations.

Mechanistic insights into the diastereoselectivity of this transformation, as well as reasons behind the enhanced stability of products **2**, were also considered employing UV-vis spectroscopy, molecular orbital and DFT theory.1

This work was supported by Russian Science Foundation (grant № 22-13-00230).

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MEMRISTIVE EFFECT IN ULTRATHIN HYBRID FILMS ASSEMBLED FROM GRAPHENE OXIDE AND POLYDIACETYLENE SURFACTANT

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Nowadays, much attention has been paid to research in organic electronics to reduce the cost of electronic devices, increase their stability, and minimise their environmental impact while maintaining high efficiency. In this context, there is a growing interest in finding new approaches to obtaining ultra-thin flexible coatings, which opens up the possibility of creating a new generation of flexible thin-film devices.

Of particular importance are ultrathin hybrid materials based on graphene oxide (GO) and organic chromophores. In such systems graphene oxide provides mechanical strength and flexibility of the materials, as well as sets the structural characteristics of the ensemble of organic molecules. In turn, the properties of the organic component determine the useful functions of the material, as they allow the tuning of the photoactive, conductive, mechanical and surface characteristics of the hybrid.

In order to obtain ultrathin GO/organic chromophore coatings, methods must be available to produce ultrathin films with a molecularly controlled structure. In this work, a simple one-step method for the preparation of GO and 10,12-pentacosadinic acid (PDA)-based ultrathin hybrid materials was proposed. For this purpose adsorption layers of GO/PDA were transferred vertically onto a PET substrate coated with indium-tin oxide (ITO) using an automatic dipper [1]. The presence of both components in the film was confirmed by Raman spectroscopy. According to atomic force microscopy the thickness of such coatings is 5-10 nm. To evaluate the electrophysical properties, the hybrids were integrated into electronic cells with PET+ITO/GO/PDA/C_{60}/BCP/Al architecture.

Analysis of the volt-current characteristics showed that such systems exhibit a pronounced nonlinear behaviour accompanied by the appearance of a hysteresis loop at positive and negative potential sweeps. The effect can be enhanced by the formation of a photocurrent at the absorption of photons by the organic polymer. It was demonstrated that the coating remains stable under repeated cycling and does not lose its functional properties after 6 months of operation. For comparison, control systems with glass+ITO/C_{60}/BCP/Al, PET+ITO/C_{60}/BCP/Al, PET+ITO/PDA/C_{60}/BCP/Al, PET+ITO/GO/C_{60}/BCP/Al structure in which this effect was not observed were made.

The hysteresis of the volt-ampere curves may be related to the large concentration of traps at the metal/semiconductor surface contact in the layered electron cell. The obtained data open up the prospect of application of ultrathin hybrid GO/PDA coatings as information storage devices (memristors).

Acknowledgements: *This work was supported by the Russian Science Foundation (project No 23-73-00095).*

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NITRO-SUBSTITUTED PHTHALOCYANINES AS BUILDING BLOCKS FOR NEXT-GENERATION FUNCTIONAL MATERIALS

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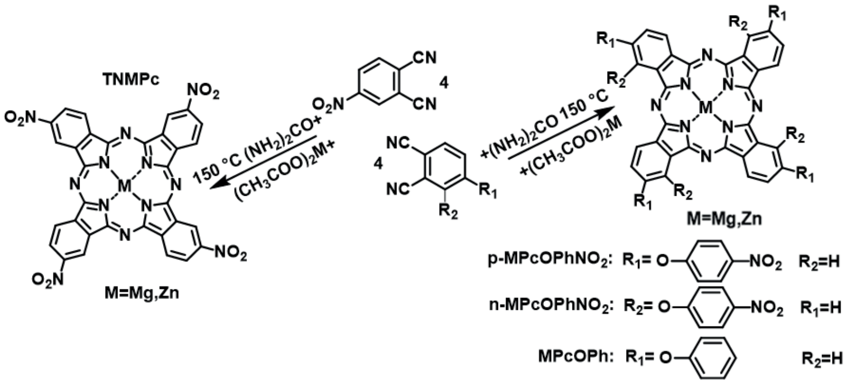
Phthalocyanines, which are a class of macroheterocyclic compounds, possess an extended π-electron system, which accounts for their great potential for use in various fields of human life. A common limiting factor in the study and application of this class of compounds is aggregation - overlapping π-systems of two or more molecules. Also the properties of phatlocyanines strongly depend on the nature, number and position of the substituents in the macroring. The high architectural flexibility makes it possible to vary the substituents and the central metal atom [1,2], which gives space for molecules with diverse properties and increased solubility due to functional groups.. For example, the introduction of a sulfo group gives complexes solubility in water [2], alkoxy- and aryloxy substituents high solubility in organic solvents [3]. A distinction is made between non-peripheral and peripheral positions of substituents in the phthalocyanine molecule. Nitro groups bring to the molecule a high potential for structure modification, immobilization on various carriers, and an important factor is the cheap cost of precursors for the synthesis containing nitro groups.

There are many approaches to the synthesis of phthalocyanine complexes, but they all have in common the presence of a template in the system, around which the phthalocyanine molecule is built up, this feature determines the pre-organisation of the molecule, and as a consequence, the small number of impurities during the synthesis, the ease of compound identification and the ability to predict the reaction product before the synthesis.



Scheme 1. Synthesis of zinc and magnesium phthalocyanite complexes

As a method of synthesis was chosen template condensation in the melt of initial phthalonitrile with metal acetates in the ratio 4 : 1, in the presence of urea. The synthesis was carried out at 150 °C until complete solidification of the mixture (20 minutes). Then the reaction mixture was purified by Soxhlet extraction with chloroform (for the nitro-substituted complexes, due to their poor solubility in chloroform), or by column chromatography on silica gel with chloroform as eluent (for other complexes). Purification was monitored by thin layer chromatography. The structure of the compounds was confirmed by ^{1}H NMR and IR spectroscopy, MALDI-TOF mass spectrometry and electron spectroscopy.

This work was supported by the Russian Science Foundation, grant 22-73-10158.

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SELF-ASSEMBLY OF HYBRID MATERIALS FROM ORGANIC CHROMOPHORES AND LOW-DIMENSIONAL INORGANIC PARTICLES

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Metal-organic frameworks (MOFs) based on porphyrins are coordination polymers widely used in gas separation, sensorics, heterogeneous and photocatalysis due to the coordination chemistry and optical properties of porphyrin complexes and high porosity. The main limitation in the creation of new materials based on MOFs is the insufficient chemical and mechanical stability of such structures due to the weak coordination bonds between the porphyrin molecules and the metal clusters forming them. A possible strategy for solving this problem is the assembly of thin films of MOFs on the solid surface (SURMOF) of planar inorganic nanoparticles based on such compounds as layered europium hydroxochloride (LEuH) and molybdenum disulfide (MoS2). This approach makes it possible to combine the functional properties of porphyrinic MOFs with those of inorganic carrier solids into a single hybrid structure. At the same time, the key challenge is to obtain aqueous dispersions of chemically pure planar nanoparticles of LEuH and MoS2 suitable for the assembly of SURMOF films on their surface.

In this work a new method of liquid-phase exfoliation in a hot saturated aqueous solution of 2-methylimidazole under ultrasonic treatment was proposed, which demonstrated its efficiency on both types of inorganic matrices. By transmission electron and atomic force microscopy, X-ray microanalysis, thermogravimetry, and X-ray diffraction, it was found that the obtained particles had an average thickness of one molecular layer, had a narrow distribution of lateral sizes, and that the cleavage agent was easily removed from their surface upon completion of synthesis. The synthesis of SURMOFs based on 5,10,15,20-tetrakis(4-carboxyphenyl) zinc porphyrinate (ZnTCPPP) and a zinc acetate bidentate complex on the surface of LEuH and MoS_2 nanoparticles was performed in hydrothermal conditions in a mixed water-alcohol solution of SURMOF components after preliminary adsorption of a zinc acetate anchoring layer on the nanoparticle surface, which provided further self-assembly of the SURMOF.

We studied the catalytic activity of the SURMOF/LEuH material during the hydrolysis of bis(4-nitrophenyl)phosphate as a model reaction for DNA phosphodiesterase and its artificial analogues. By studying the kinetics of the catalyzed hydrolysis using spectrophotometry, we showed that the hybrid material is an effective catalyst compared to the catalytically inactive initial bulk LEuH and bulk ZnTCPPP-based MOFs. Changes in the structure and chemical composition of the catalyst were studied by Raman and IR spectroscopy, spectrophotometry, MALDI-TOF mass spectrometry and X-ray diffraction.

The obtained results indicate that the hybrid material exhibits symbimetic properties, i.e. it mimics the behavior of biological symbiont organisms due to mutual stabilization of the components in the reaction medium. [1] Mutual stabilization of the components ensures catalytic synergy of the hybrid material, since only mutually integrated porphyrinic MOFs and LEuH can effectively catalyze the hydrolysis of organic phosphates. We believe that this strategy opens new horizons for the rational design of efficient hybrid materials on planar solid carriers.

Acknowledgements:
This work was supported by the Russian Science Foundation (project No 23-73-00095).

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NEW Fe(III) DINUCLEAR COMPLEXES BASED OF SALEN-TYPE (THIA)CALIX[4]ARENE LIGANDS: A CONTROL OVER MAGNETIC PROPERTIES VIA RATIONAL DESIGN OF MACROCYCLIC LIGAND

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The ability of a molecular system to exist in two different electronic states, is a particularly interesting property since logic operations can be executed. One of the most fascinating example of molecular bistability is certainly given by the spin crossover [1]. The spin crossover (SCO) or spin transition (ST) phenomenon is known as the inter-conversion between the electronic spin states occurring in coordination compounds of *3d* elements with electron configurations *d*4–*d*7. In the high spin (HS) and low spin (LS) configurations the compounds present distinct metal-donor atom distance (molecular volume), magnetic, dielectric and optical properties. Switching between the spin states can be induced by an external perturbation such as variation of temperature, application of pressure, magnetic field, light irradiation or electron pumping [2].

The chemistry of calix[4]arenes [4] and thiacalix[4]arenes is rapidly developing, and a large majority of calix[4]arene or thiacalix[4]arene based coordination compounds with 3*d*- and 4*f*-cations were investigated in the crystalline phase presenting the formation of discrete homo- and heterometallic polynuclear clusters or extended *1D-3D* coordination polymers when adopted a *cone* or *1.3-alternate* conformation able to exhibit smart properties such as tunable slow magnetic relaxation (Single Molecule Magnets, SMM), adsorption or catalytic behavior [3].

Here, we reports on the synthesis of new polydentate salen-type (thia)calix[4]arene Schiff bases ligands and their complexes with Fe (III). The complexes were characterized using X-ray diffraction on single crystal and powder and ^{57}Fe Mössbauer spectroscopy. The influence of alkyl spacer length and the presence of a methoxy group at *orhto* position of coordinating centre (OH-group) at the lower rim substituent of macrocycle backbone on the magnetic behavior of the obtained complexes has been studied.

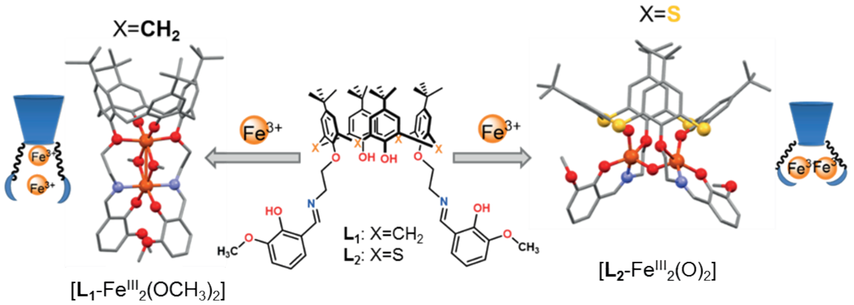

Figure 1. Crystal structure of new dinuclear Fe(III)-complexes based on calix[4]arene and thiacalix[4]arene derivatives.

Acknowledgements. This work was supported by the Russian Science Foundation (grant № 22-73-10139).

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CARBORANE-CONTAINING FOLIC ACID AND BIOTIN DERIVATIVES FOR BORON DELIVERY TO TUMOR CELLS

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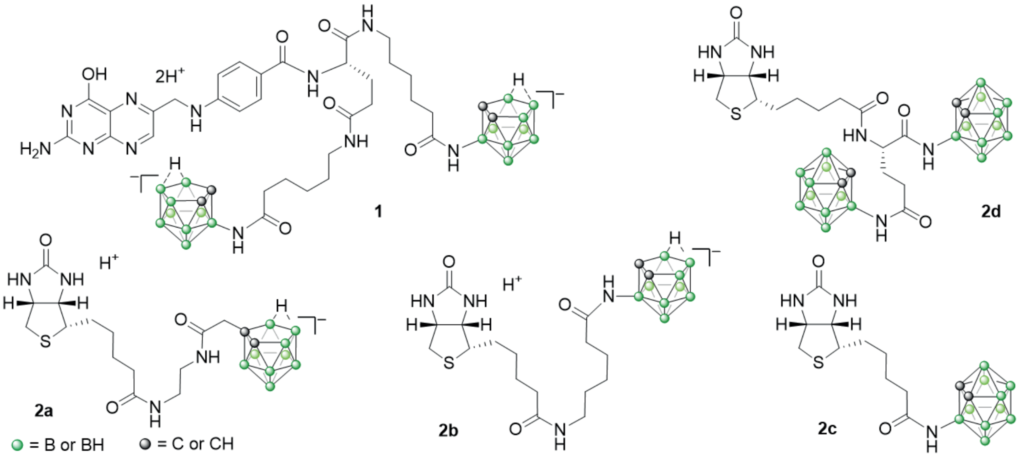
Boron neutron capture therapy (BNCT) is a modern approach to cancer treatment; it is based on the combined use of boron-containing compounds and neutron irradiation. The 1,2-dicarba-*closo*-dodecaborane and 7,8-*nido*-undecaborane derivatives (*closo*- and *nido*-carboranes) are widely used in the design of novel agents for tumor-targeting boron delivery that ensures successful application of BNCT [1]. Carboranes are characterized by high boron content, high stability and lipophilicity.

Folic acid (FA, vitamin B_9) and biotin (BT, vitamin B_7) are well-known tumor-tropic biomolecules. The FA and BT receptors are over-expressed in various types of tumor cells (including ovarian, brain, and breast cancers). Therefore, the derivatives of FA and BT are actively studied as tumor-targeting therapeutic, diagnostic and theranostic agents.

We have developed synthetic approaches to novel carboranyl derivatives of FA **1** [2] and BT **2a-d** [3] as potential agents for boron delivery to tumor cells. Compounds **1** and **2a-d** were obtained by the coupling reaction of FA or BT to primary amines containing *closo*- or *nido*-carborane residues by the carbodiimide or mixed anhydrides method.

nido-Carborane-containing FA and BT derivatives **1**, **2a** and **2**b with high solubility in 0.5% aqueous $NaHCO_3$ were moderately toxic against various tumor cells and BJ-5ta human fibroblasts (MTT assay). FA *bis*-amide 1 demonstrated a good ability to deliver boron to U87 MG human glioblastoma cells (up to 7.0 µg B/10^6 cells according to ICP-OES) [2].



Thus, it has been demonstrated that carborane derivatives containing folic acid and biotin moieties can be considered as promising compounds for design of novel BNCT agents.

The work was financially supported by the Russian Science Foundation (project no. 21-73-10073).

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SALTS CONTAINING DIFFERENT AMINO ACIDS AS A SOURCE OF NEW MATERIALS

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The search and investigation of new salts of amino acids is of great interest because these crystals display numerous applicable physical properties such as nonlinear optical and electro-optical activity, piezoelectricity, pyroelectricity, and ferroelectricity. Amino acid salts are known for a long time and have been thoroughly investigated. In particular, simple salts, salts with dimeric cations and salts with different anions are known [1]. Thus, a huge amount of information has been accumulated in this field. We had supposed, that salts containing two different amino acids may exist; this assumption was confirmed when a new class of amino acid salts was revealed [2,3,4]. To date, 69 representatives of these salts have been synthesized. Salts containing different amino acids may be classified into eleven distinct types. The majority of salts (47) belong to the [A(1)+···A(2)]X- type and the following 13 dimeric cations have been revealed: (Gly+···Sar), (Gly+···DMG), (Sar+···DMG), (DMG+···Sar), (Sar+···Bet), (Bet+···Sar), (DMG+···Bet), (Bet+···DMG), (L-Pro+···Sar), (β-Ala+···l-Pro), (β-Ala+···Sar), (β-Ala+···DMG) and (β-Ala+···Bet). 38 salts are non-centrosymmetric, 26 of which have polar symmetry. Thus, these compounds are potential nonlinear optical, pyroelectric and ferroelectric crystals. Furthermore, iodides can be used in medicine as regulators of thyroxine synthesis in the body [5].

Among these salts, an interesting phenomenon is observed when, depending on the anion or solvent, two amino acids can form two different dimers and either one or the other amino acid can be protonated. Three such pairs were observed: (Sar+DMG), (Sar+Bet), and (DMG+Bet). There are, for example, two representatives (Sar^{+}···DMG)ClO4 and (DMG^{+}···Sar)ClO$_4$, the first of which was precipitated from an aqueous solution and the second one from an acetic acid solution. Other examples are (Sar^{+}···Bet)I, (Sar^{+}···Bet)Br, (Sar^{+}···Bet)BF$_4$, (Sar^{+}···Bet)ClO$_4$ vs. (Bet^{+}···Sar)NH$_2$SO$_3$·0.5H$_2$O, and (DMG^{+}···Bet)BF$_4$·H$_2$O, (DMG^{+}···Bet)ClO$_4$·H$_2$O vs. (Bet^{+}···DMG)NO$_3$, (Bet^{+}···DMG)I.

Salts containing different amino acids are new materials with exciting properties, which still need further study, and new types of these phases may be revealed. Actually, it is a new path of synthesis of materials for various applications.

Acknowledgments

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HIERARCHICAL HALLOYSITE-BASED ALUMINOSILICATES AS A SUPPORT FOR HIGHLY EFFICIENT HYDROTREATING CATALYSTS

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Currently, oil refining faces two important tasks: meeting the ever-growing demand for high-quality motor fuels that meet strict environmental requirements, as well as the problem of processing heavy secondary petroleum cuts, the quality of which does not allow obtaining products that meet modern requirements. The hydrotreatment process makes it possible to effectively remove undesirable components from the processed raw materials, in particular, sulfur-containing substances. The main direction of increasing the efficiency of the hydrotreatment process is the improvement of the applied catalytic systems.

Traditional composition of hydrotreating catalysts includes a composition based on Co(Ni) and Mo(W) metals deposited on a porous carrier - γ-Al_2O_3.

One way to improve catalysts is to use modified composite supports. One of the promising materials-components of catalysts is halloysite (HNT) - aluminosilicate nanotubes with a number of features: large mesopore size - 20-50 nm, chemical anisotropy of the surface and internal cavities of the material. This material can be modified in many ways, in particular on the surface or inside the tubes, a silicate material of the MCM-41 type can be obtained.

Halloysite and MCM-41 materials were described as promising component of high-active hydrodesulfurization catalyst [1,2]. The reason for the increased activity of the catalyst is the formation of “nano-reactors” from sulfide particles stabilized by the porous structure of nanotubes or ordered silica. On the other hand, the presence of Brönsted acid sites leads to a weakening of the interaction between the active phase and the support, which leads to the formation of a larger number of highly active type II phase CoMoS particles.

In this work, sulfide CoMo catalyst on traditional and composite halloysite supports were investigated. Composite supports were Al_2O_3-HNT, Al_2O_3-deAlHNT (dealuminated halloysite), Al_2O_3-MCM-41/HNT (MCM-41 material outside of HNT) and Al_2O_3-MCM-41@HNT (MCM-41 material inside of HNT) materials. The obtained materials were characterized by a wide range of physicochemical methods: TPR, porosimetry, TEM, XPS, XRD, FTIR Py. The catalysts were investigated in the hydrotreatment of straight-run diesel fraction and mixed feedstock with 40% light catalytic cracking gas oils. The influence of technological parameters on the efficiency of the process was investigated. Catalysts based on composite supports showed higher activity compared to traditional ones. The resulting catalysts make it possible to obtain raw materials with a sulfur content of less than 10 ppm at lower temperatures. In this case, the degree of hydrogenation of polyaromatic compounds is much higher.

As a result, an increased efficiency of catalysts based on halloysite nanotubes was shown. The main reason may be the improvement of diffusion properties due to the system of large transport pores.indicated. On the other hand, the presence of Brønsted acid sites promotes the occurrence of transalkylation reactions that contribute to the removal of sterically hindered molecules, which was confirmed by studying the conversion of model feed containing 2,6-dimethyldibenzothiophene.

Acknowledgement.
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THE MECHANISM OF ACTION ON LIPID MEMBRANES OF THE ANTIMICROBIAL PEPTIDE TRICHOGIN. MD SIMULATION

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Peptaibols belong to the class of antimicrobial peptides (AMPs) that are produced by living organisms and act as the first defense against pathogens. They are unique due to containing non-standard amino acid residues such as α-aminobutyric acid (Aib) and C-terminal aminoalcohols. Alamethicin is an example of a peptaibol that shows membrane perturbing activity. Peptides such as long peptaibols permeate the lipid bilayer of the membrane, nonselectively creating channels in it. The resulting pores allow water and ions to traverse the membrane, what can lead to the permeation of the cellular contents.

Some peptaibols are smaller in size comparing to common transmembrane AMPs and can be as small as half the thickness of the lipid bilayer but still have antibacterial activity. The working mechanism of such peptaibols is still unclear despite the large number of experimental studies. To solve this problem, it is necessary to understand the behavior of small peptaibols in the membrane at the molecular level.

The object of our study is the peptaibol Trichogin GA IV, which consists of 10 amino acid residues. We have performed full-atom MD simulations of these molecules in different solvents. First of all, we have parameterized its molecule using quantum-chemical calculations since some of its amino acids are not included into the libraries of known force fields. The resulting molecule successfully has passed all stages of MD relaxation and has showed strong agreement with the known experimental properties. A simulation of the Trichogin has been performed in water, nonpolar solvent (hexane) and in a DOPC lipid bilayer.

The behavior of both individual molecules and their clusters of four molecules have been analyzed. Based on our analysis, we have shown that the Trichogin molecule is characterized by the ability to diffuse spontaneously into the membrane from the bulk water; the most frequently observed position is under lipid heads. A four-peptide complex formed in a nonpolar solvent and then placed in the center of the lipid bilayer have been found to be stable, in contrast to the complex obtained in water. Empty volume in the bilayer have been analyzed in the presence of a four-peptide cluster. It has been shown this cluster simplifies the penetration of water molecules into the bilayer. This behavior can be explained by the presence of hydrogen bonds between Trichogin molecules which has been made possible by the loss of their helical structure.

POSTER PRESENTATIONS

1-ARYL-3-NITROPROP-2-EN-1-ONES IN REACTIONS WITH SUBSTITUTED HYDRAZINES

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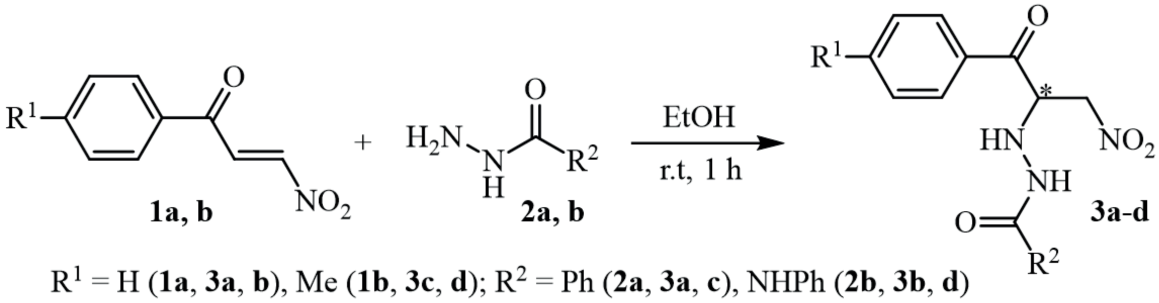
1-Aryl-3-nitroprop-2-en-1-ones, containing in their structure a C=C bond conjugated with two acceptor substituents, are attractive substrates in reactions with nucleophilic reagents.

It has been previously shown that structurally similar alkyl 3-nitroacrylates react with carboxylic acid hydrazides and hydrazinecarboxamide to form Michael adducts [1, 2].

We have studied the interaction of 1-aryl-3-nitroprop-2-en-1-ones **1a, b** [3] with representatives of substituted hydrazines – benzohydrazide **2a** and *N*-phenylhydrazinecarboxamide **2b**. The reaction proceeds in ethanol solution at room temperature and leads to the formation of corresponding aza-Michael adducts **3a-d** with yields up to 92%.



R^1 = H (**1a**, **3a**, **b**), Me (**1b**, **3c**, **d**); R^2 = Ph (**2a**, **3a**, **c**), NHPh (**2b**, **3b**, **d**)

The structure of synthesized compounds **3a-d** was characterized by a complex of physicochemical methods (IR, NMR ^{1}H, ^{13}C spectroscopy with ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC experiments). The structural feature of adducts **3a-d** is the presence of an asymmetric carbon atom, which causes the manifestation diastereotopy effect in the ^{1}H NMR spectra of protons of the CH_2NO_2 group.

This work was financially support by the Ministry of Education of Russia (project no. VRFY-2023-0003).

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DESIGN AND SYNTHESIS OF NOVEL (METHOXYPHENYL)-TETRAHYDROPYRANYL-SUBSTITUTED 1,3,4-OXADIAZOLES

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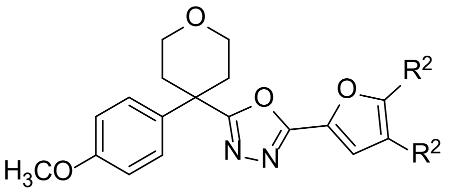
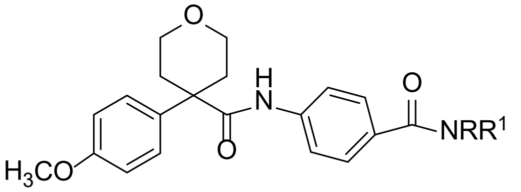
The 1,3,4-oxadiazole ring is an important structural fragment of many biologically active compounds that exhibit antibacterial, anti-inflammatory, anticonvulsive, antitumor, antihypertensive, and other properties. Aryltetrahydropyran derivatives, too, show diverse biological properties: among them, compounds that act as α- and β-adrenoblocking, as well as antimonoaminooxidase, antibacterial, and antihistamine agents were found [1].

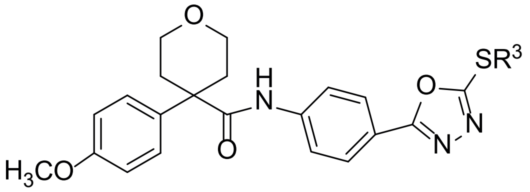
In the present work we set ourselves the goal to synthesize previously unknown compounds, in which the 1,3,4-oxadiazole ring is linked to the aryltetrahydropyran fragment, both directly and via an amidobenzyl linker. To this end, we had first to prepare 4-(4-methoxyphenyl)tetrahydro-2*H*-pyrancarboxylic and 4-[4-(4-methoxyphenyl)tetrahydro-2*H*-pyran-4-carboxamido]benzoic acid hydrazides through the corresponding esters [2].

Oxadiazoles, in which the tetrahydropyran ring is directly attached to the oxadiazole ring, were synthesized starting with furan- and 4,5-dimethylfurancarboxydrazides and disubstituted hydrazides were cyclized by phosphorus oxychloride to obtain the target unsymmetrical 2,5-disubstituted 1,3,4-oxadiazoles.

The synthesis of 1,3,4-oxadiazoles containing a 4-(4-methoxyphenyl)-*N*-phenyltetrahydro-2*H*-pyran-4-carboxamide fragment was performed starting from ethyl 4-[4-(4-methoxyphenyl)- tetrahydro-2*H*-pyran-4-caroxamido]benzoate. The condensation of letters with hydrazine hydrate gave hydrazide. which was reacted with CS_2 to obtain 5-sulfanyl derivative, which was used in further syntheses, in particular, alkylation reactions [3].







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HOMOGENIZING ROLE OF HYDROGEN IN THE SYNTHESIS OF MULTICOMPONENT MATERIALS OF TRANSITION METALS IN THE COMBUSTION MODE

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Multicomponent interstitial phases - carbides, nitrides, carbonitrides, etc. - have a valuable combination of important physical and mechanical properties that determine their use in modern materials science. They are multi-purpose materials.

Along with alloying metals, hydrogen, as a temporary alloying element, is unique to group IV–VI metal carbides and nitrides because it can be easily added and removed without melting, unlike other alloying elements. Alloying of alloys with hydrogen is attractive in the industry for improving performance, including machining, powder production, sintering, densification, ductility, etc.

Systematic studies of combustion processes in multicomponent systems based on transition metals of groups IV, V and VI of the periodic system with carbon in an atmosphere of argon, hydrogen, nitrogen and in a nitrogen-hydrogen mixture have been carried out. Numerous compounds have been synthesized, and the effects of various metals and non-metals on combustion processes, phase composition, and their absorption properties for hydrogen have been studied.

Single-phase products were synthesized in one technological stage by the SHS method in the systems: Zr-Nb-N, Zr-Nb -N-H, Zr-Nb -C, Zr-Nb-C-H, Zr-Nb-C-N, Zr-Nb-C-N-H, Ti-V-C, Ti -V- C-H, Ti-V- C- N, Ti -Nb -V-C, Ti -Nb -V-C-H, Ti-Nb -Cr-C, Ti-Nb-Cr-C-H, Ti-Nb -W-C, Ti -Nb -W-C-H.

The optimal conditions for the synthesis of multicomponent single-phase carbides, carbohydrides, nitrides, nitride hydrides, and carbonitride hydrides are determined. Some characteristic phenomena occurring in the combustion regime in a hydrogen atmosphere are revealed. Some characteristic phenomena occurring in the combustion regime in a hydrogen atmosphere are revealed. The effect of hydrogen on the formation of single-phase products in the SHS regime has been studied.

It has been established that in all the systems studied, combustion in a hydrogen atmosphere leads to homogenization of the final products of synthesis, and hydrogen is an active factor influencing structural processes.

It is shown that, during combustion in argon, two-phase carbides with an FCC structure are mainly formed. The combustion of the same compositions in a hydrogen atmosphere leads to the synthesis of single-phase carbohydrides. During the combustion of transition metals at high nitrogen pressures, the products are multiphase, and during the repeated combustion of these multiphase nitrogen-containing compounds in hydrogen, single-phase nitridohydrides are formed. It has been established that after the removal of hydrogen, the single-phase structure is not disturbed.

The presence of hydrogen in the crystal lattice of refractory carbides, nitrides makes it easy to disperse these compounds up to 10-20 microns. The present results may be of commercial importance in powder metallurgy in the production of refractory materials.

SYNTHESIS AND BIOLOGICAL SCREENING OF NEW THIOALKYLDERIVATIVES OF PYRIDINE

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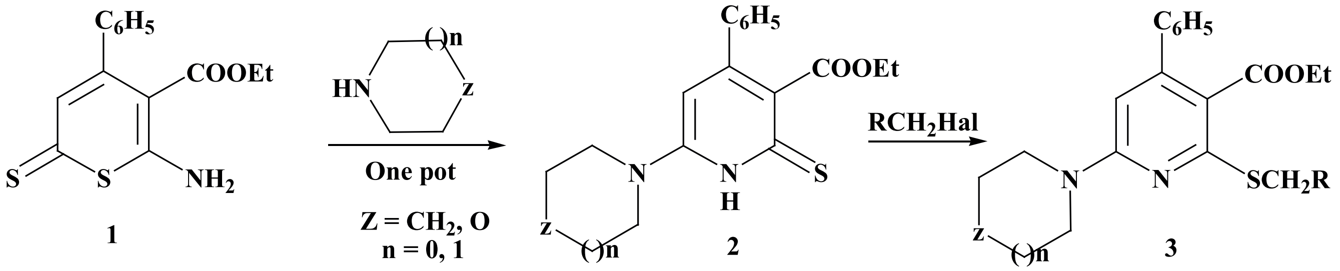
Pyridine and pyridine-derived structures are important in medicinal chemistry due to their ability to bind to biological targets and influence their activity. They have been used as scaffolds for the development of numerous drugs, including antihistamines, antidepressants, and antipsychotics. Pyridine derivatives also offer a degree of structural diversity, which can be useful in optimizing the pharmacological properties of a drug [1-3]. In continuation of the work on the synthesis of biologically active compounds containing pyridine ring, we have developed methods for obtaining new thioalkylderivatives of pyridine and predicted potential biologically activity of them. Thus, a one-pot method for obtaining 2-amino substituted thiopyridine derivatives **2** based on ethyl ester of 6-amino-4-phenyl-2-thioxo-2*H*-thiopyran-5-carboxylic acid **1** was developed. Based on 2-amino substituted thiopyridine derivatives **2** and alkylating agents ethyl 2-thioalkyl-4-phenyl-6-cycloamine-pyridine derivatives **3** were synthesized in high yield (96-98%). The biological spectrum of the synthesized new pyridine derivatives was predicted by in silico method. Some compounds have been found to exhibit potent anti-cancer, anti-ulcer, anti-arthritic and anti-diabetic effects



This work was supported by the Science Committee of RA (Research project № 20TTWS-1D032).

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C–H SULFENYLATION OF AZOLOPYRIMIDINES IN THE DESIGN OF NOVEL ANTIVIRAL TRIAZAVIRIN® CONGENERS

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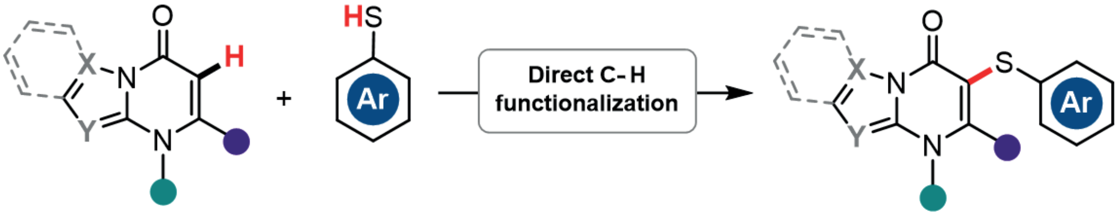
Since the beginning of the COVID-19 pandemic, the urgency for the development of new effective antiviral drugs has become more apparent than ever before. In this connection, high hopes are placed on designing convenient synthetic pathways to achieve original small molecules with high antiviral potential. Among the manifold of relevant organic scaffolds, azoloazine core has emerged as one of the most promising ones; for example, azoloazine-based drug Triazavirin® (INN Riamilovir) has been successfully exploited in Russia during the pandemic to treat the SARS-CoV-2-induced pathological conditions.[1] The latter determined the focus of the current study, being aimed at the elaboration of new Triazavirin® structural derivatives with improved pharmacological characteristics.

During the literature analysis, it was found that the introduction of an aromatic thioether moiety into the azoloazine scaffold could govern the desired enhancements.[2] However, the appropriate synthetic approach was required to be designed to provide the expedient access to such compounds. In the course of our investigation, we have managed to achieve the target molecules by employing direct transition-metal-free cross-dehydrogenative coupling of azolopyrimidines **1** with (hetero)aromatic thiols **2**. As a result, a series of 18 sulfenylated heterocyclic derivatives **3** have been obtained in yields of up to 87%, and their structures were confirmed by 2D NMR, IR, and mass analyses.



1 **2** **3**

X, Y = N, CH, CR

Affinity of the compounds **3** towards the key target of SARS-CoV-2, main protease Mpro, was assessed by an *in silico*-analysis. According to the results of molecular docking, some of the synthesized structures demonstrate the binding energy values almost identical to a known inhibitor X77 (PDB ID: 6W63) used as a native ligand, and much lower than that of Triazavirin®. Thereby, our current efforts are focused on in-depth evaluation of the antiviral activity of these compounds (involving experiments *in vitro* and *in vivo*), as well as on improvement of their pharmacokinetic properties.

This research was funded by the Ministry of Science and Higher Education of Russia
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NITROGEN DIOXIDE SORPTION BY METAL-ORGANIC FRAMEWORKS

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Nitrogen oxides NO_2 and NO (NO_x) are toxic gases that are produced in large quantities by human industrial activity. They are also the main cause of photochemical smog and acid rains. Reducing NOx pollution is an important and challenging problem, not least because of their strong oxidizing and corrosive properties. Thus, the search for materials capable of repeatedly sorbing nitrogen dioxide without losing sorption capacity is an important goal.

Various types of materials (such as zeolites[1], metal oxides[2] and activated carbons[3]) have been proposed for nitrogen dioxide adsorption, but they all have such drawbacks as low sorption capacity and irreversible chemical interaction due to the high reactivity of NO2 which often leads to oxidation and degradation of sorbents.

Metal-organic frameworks (MOFs) have recently gained popularity due to their structural diversity and the number of promising applications. The large amount of research devoted to these compounds because the almost unlimited possibility to vary their properties by changing a metal center or organic linkers. The wide range of materials synthesized so far could be of interest in a number of applications such as gas separation and storage, catalysis, liquid-phase separation. For example, MOFs are solid adsorbents that show promise in the sorption of harmful gases such as CO_2, NO_2 and others[4,5].

Metal-organic frameworks exhibiting high structural stability are particularly interesting for adsorption of chemically active gases, considering that many of already synthesized MOF materials are often unstable. Zirconium MOFs are particularly notable for showing the highest structural stability due to the strong Zr-O bonds.

Therefore, in this work, the interest has been focused on the zirconium MOFs with various organic linkers (fumaric acid and terephthalic acid). They were considered as NO_2 sorbents and their sorption capacity was evaluated. A spectrum of immobilized NO_2 at room temperature was obtained for the first time. The sorption mechanisms were studied by a set of different physicochemical methods (EPR spectroscopy, infrared spectroscopy, powder X-ray diffraction and gravimetry).

This work was supported by Russian Science Foundation (22-73-10239).

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INTRAMOLECULAR SPECIFIC INTERACTION OF =CH...O=C, =CH...NO_2 IN METHYL ESTERS OF 1-VINYL-3(5)PYRAZOLECARBOXYLIC ACIDS BASED ON QUANTUM CHEMICAL MODELING AND X-RAY DIFFRACTION ANALYSIS

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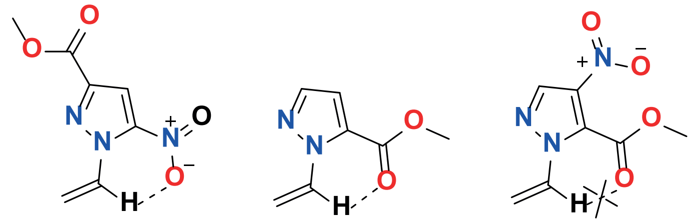
According to ^1H and ^{13}C NMR data and based on AB initio quantum chemical calculations, the molecules of 1-vinyl-2-formylimidazoles and 1-vinyl-2-formylbenzimidazoles have specific intramolecular interactions (C–H...O=C) [**1**].

Using the semi-empirical quantum-chemical GFN2-xTB method, a conformational analysis of structures **1-3** was carried out (**Scheme**) [**2**].



1 **2** **3**

During the simulation, all conformers **1-3** were found by rotating all substituents connected with the pyrazole ring. Conformational analysis based on quantum chemical modeling showed that for compounds **1** and **2** in solution, low-energy conformers can be formed. In particular, all substituents at the pyrazole ring laid in the ring plane and formed a hydrogen bond of the characteristic structure with α-H-atom of the vinyl group. On the other hand, compound **3** in a DMSO solution has low-energy conformers in which the formation of a strong intramolecular hydrogen bond is impossible. At the same time, for compound **3**, the formation of intermolecular hydrogen bonds may be facile, which was confirmed by X-ray diffraction study (**Fig.**).

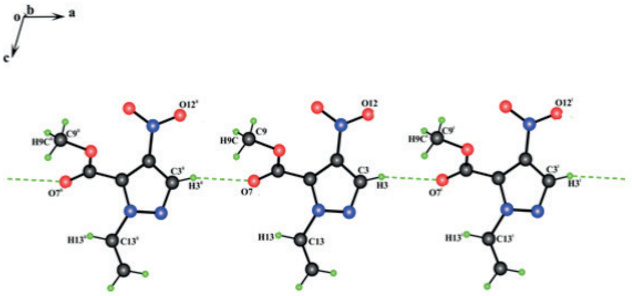


Fig. Chain along [1 0 0] formed by intermolecular hydrogen bonds, symmetry code (i=1+x; y; z, ii= -1+x; y; z). Hydrogen bonds are shown by dotted lines.

This work is supported by the RA MES Committee of Science in the frames of research project № 21T-1D020.

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SYNTHESIS AND CONVERSIONS OF BENZ-SUBSTITUTED 4-[2-METHYL-4-(METHYLTIO)-QUINOLIN-3-YL]PROPAN-2-ONES

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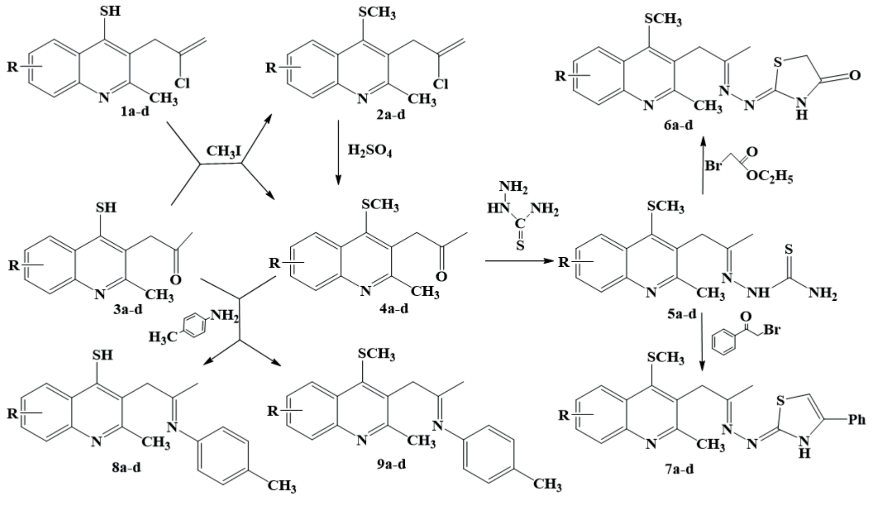
Quinoline and its derivatives have consistently captured the interest of synthetic and biological chemists due to their significant role as a biologically important moiety, exhibiting a wide range of biological properties including antimalarial, antidepressant, antibacterial, antihypertensive anti-inflammatory, anti-arrhythmic and antituberculosisactivities [1,2].Based on this perspective, we have developed novel series of quinoline derivatives. The conceptual designs of these derivatives are illustrated in Scheme 1.In this study, we present an affordable and cost-effective approach for synthesizing novel derivatives of thiazolidine and dihydrothiazoline based on 2-{1-[2-methyl-4-(methylthio)quinolin-3-yl]propan-2-ylidene}hydrazinocarbothioamide with substitution in the benzene ring (5a-d). The main starting compounds were synthesized through the reaction of 3-(2-chloroallyl)-2-methyl-4-(methylthio)quinolines (1a-d) and 1-[2-methyl-4-(methylthio)quinolin-3 -yl]propan-2-ones (3a-d) with methyl iodide.This resulted in the formation of substituted in the benzene ring3-(2-chloroallyl)-2-methyl-4-(methylthio)quinolines(2a-d) and 1-[2-methyl-4-(methylthio)quinoline -3-yl]propan-2-ones (4a-d). The latter compounds were also obtained by hydrolysis of compounds 2a-d in 96% sulfuric acid. The interaction between the obtained propanones (4a-d) and thiosemicarbazide resulted in the formation of the corresponding thiosemicarbazones (5a-5d) as syn- and anti-isomers in a ratio of 1:4 with quantitative almost yield.

Scheme 1



R = H (a); 6-CH$_3$ (b); 8-CH$_3$ (c); 8-OCH$_3$ (d)

Compounds 5a–5d were reacted with ethyl ester of monobromoacetic acid and bromoacetophenone in the presence of sodium acetate, followed by refluxing in ethanol. This reaction resulted in the closure of the 4-thiazolidinone and 2-phenylthiazolidinone rings, leading to the formation compaunds6a–d and 7a–d. The starting propanones-2 (3a-d) and (4a-d) were reacted with p-toluidine. This reaction yielded 2-methyl-3-[2-(p-tolyl-imino)-propyl]quinoline-4-thiols (8a-d) and 2-methyl-3-[2-(p-tolylimino)propyl]- 4-methylthioquinolines (9a-d).

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NOVEL N^4-ALKYLCYTIDINES AS PROMISING ANTIMICROBIAL AGENTS

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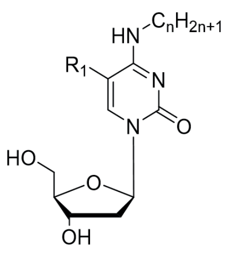
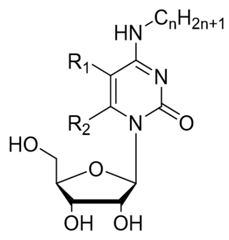
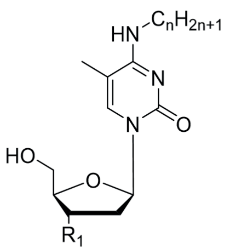
The emergence of drug-resistant strains of pathogenic microorganisms necessitates the creation of new drugs.



(1) n=8, 10, 12, 14
R_1 = H, CH_3



(2) n=8, 10, 12, 14
R_1 = H, R_2 = CH_3
R_1 = CH_3, R_2 = H



(3) n= 10, 12
R_1 = N_3, NH_2, NHC_2H_5, $NH(CH_3)_2$, $N(C_2H_5)_2$

In order to find new inhibitors of pathogenic bacteria and fungi, we synthesized a set of N^4-derivatives of (2'-deo-xy)cytidine, bearing extended N^4-alkyl groups **1-3** [1] as well as 3′-modified derivatives of N^4-alkyl-5-methyl-2′,3′-dideo-xycytiines **4** [2].

The derivatives **1-3** demonstrated activity against *Mycobacterium smegmatis* and some Gram-positive bacteria, including *Staphylococcus aureus* (MIC= 10 – 200 mM), comparable with the activities of a number of antibiotics in medical use. The most promising are low toxic N^4-dodecyl cytidine derivatives **1** (R_1=CH_3) and **2** (R_1=CH_3, R_2=H as well as R_1=H, R_2= CH_3) demonstrating high inhibitory activity not only against Gram-positive bacteria (MIC =25 mM) but filamentous fungi that can, among other things, damage works of art, such as tempera painting. In this case the fungal growth inhibitory concentration appears to be in the range of 0.5 - 3 mM.

The replacement of the 3′-hydroxyl group with amino, aminoethyl and dialkylamino groups significantly enhances the antifungal activity, most prominently towards *Aspergillus* genus. Several new compounds were able to completely inhibit growth of all the tested moulds (at 0.7 mM), previously isolated in the Moscow State Tretyakov Gallery. In particular, such compounds are promising for use as antiseptics for protecting works of art from mould fungi.

3′-Modified N^4-alkyl-5-methyl-2′,3′-dideoxycytidines **4** also demonstrate activity against gram-positive bacteria as well as mycobacteria. Unfortunately, their high cytotoxicity does not allow to consider them as potential antibacterial drugs. However, cytotoxicity is not the issue for their application on lifeless but (hopefully) eternal works of art. It appeared that our compounds display a wide range of activity against a large number of microorganisms. In this regard, the obtained substances may be an important tool for preventive treatment and scientific restoration of tempera paintings and oil paintings on canvas as biocidal coatings.

Acknowledgements: The studies were supported by Russian Science Foundation (Grant number: 23-14-00106)

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SYNTHESIS OF INTERMETALLIC Ni_3Fe COMPOUND FOR MAGNETIC APPLICATIONS BY SOLUTION COMBUSTION SYNTHESIS METHOD

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Alloys based on iron and nickel are of great interest from scientific point of view due to their catalytic and multifunctional properties. In particular, the intermetallic compound Ni_3Fe has received great interest due to its catalytic properties for the electrolysis of water [1] Due to high magnetic permeability it is used in creation of magnetic sensors, transformers, electric motors, etc. [2]. The utilized synthesis methods of Ni_3Fe contain time- and energy intensive multiple high-temperature steps.

In this study a new approach for the synthesis of intermetallic compound based on Ni-Fe with a homogeneous structure was developed. To synthesize Ni_3Fe the solution combustion synthesis (SCS) approach was applied [3]. SCS is a type of combustion synthesis method and, in particular, it is considered a special type of high-temperature self-propagating synthesis (SHS) method. It is a fast, energy-saving, ecologically clean, single-phase, reproducible way of obtaining materials. The process takes several minutes and is characterized by high combustion temperatures, which ensure the crystallization and purity of the final product. In this process the raw materials are mixed at the molecular level providing homogeneity of the final product. During the process large amount of gases are released, which prevent the growth of particles and contributes to the formation of porous, nano-size particles.

In this work combustion process was realized in aqueous solutions of the $Ni(NO_3)_2 + Fe(NO_3)_3 + nC_6H_{12}N_4$ mixture in nitrogen atmosphere. X-ray examinations have shown (Fig.1A) that at n=6 mol, a single-phase target product Ni_3Fe is obtained, and electron microscopic studies indicated that the product is characterized by a pronounced porous structure (Fig.1B) due to abundant gas evolution during the SCS process. The magnetic characteristics of the synthesized substance also have been studied.

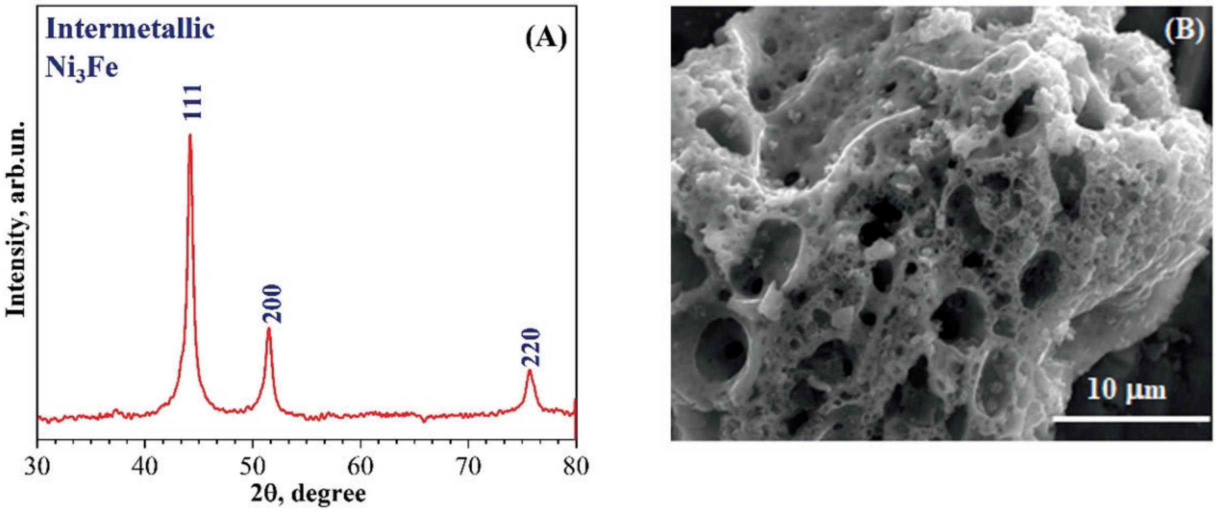

Fig. 1. XRD pattern (A) and SEM image (B) of the Ni_3Fe intermetallic compound prepared by SCS

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G-QUADRUPLEX LIGANDS BASED ON 4,11-DIAMINOANTHRA[2,3-*d*]THIAZOLE-5,10-DIONES: SYNTHESIS AND BIOLOGICAL PROPERTIES

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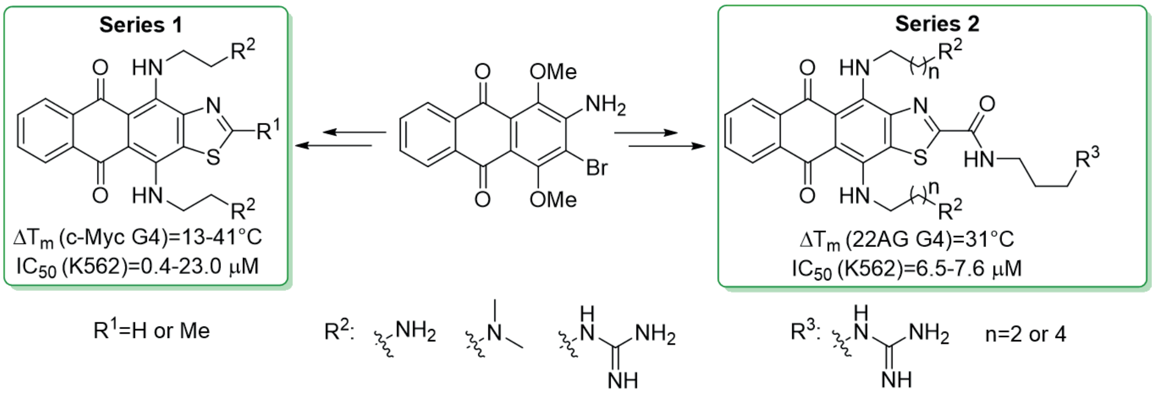
Anthraquinone moiety is one of the first and productive scaffolds for the design of G-quadruplex (G4)-targeting compounds [1]. Previously, derivatives of heteroarene-fused anthraquinones (namely, anthrathiophenes and anthrafurans) containing aminoalkyl substituents at the *peri*-positions and a side chain at the 2 position were identified as potent G4 binders [2]. Lead derivatives are able to target G4 from human telomeric sequences, as well as to stabilize quadruplexes in the oncogene promoters (H-Ras and K-Ras) [3, 4]. To study the effect of the heterocycle on biological properties, thiazole-fused anthraquinone derivatives were obtained.

Target G4 ligands bearing aminoalkyl substituents at the positions 4, 11 (series 1), and compounds substituted with an additional side chain at the position 2 (series 2) were synthesized from 2-amino-3-bromo-1,4-dimethoxyanthracene-9,10-dione. Preliminary screening of antiproliferative activity of new derivatives against K562 leukemia cell line was carried out. Compounds with ethylenediamine and *N,N*-dimethylethylenediamine substituents suppressed growth of tumor cells in the range from submicromolar to micromolar concentrations; thiazoles substituted at positions 2, 4, and 11 showed a moderate antitumor effect.

Interaction of new ligands with different topologies of nucleic acids was studied by the FRET-melting assay. The results showed that selected derivatives from series 2 have high values of stabilization shift (up to 31°C) and selectivity of action towards telomeric G4 (22AG). The guanidino derivatives of series 1 had the highest binding affinity to c-Myc G4 (up to 41°C). It should be noted that all new derivatives did not show significant affinity for duplex DNA.



The study was performed with partial financial support of the Russian Science Foundation grant No. 22-23-01073, https://rscf.ru/project/22-23-01073/

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INVESTIGATION OF THE STABILITY TO ATOMIC OXYGEN OF LADDER POLYPHENYLSILSESQUIOXANES AND COMPOSITES BASED ON THEM

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It is well known that the near-satellite environment at altitudes of 200–800 km is aggressive with respect to polymeric materials and small spacecraft (SSC) coatings: high vacuum, ultraviolet radiation, temperature drops, charged particles, micrometeorites, atomic oxygen (AO), etc [1, 2]. Among these factors, the greatest danger for polymers used in the external elements of the SSC design is AO, whose incoming flow causes their erosion and degradation, which leads to a reduction in the service life of the SSC [3]. Research in such areas as diversification of materials that can work in outer space and be used in the development of SSC is in line with global trends in the development of materials chemistry.

Siloxane polymers are a class of non-carbon materials, whose erosion rate when exposed to AO is one to two orders of magnitude lower than that of organic polymers in low Earth orbit [4]. In addition to a lower erosion rate upon exposure to AO, siloxane polymers form a protective barrier layer of silicon dioxide, consisting of SiO_x fragments (where x ranges from 1.8 to 2.0) [5, 6]. With constant exposure to AO, the inorganic surface layer prevents further degradation of the polymer underneath. However, this siloxane-to-silica surface transformation tends to create tensile stresses leading to coating cracking and loss of its integrity [7, 8].

In this work we studied the resistance to atomic oxygen of ladder polyphenylsilsesquioxanes with molecular weights $M_w = 322 \cdot 10^3$ and $1060 \cdot 10^3$, as well as composites based on them. Both initial and filled ladder polymers exhibit low erosion coefficients in the region of 10^{-26} cm^3/atom O at a fluence of atomic oxygen (AO) of $1.0 \cdot 10^{21}$ atom O/cm^2. When exposed to an oxygen plasma flow, the films retain their integrity and do not crack, i.e. they are free from the limitation typical of linear siloxanes. Both unirradiated and irradiated ladder polyphenylsilsesquioxane films retain high transparency. Exposure to high AO fluence does not lead to oxidation or degradation of both polymers and composites based on them.

This work was supported by the Russian Science Foundation (project no. 23-13-00244).

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PLATINUM AND RUTHENIUM ANTIPROLIFERATIVE COMPLEXES WITH PHENOSANIC ACID BASED LIGANDS

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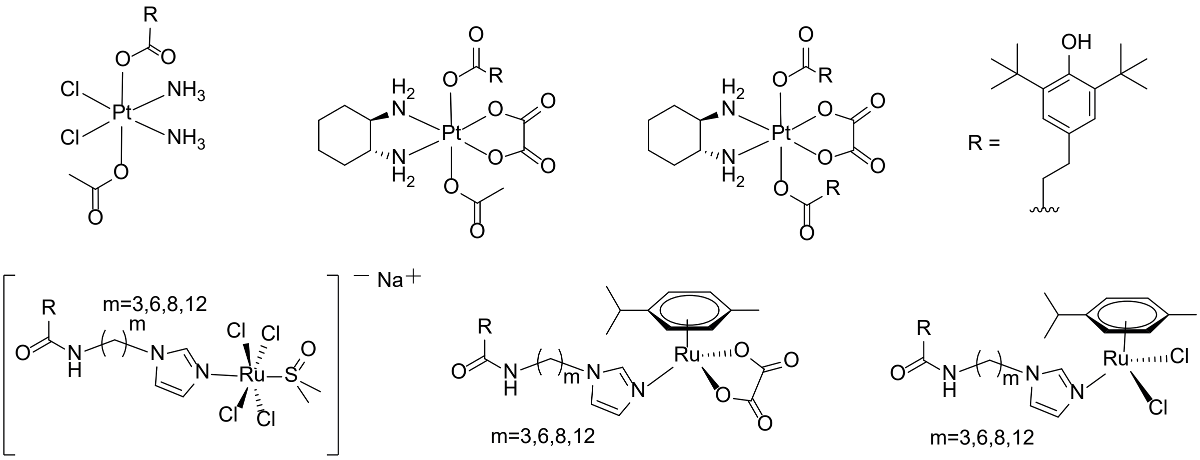
Platinum (II) compounds, such as cisplatin, carboplatin and oxaliplatin , are widely used in chemotherapy. due to their high effectiveness. However, their use is limited by severe side effects and the development of resistance in certain cancer types. Thus, the development of novel anticancer agents that overcome these limitations represents a significant and urgent challenge in modern medicinal chemistry. Metal-containing anticancer compounds are developed using various strategies, including modifying the metal center and its ligand environment. One promising area of research is the development of Pt (IV) compounds, which serve as prodrugs demonstrating lower toxicity compared to the parent Pt (II) compounds. Another approach for modification involves transitioning to a different metal. Ruthenium compounds are particularly intriguing as potential anticancer drugs, as they offer the potential to mitigate the challenges associated with high general toxicity and resistance.

The aim of this study was to synthesize and evaluate Pt (IV) prodrugs, as well as Ru(II) and Ru(III) compounds with organic ligands based on phenosanic acid. The introduction of this antioxidant moiety has the potential to soften the toxic effects of the compounds on healthy cells.



The obtained compounds were fully characterized using NMR spectroscopy, mass spectrometry, and elemental analysis. The *in vitro* antiproliferative activity of the compounds was assessed using the MTT assay on A549, MCF7, HCT116, and WI38 cell lines. The platinum complexes exhibited superior activity compared to the reference compound cisplatin. The ruthenium compounds demonstrate activity within the micromolar concentration range. The ability of several compounds to induce apoptosis was studied.

Furthermore, the antioxidant activity of all compounds was evaluated through DPPH and CUPRAC assays, demonstrating their promising potential as antioxidants.

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CYCLIC MERCURIC DERIVATIVES OF HALOGEN SUBSTITUTED *ortho*-CARBORANE

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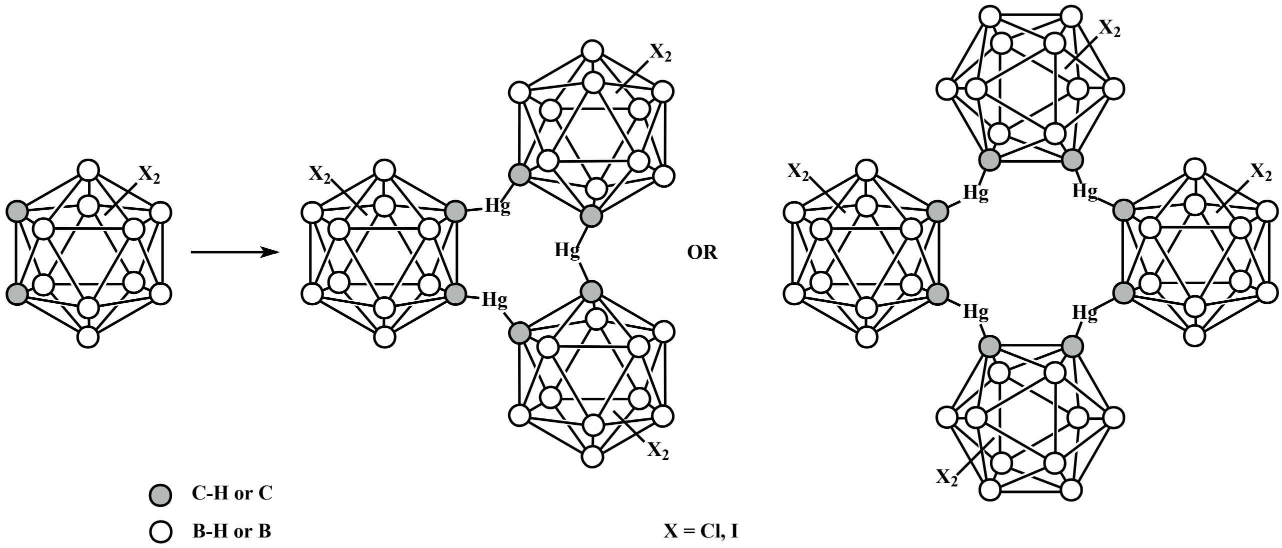
Molecular recognition is an actively developing area of supramolecular chemistry due to possible applications in the creation of various molecular devices such as sensors, extraction systems, simple and transmembrane transporters, catalysts based on transition metals, organocatalysts, etc. Therefore, one of the fundamental problems of modern chemistry is the directed design of supramolecular systems in which the binding of components occurs through intermolecular (non-covalent) interactions.

One of the most well-known types of supramolecular receptors for binding anions are macrocyclic anticrowns with mercury atoms linked together by various electron-withdrawing groups, which increase their Lewis acidity. An example of such an anticrown is cyclic trimeric tris(perfluoro-*ortho*-phenylenemercury) (o-$C_6F_4Hg)_3$ [1,2], which is capable of forming polymer and sandwich complexes with halide anions in which the anions are located above/below the Hg_3 plane (the "nest" type structure). Complexes of halide anions with tris(*ortho*-carboranylmercury) (o-$C_2B_{10}H_{10}Hg)_3$ have a similar structure [3].

In this work we discuss carborane-containing anti-crowns carborane backbone modification by replacing hydrogen atoms in positions 9/12 or 3/6 with halogen atoms in order to increase its Lewis acidic properties.



Scheme 1.

This work was supported by Russian Science Foundation (№ 21-13-00345).

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SYNTHESIS AND PROPERTIES OF HYBRID DENDRIMERS BASED ON A CARBOSILANE CORE AND AROMATIC SHELL

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Dendrimers and structures based on them typically consist of blocks of the same type. Previously, our group demonstrated the possibility of synthesizing core/shell dendrimers by combining hard polyphenylene and soft carbosilane blocks [1,2]. The advantage of the Cu-catalyzed core-shell azide-alkyne cycloaddition reaction is total conversion and the absence of many side processes.

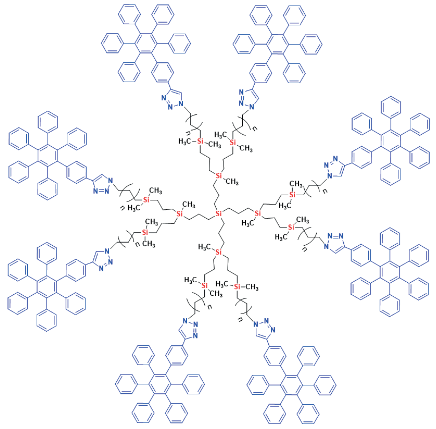

Figure 1 - An example of a hybrid dendrimer based on a carbosilane core of the 1st generation and a dendron from hexaphenylbenzene with different spacer lengths

Our research is focused on the synthesis and study of the properties of carbosilane dendrimers of the 1st and 2nd generation with a polyphenylene dendrons in a shell [3]. A spacer of various lengths between the carbosilane core and the polyphenylene shell was used. We study the effect of a change in the length of the spacer, as well as the presence of a rigid triazole fragment, on the different ordering of hybrid systems. The influence of the number and density of GPB groups in the dendrimer shell on the degree of crystallinity of macromolecules and the packing density in the crystal structure, as well as the phase and thermal behavior, is shown.

Acknowledgments. This work was supported by RSF, Project No. 22-13-00459

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INFLUENCE OF THE COMPOSITION OF THE INITIAL MIXTURE ON THE REGULARITIES OF PROPANE OXIDATION IN THE MODE OF A STABILIZED COOL FLAME

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The problem of rational use of natural resources, including hydrocarbon raw materials, is still very relevant. Interest in the mechanism of complex processes of hydrocarbon oxidation is determined by two main factors: the need for further development and refinement of the theory of degenerate branched chain reactions and the search for ways to more efficiently use hydrocarbon raw materials both in the energy sector and for the production of valuable oxygen-containing compounds. Numerous experimental data obtained in the study of hydrocarbon oxidation reactions indicate that this class of reactions has a number of characteristic features, such as the appearance of cool flames and the existence of a region of negative temperature coefficient (NTC) of the maximum reaction rate. However, despite a large number of studies, the detailed mechanism of these phenomena, which are closely related to the processes of hydrocarbon processing, still remains unclear.

Propane occupies a special place among saturated hydrocarbons. On the one hand, it is the simplest among hydrocarbons that are beginning to show common features with heavier alkanes during chemical conversion in both low and high temperature ranges. On the other hand, it is an intermediate product between light (CH_4 and C_2H_6) and heavy (C_4H_{10}, C_5H_{12}, etc.) alkanes. It has been experimentally shown that the parameters of a stabilized cool flame of propane depend significantly on the ratio of reactants in the initial propane-oxygen mixture.

The experiments were carried out in two-section quartz reactor at T=350°C, pressure P=340 Torr, and residence time of the mixture in the second section of the reactor 18.2 s. The experiments were carried out with five compositions of initial reagents C3H8:O2 = 1:1, 1:2, 1:3, 1:4, and 1:5.

It was shown that in the studied range of mixture compositions, an increase in the oxygen content leads to a decrease in the intensity of stabilized cool flame. The change in intensity is evidenced by the change in heating and luminescence of the stabilized cool flame. When the C_3H_8:O_2 ratio is reached from 1:1 to 1:4, the stabilized cool flame becomes extremely unstable, and when the composition of the mixture C_3H_8:O_2 = 1:5, the flame dies out.

At the same time, in the high-temperature region (above 530°C), in contrast to the cool flame regime, an increase in the oxygen concentration during propane oxidation increases the intensity of the process. It has been established that the color and brightness of the glow depend both on the composition of the initial mixture and on the temperature in the second section of the reactor. It has been shown that with an increase in the oxygen content, the selectivity of formaldehyde and acetaldehyde formation increases, while the selectivity of methanol formation decreases, which can be explained by the competition of the corresponding reactions.

SYNTHESIS OF (4-(BENZO[d][1,3]DIOXOL-6-YL)-TETRAHYDRO-2*H*-PYRAN-4-YL)METHYLSUBSTITUTED AMINOAMIDES, SULFANILAMIDES AND ARYLOXYPROPANOLAMINES

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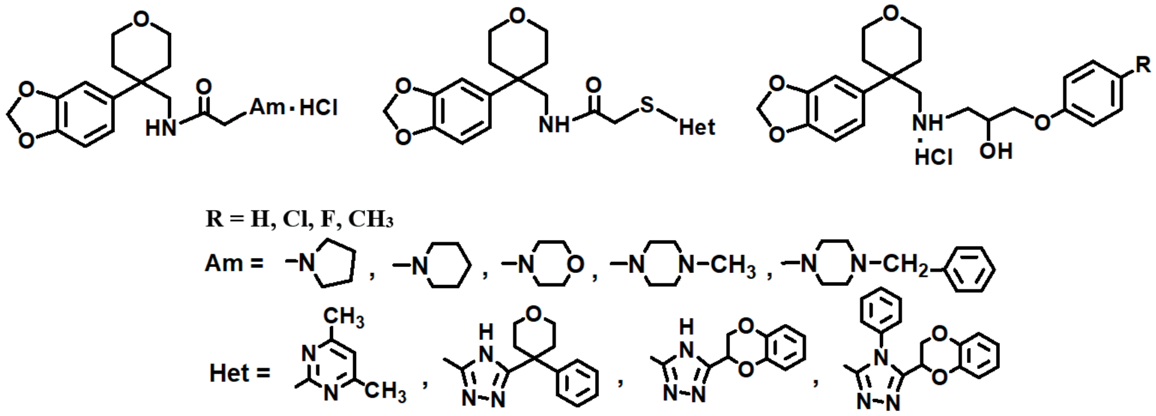
The structure of benzo[d][1,3]dioxol is a constituent of many natural and synthetic compounds with a wide spectrum of biological activity. In particular, they exhibit sedative, hypotensive, anticonvulsant, antibacterial, antitumor, antispasmodic and other activities [1,2]. Recent studies have revealed compounds with a wide spectrum of activity also among phenyltetrahydropyranmethylamine derivatives [3]. At the same time, one of the most common pharmacophore fragments in biologically active compounds are amide, aminoamide, and aminopropanol groups. The present work is devoted to the synthesis of new derivatives of (4-(benzo[d][1,3]dioxol-6-yl)tetrahydro-2*H*-pyran-4-yl)methylamine with aryloxypropanol, aminoacetyl and heterylsulfanylacetyl substituents.



The reaction of (4-(benzo[d][1,3]dioxol-6-yl)tetrahydro-2*H*-pyran-4-yl)methylamine with aryloxymethyloxiranes gave the corresponding aryloxypropanolamines. The reaction of the same amine with chloroacetyl chloride isolated chloroacetamide, the interaction of which with secondary amines and heterylthiols synthesized substituted amino- and sulfanylacetamides.

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INTERACTION OF N-ARYLAMIDOETHERS OF MALONIC ACID WITH ELECTROPHILIC ALKENES. INTRAMOLECULAR HETEROCYCLIZATION

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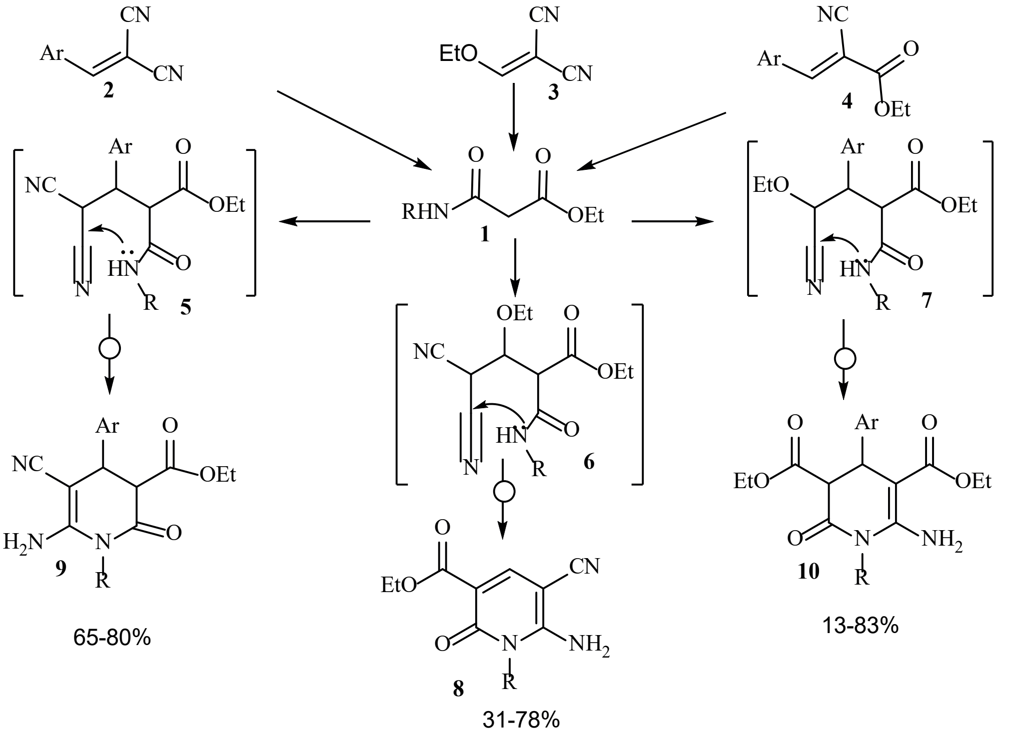
The search for new accessible methods for the synthesis of azaheterocycles derivatives, in particular, pyridines that occur most frequently in natural and synthetic biologically active compounds, is an urgent task [1]. We have investigated the interactions of N-arylamidoethers of malonic acid **1** (nucleophile) with various electrophilic alkenes, in particular arylmethylidene malononitrile **2**, ethoxymethylidene malonitrile (**3**) and arylmethylidenecyanoacetic ester **4** in order to obtain new pyridine analogues and to clarify the regioselectivity of intramolecular cyclization by Michael adduct **5**, **6**, **7**. It was shown that by changing the reaction conditions 1,2-dihydropyridine derivatives **8** [2] and 1,2,3,4-tetrahydropyridine derivatives **9**,**10** with different biological activity were obtained [3,4].



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PIPERAZINE DERIVATIVES AS A MULTITARGET MODULATORS OF ALZHEIMER DISEASE

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Among the several neurodegenerative diseases that cause difficulties in middle-aged and elderly people are Alzheimer's disease and cerebral ischemia. For these illnesses, there are no efficient treatments that can prevent them. The TRPC6 channel has emerged as a viable molecular target for the creation of neuroprotective agents, according to recent in vitro and in vivo investigations. A non-selective cation plasma membrane channel such as TRPC6 is permeable to Ca^{2+}. The stabilization and defense of excitatory synapses is a result of its Ca^{2+}-dependent pharmacological effect. In models of Alzheimer's disease and brain ischemia, both down and upregulation of TRPC6 channel functions have been studied. Appropriate TRPC6 channels modulators must therefore be used to protect neurons from Alzheimer's disease and cerebral ischemia. TRPC6 channels modulators are a developing research area, and new chemical structures modulating the activity of TRPC6 channels are currently being studied and discovered [1]. The second protein of interest to us is acetylcholinesterase (AChE). Acetylcholinesterase (AChE) inhibitors have dominated Alzheimer's disease treatment. By acetylcholine (ACh) turnover and restoring synaptic levels of this neurotransmitter, these medications make up for the loss of cholinergic neurons and provide symptomatic relief. AChE has recently been linked to the etiology of Alzheimer's disease, though. Numerous studies have shown that cholinergic modulation and other functional consequences of AChE inhibition may cause the processing of amyloid precursor protein and protect neurons from a variety of insults [2]. Our result show in virtual screening based on pharmacophore of structure 51164 with the TRPC6 monomer yielded 5 leading compounds that interacted with TRPC6 in the active site.

The best result in the top 5 was given by the compound N1, which we chose for the next step. The next step in our journey is molecular dynamics with the TRPC 6 polymer structure and the compound N1 with the control compound hyperforin. The result of molecular dynamics in the active site, based on the interaction energy, is positive, the type of interaction is predominantly hydrophobic [4]. Interaction at the peripheral binding site is not stable. our next step was to study the activity of our leaders in interaction with acetylcholinesterase. All 5 compounds, as a result of molecular docking, showed interaction with the ATP binding site in the active center of the protein, but the amino acids of the catalytic triad involved in the process of ATP catalysis did not interact with the conformers of the leader compounds. Molecular dynamics showed identical results for all compounds, they all had a stable interaction with the active site of acetylcholinesterse, interaction types were hydrogen, van der Waals interactions and hydrophobic interactions.

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SYNTHESIS AND STUDY OF ANTICHOLINESTERASE PROPERTIES OF NEW FUNCTIONALLY SUBSTITUTED ETHYLIDENE HYDRAZINE-1-CARBOTHIOAMIDES AND THEIR DERIVATIVES

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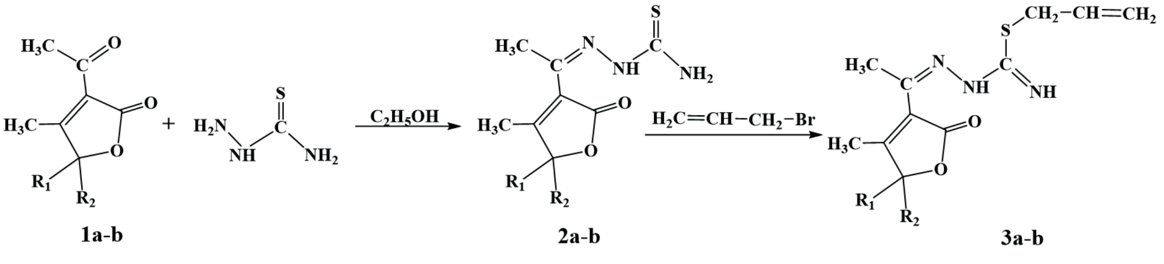
It is known that a 2-oxo-2,5-dihydrofuran fragment is a structural unit of many natural and synthetic biologically active compounds. Furan-2(5*H*)-one derivatives have found wide application in medicine, agriculture, perfumery, etc. [1]. On the other hand, functionally substituted furan-2(5H)-ones offer a great potential for organic synthesis [2].

In recent years, unfortunately, many senile diseases, which characterized by dysfunction of the cholinergic system of the body, have become younger. In particular, Alzheimer's and Parkinson's diseases, which are accompanied by a deficiency of the mediator acetylcholine. The latter explained by the increase in the activity of acetylcholinesterase and butyrylcholinesterase enzymes. In the literature, there is evidence that a number of compounds with anticholinesterase activity contain a furan ring in their composition [3]. Therefore, the search for new cholinesterase inhibitors is an urgent task.

In continuation of our study in this field and with the aim of synthesizing new biologically active derivatives of furan-2(5*H*)-one, herein we report the reaction of 5,5-substituted 3-acetyl-4-methylfuran-2(5*H*)-one (1a-b) with thiosemicarbazide. The reaction proceed at an equimolar amount of reagents by refluxing in absolute ethanol for 3 h to afforded 2-(1-(5,5-substituted 4-methyl-2-oxo-2,5-dihydrofuran-3-yl)ethylidene)hydrazine-1-carbothioamide (2a-b) with high yields.

Then the reaction of synthesized compounds (2a-b) with allyl bromide by heating in acetonitrile at 60-65°C for 4 h in presence catalytic amount of methanolic solution of sodium methoxide. According to the IR, ^{1}H and ^{13}C NMR data, the products were the corresponding S-allyl derivatives – allyl 2-(1-(5,5-substituted 4-methyl-2-oxo-2,5-dihydrofuran-3-yl)ethylidene)hydrazine-1-carbimidothioate (3a-b) were formed.



$R_1=R_2=CH_3$; $R_1+R_2=C_5H_{10}$

The anticholinesterase properties of the synthesized compounds against human erythrocyte acetylcholinesterase (AChE) and human plasma butyrylcholinesterase (BChE) were studied. Compounds (2a–2b), were found to exhibit low inhibitory activity against AChE, but high inhibitory activity against BChE. Allyl derivatives (3a-b) show moderate inhibitory activity against both AChE and BChE.

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NANOSTRUCTURAL ANOMALIES AND HETEROGENEITIES IN ZWITTERIONIC LIQUIDS REVEALED BY EPR

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Zwitterionic liquids (ZILs) represent a kind of ionic liquids whose molecules are composed of covalently bonded cationic and anionic species. ZILs have been extensively researched for applications such as surfactants, surface coatings and catalysts, electrochemistry, etc. For instance, due to their structure ZILs possess the less mobility and they can provide higher Li^+ conductivity compared to ILs. It makes ZILs a fascinating electrolyte component.

The electron paramagnetic resonance (EPR) spectroscopy provides unique information about the structural organization at the molecular level. In this approach, the paramagnetic probe (in most cases, nitroxyl radicals) has to be dissolved in the sample in negligible "non-perturbing" concentrations.

Our group had recently developed a versatile EPR approach to study IL heterogeneities and, in particular, nanostructuring at temperatures below the glass transition points (*Tg*) [1,2]. Unprecedented suppression of molecular mobility was evidenced near the glass transition, which was assigned to unusual structural rearrangements of ILs on the nanometer scale. Indeed, pulse and continuous wave EPR clearly indicated the occurrence of heterogeneities near *Tg* in a rather broad temperature range of ~50 K.

The current work is focused on the investigation of molecular mobility and nanostructuring in imidazolium based ZILs. The obtained trends were compared with the ones obtained for corresponding ILs with separated cationic and anionic species.

The work was supported by Russian Science Foundation (№ 19-13-00071-П).

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ELECTROINITIATED DISMUTATION OF BENZOPINACOLE

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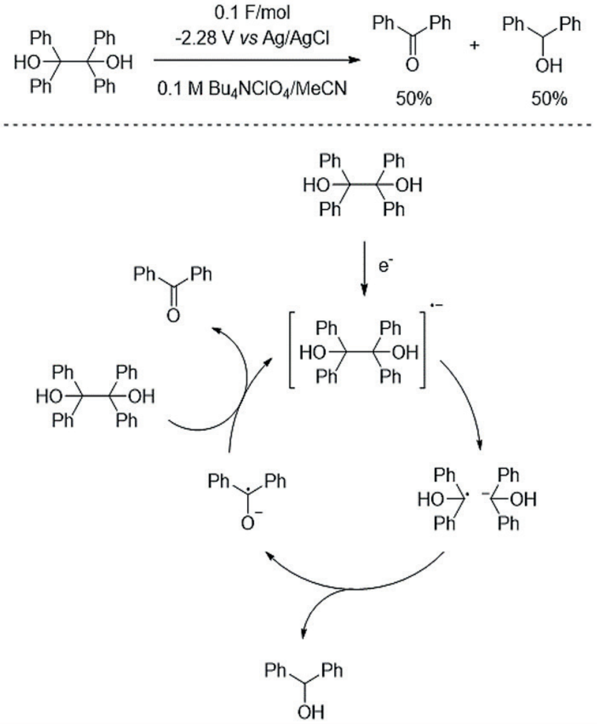
The breaking of a chemical bond during the transfer of an electron to an organic molecule is one of the most typical electroinitiated reactions [1, 2]. However, examples of carbon-carbon bond breaking are few.

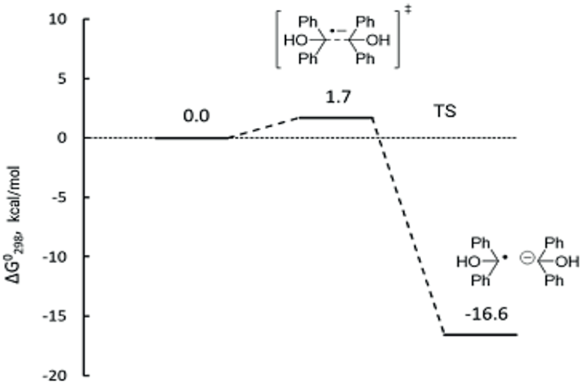
When studying the electrochemical behavior of benzpinacole, we found that it undergoes electrically initiated dismutation to benzophenone and benzhydrol. Therefore, this work is devoted to a discussion of this reaction, its mechanism, and factors affecting it.



Using cyclic voltammetry, chronoamperometry, electrolysis at a controlled potential with chromatographic characterization of products and ab initio quantum chemical calculations, it was shown that the electrochemical reduction of benzpinacole in aprotic solvents (DMF, MeCN, THF) using Bu_4NClO_4 as a supporting electrolyte is accompanied by the subsequent cleavage of the central C–C bond after electron transfer. This initiates a chain process whose products in an equimolar ratio are benzophenone and benzhydrol.

The presence of proton donors (phenol, benzoic and acetic acids, etc.) in the solution at concentrations close to the concentration of the substrate suppresses decomposition. The addition of salts of divalent metals, in particular $Mg(ClO_4)_2$, leads to a similar effect, while the presence of singly charged cations ($LiClO_4$, etc.) in the solution does not suppress the decomposition of benzopinacole.

Quantum-chemical calculations show that the reaction of breaking the central C-C bond of the benzopinacole radical anion with the formation of a radical and anion has a very low barrier (1.7 kcal/mol) and is very favorable thermodynamically ($\Delta G^0_{298} = -16.6$ kcal/mol), which explains its effectiveness.



This study was supported by the Russian Science Foundation (Project No. 20-73-10234-P).

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NONCOVALENT BONDING NAVIGATION IN Si-CONTAINING COMPOUNDS AND 2D MATERIALS

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At modeling multicomponent chemical systems, the reliable prediction of noncovalent interactions and the strategy for choosing methods for simulation the structure and properties come to the fore. The electron density and its gradients, in turn, are the most important for theoretical investigation of chemical bonds, and, consequently, the reactivity of compounds, the properties of crystals, surfaces, macromolecules and interfaces, which impossible to do without structure simulation based on periodic boundary conditions. The methods based on the orbital-free quantum crystallography [1] allows one to obtain the kinetic and static electronic potentials and forces acting in the system [2] via electron density and its derivatives. Such information about the electronic structure of multicomponent system should provide not only a reliable level of the structural characteristics, but, in some cases, be an effective tool for prediction of the macro-properties of the material.

In our study, we have considered multicomponent systems with defective graphene containing a vacancy or Si substituents replacing C-positions in different ratios: a point Si-defect, 25% and 50% substitution. The variety of bond types that Si atoms can form inside the Si-defect substrate, opens up the possibility for generating more optimal patterns of defects that can lead to the most efficient fixation of a sorbate. Interactions of silicaten with metalatranes capable of functioning as immobilizers [2] were investigated. All systems were described by 2D periodic density functional theory calculations and studied for their bonding potency with sorbates.

For the nuanced examination of the nature of the noncovalent interactions building these systems we applied an innovative technology of the joint analysis of the electrostatic and fermionic [3] potentials. Among other things, this powerful tool allowed us to reveal: (i) a peculiar intralayer tetrel bond in the area of the vacancy of the defected graphene; (ii) impact of the Si…π interactions on the electron delocalization in the interacting Si-defected graphene and epoxy-diane compound; (iii) the nature of noncovalent oxygen-oxygen bonds formed between atoms in silicaten and silatrane. Analyzing the positions of the minima of electron density and electrostatic potential along the line between interacted oxygens, we concluded that oxygen in silatrane acts as a nucleophilic site. A comparison of noncovalent interactions occurring between silicaten and adsorbed silatranes or germetranes was performed as well.

This work has supported by the Russian Science Foundation, №22-13-00170.

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METAL PHTHALOCYANINES AND THEIR HYBRID MATERIALS WITH GOLD AND IRIDIUM NANOPARTICLES AS ACTIVE LAYERS OF GAS SENSORS

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Gas sensors have a wide range of applications in various fields, including the chemical industry, food and cosmetics production, and agriculture and environment monitoring. Another important area of application for gas sensors is non-invasive medical diagnostics. The exhaled breath contains a large number of volatile organic compounds, sulfur-containing compounds, halogen-containing compounds, nitrogen-containing compounds, etc. [1]. Among the gases considered as biomarkers is nitric oxide. An increase in the concentration of nitric oxide in exhaled air indicates the course of inflammatory processes in the respiratory tract [2]. The level of nitric oxide in the breath of healthy people is below 25 ppb, and elevated concentrations are found in the exhaled air of patients suffering from lung diseases [3].

Metal phthalocyanine (MPc) films and their hybrid materials are widely studied as active layers of chemiresistive sensors to determine low concentrations of various gases, including nitrogen oxides NO_x [4].

The main goal of this work is to study cobalt phthalocyanine (CoPc) films and new heterostructures based on CoPc and gold (AuNPs) or iridium (IrNPs) nanoparticles and to evaluate the prospects of their use to determine low concentrations of nitric oxide. For this purpose, CoPc films were decorated with AuNPs and IrNPs by gas-phase methods, viz. Metal Organic Chemical Vapor Deposition (MOCVD) or physical vapor deposition (PVD), and their chemiresistive sensor response to low concentrations of NO (10–50 ppb) was investigated. A comparative analysis of the characteristics of heterostructures depending on the preparation methods was carried out. The composition, structure, and morphology of the resulting hybrid films were studied by X-ray photoelectron spectroscopy and inductively coupled plasma atomic emission spectroscopy, as well as electron microscopy methods to discuss the effect of these parameters on the sensor response of hybrid films to nitric oxide.

It was shown that regardless of the deposition method (CVD or PVD), the chemiresistive response of Au/CoPc to NO increased with increasing gold concentration. In the case of Ir/CoPc hybrid structures, the sensor response to NO depended on not only on the Ir concentration but also on the condition of the MOCVD process, e.g. the type of the gas-reactant (H_2 or O_2) and its ratio to the carrier gas ($Ar/H_2 = 0.5\text{-}2$). The prepared heterostructures exhibited a limit of NO detection of up to 4 ppb.

This work was funded by the Russian Science Foundation (grant 21-73-10142).

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SYNTHESIS AND COLOR PROPERTIES OF V-DOPED ZIRCON PIGMENTS

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Owing to its high thermal and chemical stability, vanadium-doped zircon V-$ZrSiO_4$ is one of the blue pigments widely applied in ceramic industry for decades [1]. Besides the traditional ceramic method performed via the solid-state processing of SiO_2 and ZrO_2 oxides at high temperature (1200 °C and more) for hours (12 h and more) in the presence of NaF [2], sol-gel techniques are often suggested in order to produce V-$ZrSiO_4$ pigments with controlled morphology at lower temperatures [3]. The involvement of silica hydrogel (SiO_2 6%) derived from serpentine minerals has allowed developing another simplified method consisting of precipitation procedure and calcination for V-$ZrSiO_4$ synthesis.

Gel-like intermediates with $Zr_{1-x}V_xSiO_4$ compositions where x = 0.03–0.06 were prepared via an hour stirring of the boiling mixture prepared from the silica hydrogel above mentioned, NaOH crystals, $ZrOCl_2{\cdot}H_2O$ and VO_2 with SiO_2:Na_2O:ZrO_2:V_2O_5=1:0.5:0.97:0.03–0.06 molar ratios and then dried for 24 h. Intermediates dried were heated at temperatures from 700 to 1100 °C in order to investigate the color evolution observable in the synthesized pigments (Fig). *L*a*b**chromatic parameters of CIE lab system were determined from the UV-Vis absorption spectra recorded for all the $Zr_{1-x}V_xSiO_4$ samples.

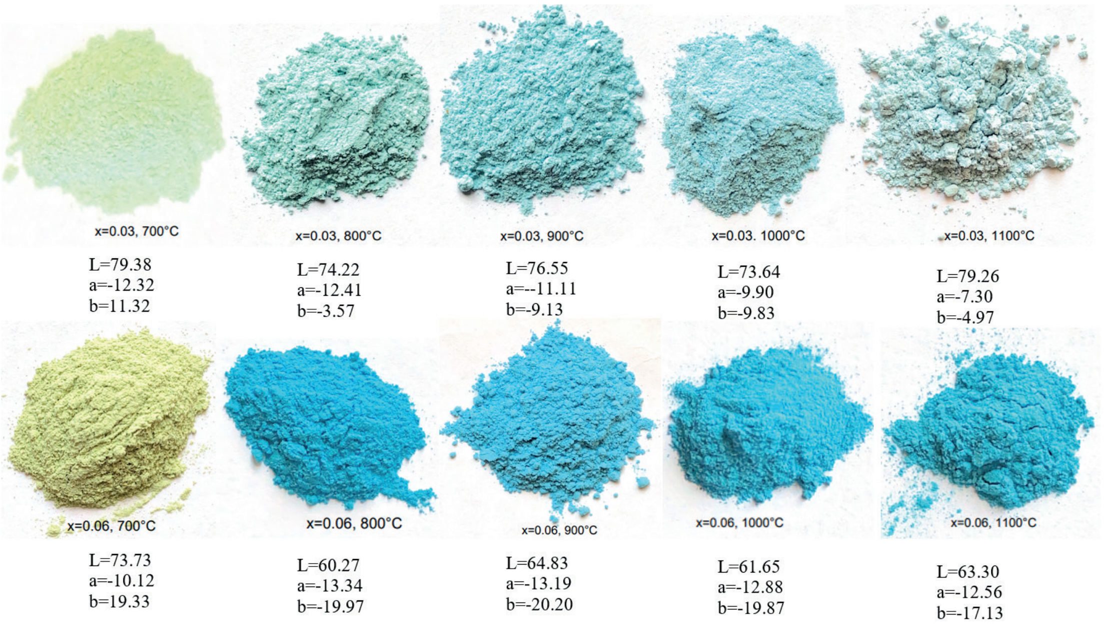

Fig. Digital images of the synthesized pigments with $Zr_{1-x}V_xSiO_4$ compositions.

Acknowledgement. The work was supported by the Science Committee of RA,
in the frames of the research projects № 21SCG-1D013 and № 21T-1D131.

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ELABORATION AND CHARACTERIZATION OF $Zn_{2-x}Co_xSiO_4$ PIGMENTS

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Using silica hydrogel (SiO_2 up to 6%) derived from serpentine minerals, a simplified route including precipitation procedure followed by calcination was developed for the syntheses of a number of silicate compounds, including willemite Zn_2SiO_4 [1]. Promising results encouraged us to apply this method for introducing cobalt ions into willemite crystalline lattice thereby producing Co-doped willemite pigments $Zn_{2-x}Co_xSiO_4$. This type of pigments is of great value because conventional blue colorants $CoAl_2O_4$ and Co_2SiO_4 need replacing with alternative pigments with reduced content of expensive and harmful Co [2, 3].

A series of experiments was performed for the investigation of optical properties evolution observable in $Zn_{2-x}Co_xSiO_4$ samples where x varies in the range from 0.1 to 0.7. Intermediates previously precipitated in SiO_2 (silica hydrogel)–NaOH–$ZnCl_2$–$CoCl_2$–H_2O system via stirring for 120 min at 95 °C underwent one-hour heat-treatment at 900 °C. Diffuse spectral reflectance measurements of the final samples were done on Agilent Cary 60 UV-Vis spectrophotometer.

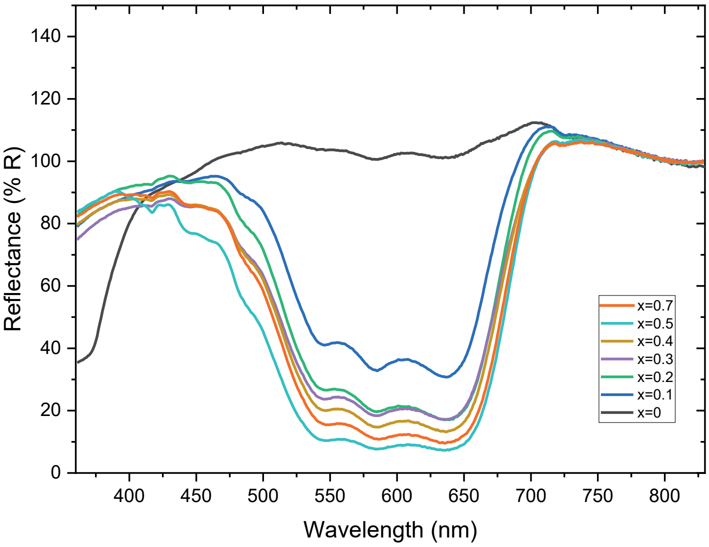

Fig. Reflectance spectra of $Zn_{2-x}Co_xSiO_4$ samples

The appearance of a triplet of bands with signals at 545, 584 and 636 nm in the reflectance spectra (%R) of all the doped samples reveals Co ions introduced in willemite lattice thus proving $Zn_{2-x}Co_xSiO_4$ formation (Fig.) [2, 3]. A gradual decrease in the %R value observable with the increase of Co concentration is interrupted when Co amount reaches 25mol% (x=0.5). The sample with $Zn_{1.5}Co_{0.5}SiO_4$ composition displays the minimum equal to 7 % thereby pointing to the highest absorbance. Subsequent increase of Co amount (x=7) leads to the %R increase conditioned by absorbance decreasing. The results allow concluding that Co content variation in the initial mixture has an essential influence on the optical behavior of the synthesized pigments, providing the highest absorbance in the sample with $Zn_{1.5}Co_{0.5}SiO_4$ composition.

Acknowledgement *The work was supported by the Science Committee of RA, in the frames of the research projects № 21SCG-1D013 and № 21T-1D131.*

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PREPARATION OF FUNCTIONAL POLYORGANOSILOXANES WITH DIFFERENT CHEMICAL STRUCTURES THROUGH CUAAC REACTION

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Polyorganosiloxanes of various structures are the most important class of organosilicon polymers of great practical importance. The introduction of organic substituents and functional groups of various nature into the structure of polyorganosiloxanes is, in turn, a defining synthetic step on the way to the creation of materials based on them. The reaction of azide-alkyne cycloaddition (CuAAC), which is one of the simplest in terms of implementation, tolerant to the presence of various functional groups and easily passes on most substrates, is excellent for this.

In this work, we show the possibility of postpolymerization functionalization of organosilicon polymers by the mechanism of azide-alkyne cycloaddition under "green" conditions: without the use of solvents or in the presence of the "green" solvent ethyl acetate, and also without the use of amines accelerating the reaction (Figure 1). All the most important functional fragments are introduced into the structure of organosilicon polymers by a single mechanism, under simple conditions, without the use of expensive catalysts, exposure to irradiation and hazardous solvents. [1].

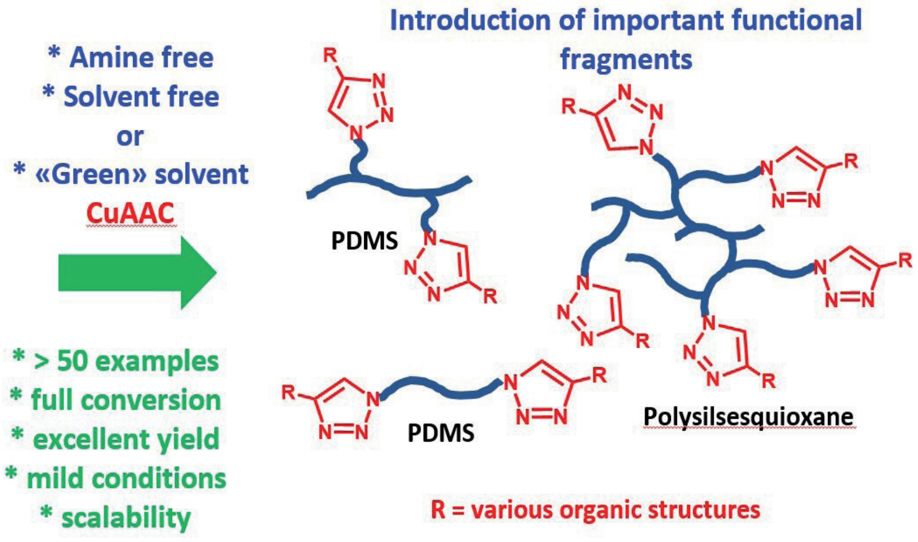

Figure 1. Functionalization of azide-containing siloxanes by the CuAAC reaction

*The work was supported by the Russian Science Foundation № 21-73-10082.*References:

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VINYLATION OF 5(3)-NITRO-3(5)-PYRAZOLE-CARBOXYLIC ACID ESTERS AND STRUCTURAL ISSUES OF THE OBTAINED PRODUCTS

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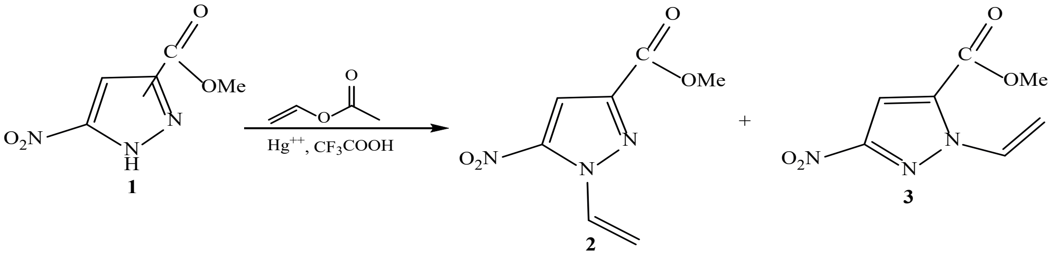
Vinyl derivatives of nitroazoles may be of interest as perspective monomers for the synthesis of high-energy polymer materials **[1–2]**. The most rational method for the synthesis of N-vinilazoles is the reaction of vinyl exchange of azoles with vinyl acetate **[3–4]**. In this work, we present the results of the synthesis of previously undescribed nitro derivatives of 1-vinyl-3(5)-pyrazole-carboxylic acid esters **2,3** by the vinyl exchange reaction using the mercury acetate-trifluoroacetic acid catalytic system.

Vinylation of 5-nitro-3(5)-pyrazolecarboxylic acid esters (**1**) with vinyl acetate with mercury acetate as a catalyst should form a mixture of isomeric esters of 1-vinyl-5-nitro-3 and 1-vinyl-3-nitro-5-pyrazolecarboxylic acids **2,3** according to the scheme.

Scheme



The formation of two isomeric 1-vinylpyrazoles **2,3** is not unexpected [**5-6**], but analysis of the ^{1}H and ^{13}C NMR spectra showed the presence of only one isomer 2. The two-dimensional ^{1}H-^{15}N HMBC experiment turned out to be a very suitable method for identifying the structure of this isomer.

In particular, one of the nitrogen atoms of the pyrazole ring had cross peaks with all the protons of the vinyl group and the pyrazole proton, while the second nitrogen atom had cross peaks only with the α proton of the vinyl group. The structure of this isomer is also confirmed by the downfield shift of the ^{1}H signal of the α-proton of the vinyl group.

This work was supported by the RA MES State Committee of Science, in the frames of research project № 21T-1D020.

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AVAILABLE METHOD FOR THE SYNTHESIS OF PHOSPHORYL-SUBSTITUTED CYCLOPROPANES AND AZIRIDINES

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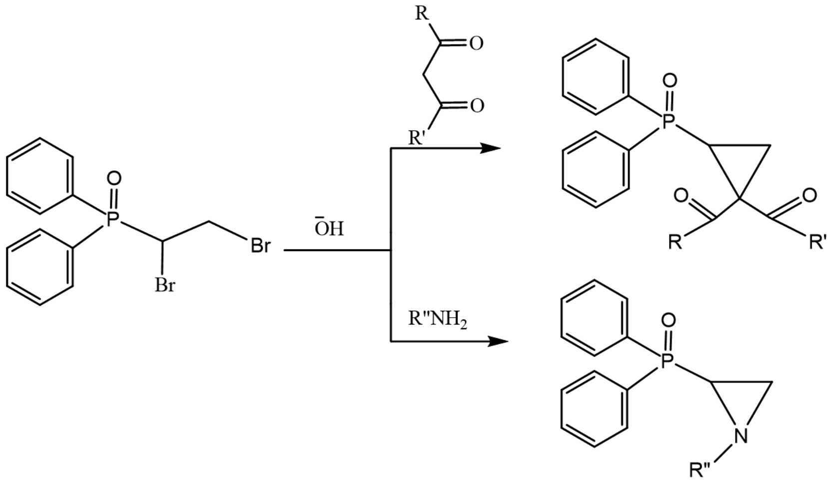
It is known from the literature data that the heteroatom-containing phosphoryl compounds have biological activity and are widely used as complexing agents, extractants of metal salts [1-3].

It is shown that the interaction of (1,2-dibrom)(diphenyl)phosphine oxide with CH-acids and primary alkyl-substituted amines in the presence of sodium hydroxide in acetonitrile at room temperature give phosphoryl-substituted cyclopropanes [4] and aziridines in high yields.



$R=R'=CH_3$; $R=CH_3$, $R'=OC_2H_5$; $R=R'=OC_2H_5$.
$R''=CH_3, C_2H_5$, i-C_3H_7, t-C_4H_9; cyclo-Hex; $C_6H_5CH_2$.

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CAGELIKE METALLASIL- AND GERMSESQUIOXANES: SYNTHESIS, STRUCTURE, AND PROPERTIES

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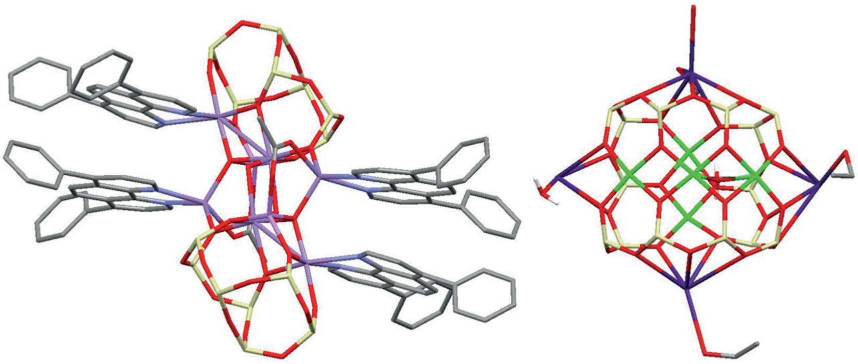
Cagelike sil- [1] and germsesquioxanes [2] are wide families of polynuclear metallacomplexes with enormous variety of compositions, structures and potential applications [3]. Lecture will discuss recent results of our group in molecular/supramolecular design of cagelike Cu-, Mn-, Fe-, Ln-based metallasesquioxanes as well as their catalytic and luminescent properties.



Molecular structures of Mn- (left) and Cu-based (right) silsesquioxane complexes

This research was funded by the Russian Science Foundation, grant number 22-13-00250

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PLATFORM OF STORING AND SEARCHING FOR CHEMICAL INFORMATION IN THE OUTPUT DATA FOR MULTICOMPONENT STRUCTURE MODELING

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Digital twins of chemical compounds and materials are formed on the basis of multilevel models that juxtapose information from macroscopic properties sets with atomic-molecular structural parameters and representations about electronic characteristics distribution [1-2]. In the case of multicomponent systems simulation, modeling method choice is the most paramount. In its turn, the level of electron density distribution calculation is the most important for describing the properties of chemical bonds, and, consequently, the reactivity of chemical compounds. Therefore, storing and searching information about the properties of electron density or recording quantum chemical calculations and wave function data are necessary procedures. At the other end of the hierarchy of properties are the functional properties of materials, and in the intermediate place are the structural and spectral characteristics of crystals, surfaces, macromolecules, and phase boundaries. When modeling them, it is impossible to do without periodic boundary conditions and time-expensive calculations [3], which do not always scale well [4]. Thus, it is more rational to store than to recalculate computer models of medium-sized and large multicomponent systems, including reproduced or predicted physical and chemical properties. Note that for an efficient prediction of properties, it is always important to ensure the transfer of information from each previous level to the next, minimizing losses.

As a solution, the platform for storing information about multicomponent atomic and molecular systems and their properties based on Data Lake is proposed. It provides storage and access to unstructured and semi-structured data of chemical experiments. High speed of loading information is provided by delayed analysis of the contents of files with useful data. The platform includes methods for organizing large volumes of data from different sources. Subsequent analysis (parsing) of the files extracts various properties of crystalline and molecular structures and organizes them into tree structures (JSON format). They are convenient for indexing and searching information in a Data Lake of “column family” type, which is a sparse matrix of search attributes. The dependences found by search and analysis algorithms between files stored in Data Lake with the results of chemical computational experiments (quantum chemical calculations, solutions of vibrational problems, trajectories obtained by methods of molecular dynamics and metadynamics, chemical reaction paths) form the structure of a graph base that allows to use in the search interfile links. The platform is available to the user through a web interface and interactive environment in Python with specialized library access methods.

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SYNTHESIS AND BIOLOGICAL EVALUATION OF ANTITUMOR CAIX INHIBITORS BASED ON SULFONAMIDE DERIVATIVES OF QUINOXALINE 1,4-DIOXIDE.

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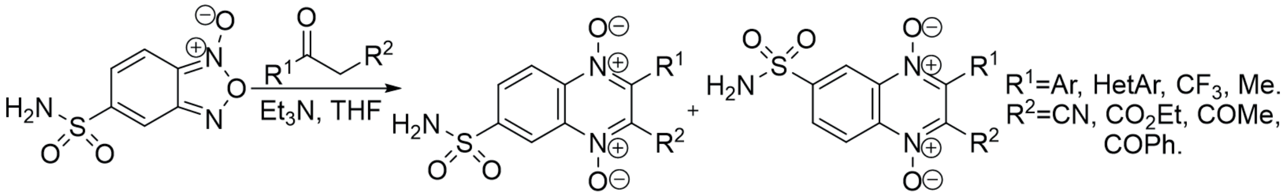
Carbonic anhydrases (CAs) are transmembrane enzymes that play an important role in intra- and extracellular pH regulation and influence proliferation, migration, and invasion. It is known that overexpression of the isoform of the enzyme CAIX is crucial for tumor cell survival and adaptation to reduced oxygen levels, tumor growth, metastasis, and angiogenesis. Several studies have demonstrated that inhibiting CAIX leads to a positive therapeutic response in aggressive hypoxic tumors [1]. In recent years, the development of CAIX inhibitors for targeting malignant tumor cells has garnered considerable attention from several scientific groups.

Quinoxaline 1,4-dioxides inhibit the expression of HIF-1α in solid tumor cells under hypoxic conditions and effectively block their growth [2]. The introduction of the sulfonamide fragment into the quinoxaline 1,4-dioxide scaffold can provide the ability to inhibit CAIX and increase their antitumor potential due to the multitargeting action on cancer cells under hypoxic conditions. Based on molecular docking results, a new 6(7)-sulfonamide-substituted quinoxaline 1,4-dioxides were developed and evaluated for both antiproliferative profile and hypoxia selectivity against MCF7 cells, as well as the ability of such derivatives to inhibit the expression of CAIX.

The Beirut condensation of 5-sufonamidobenzofuroxan **1** with 1,3-dicarbonyl compounds was used for the synthesis of the target derivatives **2** and **3**. It has been shown that, similar to their previously obtained analogs with electron-withdrawing groups [3], a mixture of regioisomers is formed, the main components of which are 6-isomers **3**. The structure of regioisomers **2** and **3** was confirmed by the analysis of the ^{13}C NMR spectra of the obtained compounds.



1 **2** (21-30%) **3** (42-60%)

Most of the obtained derivatives have high selectivity against MCF7 cells under hypoxic conditions. Sulfonamidoquinoxaline 1,4-dioxides block the activity of various isoforms of carbonic anhydrase (CAI, CAII, CAIX, and CAXII) at concentrations ranging from 2.7 to 429 nM and showed a promising profile of inhibitory activity against the key isoform CAIX. The sulfonamide of 2-carboethoxy-3-methylquinoxaline 1,4-dioxide showed the highest inhibitory effect on CAIX compared to the reference agent acetazolamide (K_i = 42.2 and 25.7 μM, respectively). It is noteworthy that the 7-sulfonamido-substituted derivatives (**2**) have low activity against CAIX, while their 6-isomers (**3**) inhibit the enzyme at micromolar concentrations. This finding depicts the specificity of the binding of this class of compounds to the intracellular target.

This work is supported by the Russian Science Foundation (grant 20-13-00402).

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HYDROGEN PEROXIDE ADDUCTS OF BIOACTIVE COMPOUNDS

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During the 20th century peroxosolvates (crystalline adducts of hydrogen peroxide) were subject of recurrent studies as perspective solid sources of H_2O_2. Some of them (e.g., urea peroxide) became extensively used bleaching and disinfecting agents with annual production volume nearing million tons. It was found that stability of peroxosolvates were determined by the number, strength and topological organization of hydrogen bonds formed by H_2O_2 molecules. Some years ago, we discovered that natural amino acids readily form adducts with hydrogen peroxide.[1] Recently, peroxosolvates of active pharmaceutical ingredients attracted renew research interest due to their enhanced biological activity resulted from synergism of API coformers and hydrogen peroxide.[2]

Furacin is an antimicrobial agent belonging to the nitrofuran class. We examined its possibility to form peroxosolvates. Crystallization of furacin from 96%, 50%, and 20% hydrogen peroxide led to three solvates $C_6H_6N_4O_4{\bullet}H_2O_2$ (**A**), $C_6H_6N_4O_4{\bullet}1.5(H_2O_2)$ (**B**), and $C_6H_6N_4O_4{\bullet}3.5(H_2O_2)$ (**C**), respectively. Surprisingly, more rich in hydrogen peroxide solvatomorphs crystallized from more diluted H_2O_2 solutions. These compounds represent the second example of solvatomorphism (peroxomorphism) among crystalline hydrogen peroxide adducts.[3] All three structures contain 1:1 cyclic supramolecular synthon formed by unprecedent bifurcate donor hydrogen bond HOOH…2(O) with nitrofuran subunit. Adduct **C** is the first example of the structure containing 2D hydrogen peroxide layers.

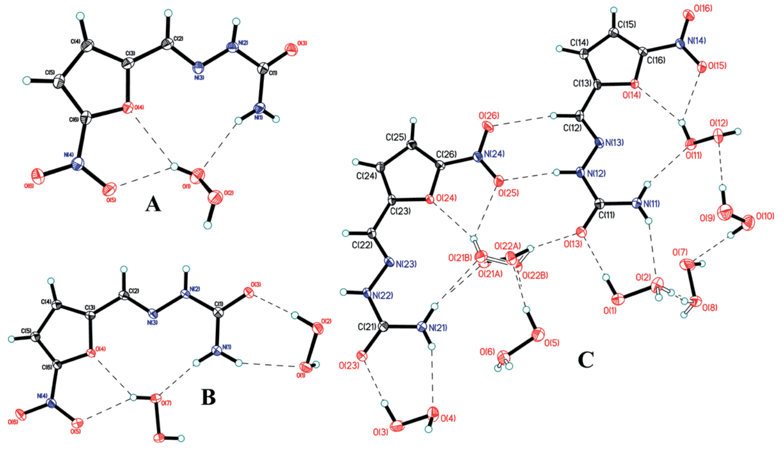

Figure 1. Asymmetric units for **A**, **B**, and **C**.

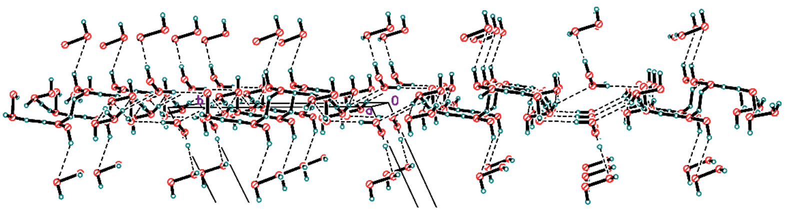

Figure 2. H-bonded layers formed exclusively by H_2O_2 molecules in **C**.

Authors thank Russian Science Foundation for financial support (grant 22-23-01101).

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SYNTHESIS AND NEUROTROPIC ACTIVITY OF NEW AND FUSED DERIVATIVES OF [2,3-B]PYRIMIDINES

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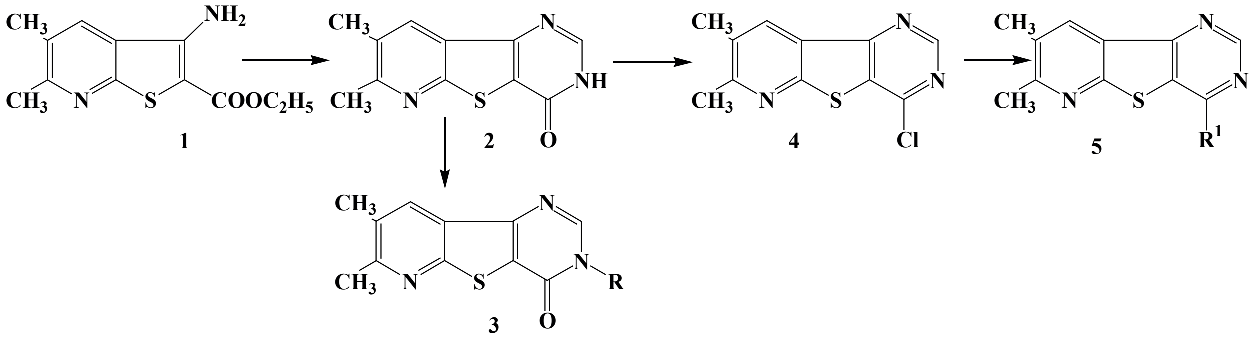
The increased interest to the chemistry and pharmacology of thieno[2,3-b]pyrimidines is due to the fact that biological studies of this class of compounds showed than many of the recently obtained derivatives have high neurotropic activity [1–3]. The synthesis was carried out on the basis of ethyl 3-amino-5,6-dimethylthieno[2,3-b]pyridine-2-carboxylate [4], which was introduced into the Nimentowski reaction to obtain a condensed thieno[3,2-d]pyrimidine-4-ons. In the latter, the ease of alkylation with halides can be emphasized; moreover, it was found that the substitution is carried out in position 3 of the pyrimidine ring. Chlorination of thieno[3,2-d]pyrimidin-4-one and further substitution with various amines allowed to obtain the target amino derivatives in high yields.

The study of the neurotropic activity of the obtained compounds revealed the anticonvulsant effect with antagonism with corazole in eight representatives. Four selected compounds had anxiolytic and activating effects.

Scheme 1



R = i-C_5H_{11}, $(CH_2)_2C_6H_5$, CH_2CONH_2, CH_2-2-Cl-C_6H_4, CH_2-2-F-C_6H_5, CH_2CONH-3-Cl-C_6H_4;
R^1 = NH-i-C_3H_7, $NH(CH_2)_2OCH_3$, 4-ethyl piperazin-1-yl, morpholin-4-yl, piperidin-1-yl, piperazin-1- yl.

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THEORETICAL STUDY OF THE REACTIONS OF HO_2 RADICALS WITH SMALL OLEFINS

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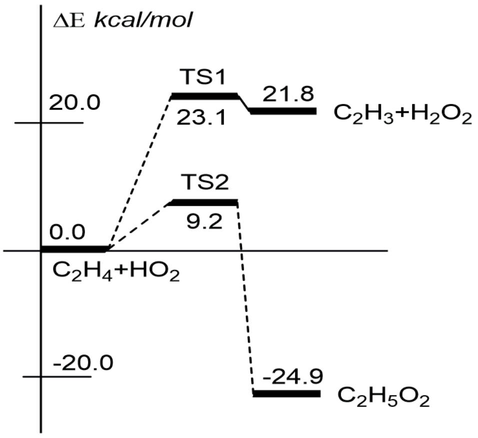
Olefin oxides are basic petrochemicals with rapidly growing industrial production of their derivatives. However, on an industrial scale, almost all of the ethylene oxide is currently produced catalytically involving complex and multi-stage manufacturing technologies based on expensive catalysts. During operations, the catalysts lose their activity due to aging and poisoning and are subject to periodic regeneration.

Non-catalytic methods are being developed for the synthesis of ethylene oxide based on the homogeneous oxidation of ethylene in the gas phase, to avoid employment of the expensive catalysts and environmentally hazardous reagents. In addition, such a method does not require source gases of a high purity, as it occurs in case of the catalytic processes.

Earlier, it has been shown that the epoxidation reaction can be effectively implemented in conjugate processes of gas-phase thermal oxidation of olefinic hydrocarbons with alkanes [1–3]. However, there are no reliable data on the reactions of key intermediate radicals HO_2, CH_3O_2, $C_2H_5O_2$ radicals with olefins to comprehend reaction pathways. Therefore, it is necessary to analyze detailed mechanism of the interaction of peroxyl radicals with olefins.

The main goal of this study was to explore the reaction mechanism of the hydroperoxyl radical with small olefins (ethylene and propylene) using quantum-chemical methods.

The calculations were carried out ($T = 298.15$ K, $P = 1$ atm) using M06-2X DFT method as it implemented in the Gaussian16 software package. Two types of reactions were primarily studied: (1) H-abstraction of olefins by HO_2 radical, and (2) addition of hydroperoxy radical to the double bond. The simplest examples are provided in the Figure below, for illustration.



$$C_2H_4+HO_2 \rightarrow C_2H_3+H_2O_2 \quad (1)$$

$$C_2H_4+HO_2 \rightarrow C_2H_5O_2 \quad (2)$$

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GENERALIZATION OF THE TERM «REACTION ORDER», ESPECIALLY FOR CONCENTRATED SOLUTIONS

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The reaction order and activation energy are basic concepts in formal chemical kinetics. They are kinetic parameters which describe the dependence of the reaction rate on the reactant concentrations and temperature. However, to our knowledge there is a lack of a strict definition for these important terms containing distinct limits of applicability. On the one hand, for an elementary reaction in an ideal homogeneous system the kinetic law of mass action (LMA) is obeyed and with good accuracy so is the Arrhenius equation. In this case both the reaction orders with respect to the reactants and the activation energy are constant parameters in these equations and in textbooks they are usually introduced as such. However, in more complicated cases (non-elementary reactions in non-ideal systems) none of these equations hold strictly. At the same time, it is said that the reaction orders and activation energy for an arbitrary reaction are to be determined experimentally. There appears some logical controversy, because these parameters are defined through certain kinetin equations (LMA and Arrhenius equation), which may not hold for the reaction under investigation. To overcome this issue, we propose that the reaction orders and the activation energy should be strictly defined through partial derivatives of the reaction rate with respect to concentrations and temperature. This approach allows determining these parameters experimentally for any given reaction, provided its rate can be regarded as a strict function of composition and temperature.

Important to note, the variation of a single concentration at fixed temperature should always be accompanied by a change of either the pressure or at least one other concentration. Depending on which parameters are kept constant and how other parameters are changed when taking the partial derivative, different types of reaction order can be determined. For example, for gas phase reactions it is more natural to keep the volume constant while reactions in solution are mostly studied at constant pressure. We classified several types of reaction orders and activation energies, which have all a clear physical meaning, and derived strict formulae, which interconnect these parameters. Moreover, we introduced a cartesian space where the logarithm of the reaction rate, the logarithms of the concentrations and the inverse temperature are plotted along the axes. In such space the kinetic equation is represented as a multidimensional surface and the different types of reaction order and activation energy are clearly represented by slopes corresponding to different directional derivatives.

SYNTHESIS OF 2*H*-IMIDAZOLE-BASED PHOSPHONIUM SALTS VIA DIRECT C–H FUNCTIONALIZATION OF NON-AROMATIC IMIDAZOLE OXIDES

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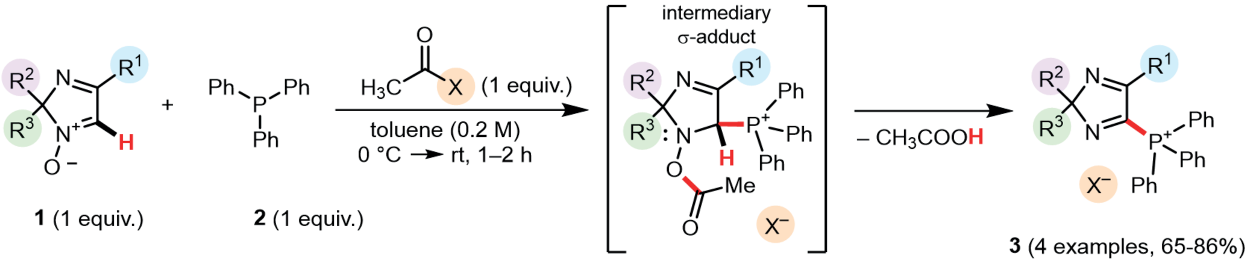
Quaternary phosphonium salts prove to be highly versatile chemical synthons capable of interacting with both various nucleophilic substrates and electrophiles; furthermore, they can act as pseudohalides in the Suzuki and Sonogashira cross-coupling reactions affording a wide range of molecules of practical interest. Besides, phosphonium salts themselves are known for their pronounced cytotoxic activity, which makes them potentially good candidates for employing as antitumor and antimicrobial agents.1 In this regard, the development of new phosphonium-containing derivatives appears to be rather sought-after.

During our ongoing research on the reactivity of azomethine C(sp^2)-H bonds, we figured out that model cyclic azomethine derivatives, non-aromatic 2*H*-imidazole 1-oxides **1**, can interact with triphenylphosphine **2** in the presence of acyl halide allowing one to obtain corresponding 2*H*-imidazole-based phosphonium salts **3**. This reaction can be considered as the eliminative nucleophilic substitution of hydrogen (S_N^H[AE]), with PPh_3 acting as a nucleophile and acetyl chloride/bromide as an activating agent contributing to the increase in *C*(sp^2)-electrophilicity of the substrate **1**. As a result, four previously unknown phosphonium salts **3** were synthesized in yields of 65-86%.



3a^{Cl} [R^1 = Me; R^2, R^3 = $(–CH_2–)_5$; X = Cl], 85%;
3b^{Cl} [R^1 = Ph; R^2, R^3 = Me; X = Cl], 86%;
3a^{Br} [R^1 = Me; R^2, R^3 = $(–CH_2–)_5$; X = Br], 84%;
3b^{Cl} [R^1 = 2-thienyl; R^2, R^3 = Me; X = Cl], 65%

Our current efforts are focused on evaluating the synthetic potential of the newly obtained compounds **3**, as well as on assessing their cytotoxic properties. The results of these studies will also define the necessity of further expansion of the reaction scope.

This research was funded by the Ministry of Science and Higher Education of Russia
(Agreement No. 075-15-2020-777).

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STEREOSELECTIVE MULTICOMPONENT SYNTHESIS OF PYRIDINIUM SALTS OF PIPERIDIN-2-ONES WITH THREE AND FOUR STEREOCENTERS

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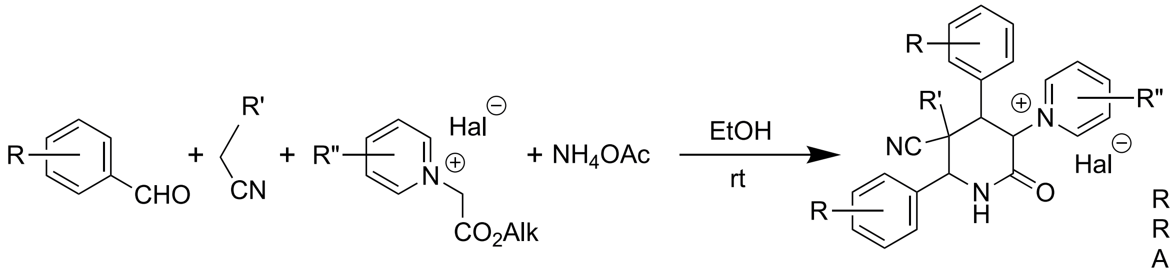
Recently, the development of new pharmaceuticals corresponding to the principles of green chemistry is an urgent task. Production of new substances with biocidal activity is a significant problem in medicinal chemistry.

We have synthesized a series of quaternary ammonium salts (QAS). An important feature of these substances is their potential biological activity. The main field of application of QAS is pharmacology.[1] These substances have antiseptic and fungicidal activities.[2] The most effective QAS containing a pyridinium cation are commercially available and widely applied in medicine.

The synthesized compounds also contain a piperidine moiety. Piperidine derivatives are used in various fields of pharmacology, such as the cancer and Alzheimer's disease treatment, and others.[3]

We have proposed a simple resource-saving synthetic approach for the multicomponent synthesis of pyridinium salts of polysubstituted piperidin-2-ones. The main advantages of our method are: a simple procedure (mild conditions, short reaction time), low solvent consumption, high atomic efficiency. This approach allowed us to obtain the target compound in high yields without further purification.

We synthesized a series of compounds containing three and four stereocenters with a predetermined configuration, the products were isolated as a single diastereomer.



R' = CN, CO_2Me
R'' = H, 3-OH, 3-Br
Alk = Me, Et
Hal = Cl, Br

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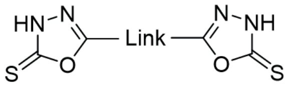
NEW BIS 1, 3,4-OXADIAZOLES, BIS 1,3,4-THIADIAZOLES AND THEIR DERIVATIVES

Dilanyan S.V.

Institute of fine Organic chemistry the Scientific Technological Center of Organic and Pharmaceutical Chemistry NAS RA

Heterocyclic rings of 1,3,4-oxadiazole and 1,3,4-thiadiazole are part of many biologically active compounds [1,2]. These data served as the basis for the creation of new compounds of this series. Introduction into the structure of the second ring 1,3, 4-oxadiazole and 1,3,4-thiadiazole, as well as various aromatic or aliphatic linkers leads to bisoxadiazolyl derivatives and bistiadiazolyl derivatives and opens up new possibilities in the rational design of drugs.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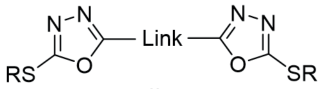
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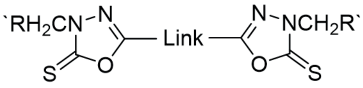
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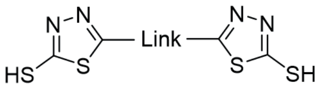
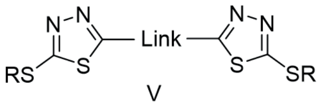
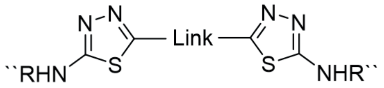

IV


V


VI

II,V, Link= $-(CH_2)_8-$, $-C_6H_4-$, R= $-CH_2COOH$, $-CH_2CONH_2$, $-CH_2COOC_2H_5$

III, Link= $-(CH_2)_8-$, R`=$-CH_2CN$

VI, Link=$-(CH_2)_8-$, $-C_6H_4-$, R``= $-C_6H_4-$, R``= $-C_6H_5$, $-CH_2CH=CH_2$

The reaction of bis hydrazide with carbon disulfide synthesized 1,3,4-oxadiazole-5-thiol (I), and the interaction with carbon disulfide in the presence of alkali synthesized a potassium salt, the sulfuric acid cyclization of which led to bis 1.3.4-thiadiazole-5-thiol (IV). It should be noted that the bisthiosemicarbazides formed by the interaction of bis hydrazide with isothiocyabates easily cyclize the corresponding bis 1.3.4- thiadiazole-2-amines (VI). Alkylation of the corresponding thiols occurs at the sulfur atom and leads to structures II,V. The cyanoethylation reaction proceeds exclusively at the *N*-position of the oxadiazole ring III.

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STEREOCHEMICAL PECULIARITIES OF CRYSTAL PACKING OF SOME NEW AMINE-CONTAINING BENZOFUROXAN DERIVATIVES

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The molecular and crystal structure of some new amine-containing benzofuroxanes was studied.

The crystal structure of new amine-containing benzofuroxanes contains two strong groups that involve in hydrogen bonding: active oxygen-containing nitro-group as acceptor and N-H-group as donor. These groups create a large number of intra- and intermolecular interactions of the N=O…H-N type. The crystals of these compounds also contain weak C-H…O-type interactions, which lead to the formation of complex three-dimensional structures.

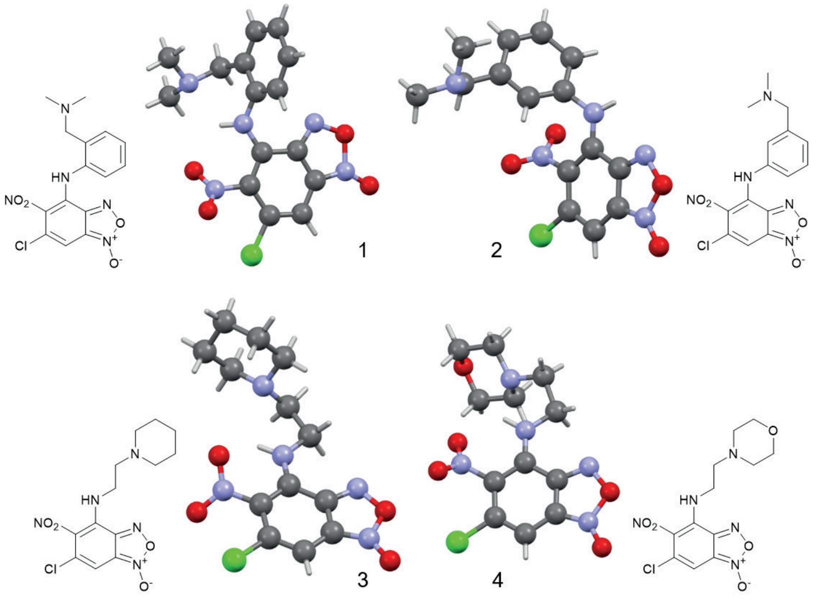

Figure 1. Molecular structures of the studied benzofuroxanes **1–4**.

The work was supported by the Russian Science Foundation (grant No 22-13-00284).

MECHANISM-DRIVEN DEVELOPMENT OF N-(QUINOLIN-8-YL)-BENZAMIDE COUPLING REACTIONS VIA C-H OR N-H

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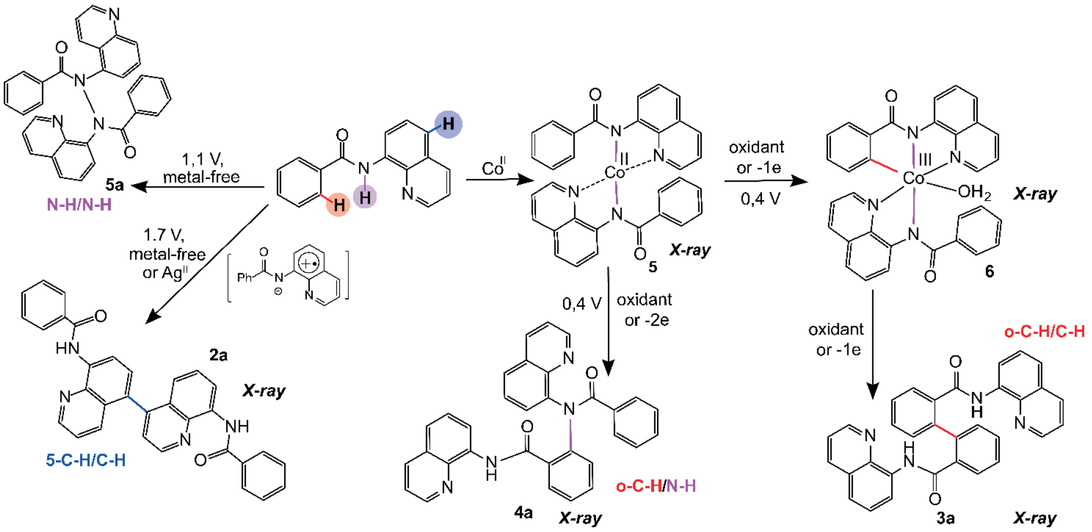
The direct functionalization of carbon-hydrogen bonds and C–H/E–H (E=C, N, P, etc.) coupling particularly provides an atom-economical and environmentally friendly synthetic method because it avoids the prefunctionalization of coupling partners. [1-3] In this regard the development of catalysts based on the naturally more abundant and, hence, cost-efficient 3d transition metal complexes, represents an attractive alternative. Although a number of metallacyclic structures have been proved for noble metals, fully characterized cobaltacycles are still rare.



Thus, manipulation of the oxidation conditions of N-(quinolin-8-yl)-benzamide makes it possible to obtain a number of coupling products: (*ortho*- or *para*- C–H/C–H; C–H/N–H; and also N–H/N–H). Intermediate Co^{II} complex and C–H-activated Co^{III} metallacycle with benzamide ligands, which are shown to oxidize at close potentials, have been isolated and characterized by various techniques, including X-ray diffraction and voltammetry.

This work was supported by the Russian Science Foundation grant no. 22-13-00017.

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HETEROSTRUCTURES BASED ON IRON PHTHALOCYANINE FILMS AND GOLD OR PLATINUM NANOPARTICLES AS ACTIVE LAYERS OF ELECTROCHEMICAL SENSORS FOR NITRITE DETECTION

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Nitrite and its salts are one of the most common food additives encountered in water, vegetables, meats and canned food [1]. Nitrite ions can also accumulate in the human body during inflammatory processes. Also, chemical reactions in the body convert nitrite ions to N-nitrosamine derivatives, which are known to be highly carcinogenic [2]. The WHO recommended monitoring the nitrite concentration in water and food to avoid its accumulation in the human body in concentrations exceeding 28.3 μM [3].

The electrochemical method is an easy-to-use approach for quantifying and monitoring nitrite ions concentration [4]. As versatile redox mediators and catalysts, transition metal phthalocyanines and their heterostructures or composites are in demand as sensor materials [5-7]. The unsubstituted iron phthalocyanine (FePc) showed the outstanding sensor responses toward NO [4], while its application for the detection of nitrite ions has not been studied in detail. On the other hand, the decoration of electrode surfaces with metal nanoparticles (MNPs) is known to increase their surface-to-volume ratio and to improve electron transport across their surfaces [8].

The main goal of this work is to investigate the application potential of unsubstituted iron phthalocyanine (FePc) films and their heterostructures with gold (AuNPs) or platinum (PtNPs) nanoparticles as electrochemical sensors toward nitrite ions. FePc films and corresponding heterostuctures AuNPs/FePc were obtained on glassy carbon electrodes (GCE) using physical vapor deposition. PtNPs were deposited on the surface of FePc/GCE using Metal Organic Chemical Vapor Deposition. X-ray diffraction, spectroscopy and microscopy methods were used to evaluate composition, distribution and sizes of gold and platinum nanomaterials to discuss the effect of these parameters on the sensor response of the prepared heterostructures toward nitrite ions. According to the data of atomic emission spectroscopy with inductively coupled plasma, the concentration of AuNPs or PtNPs in the electrodes varied in the ranges of 5–15 or 21–63 μg/cm^2. The electrochemical characteristics of FePc/GCE and a series of AuNPs/FePc/GCE and PtNPs/FePc/GCE samples were determined in 0.1M PBS solution using cyclic voltammetry (CV, 0.25–2 mM), amperometry (CA 0.5–25 or 25–250 μM) and impedance spectroscopy (IS, -180 mV, at 400 kHz –1 Hz).

It was shown that the introduction of Au or Pt nanoparticles with the sizes up to 10 nm to FePc/GCE promotes nitrite oxidation in the heterostructures, reducing the overpotentials by 75 or 100 mV compared to FePc/GCE. The sensors AuNPs/FePc/GCE (Au – 10 μg/cm^2) and PtNPs/FePc/GCE (Pt – 35 μg/cm^2) exhibited the lowest detection limits (0.022–0.029 μM) and the excellent selectivity in the presence of interfering anions.

This work was funded by the Russian Science Foundation (grant 21-73-10142).

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FUNCTIONAL SILOXANES - NEW APPROACHES TO SYNTHESIS AND PROSPECTS FOR THEIR APPLICATION

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Due to their unique properties, such as a wide operating temperature range, chemical and thermal stability, biocompatibility and bioinertness, high gas permeability, polysiloxanes are used to produce various materials: silicone rubbers, heat-resistant lubricants, defoamers, for the production of cosmetics, in pharmacology and medicine. However, over the past decades, a large number of polysiloxanes modified both by end groups and in the chain have been obtained, which has significantly expanded their applications as surfactants, biodegradable block copolymers, copolymers with low surface energy and non-linear optical properties.

This report presents the achievements of our scientific group in recent years in the field of functional polyorganosiloxanes for use in various fields [1-6]. New approaches to the synthesis and functionalization of siloxane polymers and the possibility of using natural compounds will be shown.

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SYNTHESIS AND PROPERTIES OF COORDINATION POLYMERS BASED ON DERIVATIVES OF 2,1,3-BENZOCHALCOGENADIAZOLES AND ZINC, CADMIUM AND LANTHANIDE IONS

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Metal-organic frameworks (MOFs) are a class of porous materials assembled from metal ions and organic linkers. The porous nature of MOFs determines their main scope in the field of sorption and separation of different gases or liquids. Furthermore, metals and ligands used in the synthesis determine many other important physical properties: magnetic, luminescent, catalytic, etc. Recently, much research has been devoted to obtaining luminescent MOFs capable of detecting different toxic substances in various environments. The use of MOFs as such sensors has several advantages: high selectivity, the possibility of performing express tests and sample regeneration.

Our group previously had obtained new ligands based on 2,1,3-benzochalcogenadiazole derivatives. Due to the extended π-system, such compounds often exhibit bright luminescence and can be used for the synthesis of MOFs with luminescent properties. In this report, we discuss the preparation of four new ligands: 4,7-di(4-carboxypyrazol-1-yl)-2,1,3-benzochalcogeadiazoles (**4,7-bXdbpdc,** X = S, O) and 4,6-di(4-carboxypyrazol-1-yl)-2,1,3-benzochalcogeadiazoles (**4,6-bXdbpdc,** X = S, O).

Their interaction with lanthanide salts leads to the formation of two new series of MOFs **$[Ln_2(4,7\text{-bodbpc})_3(H_2O)_3]$** (1) and **$[Ln_2(4,7\text{-btdbpc})_2(4,7\text{-btdbpcH})_2(H_2O)_4]$** (2) (fig. 1). Interestingly, different MOFs are formed (2D-layers, if X=O, and 1D-chains, X=S) despite the similar conditions of the preparation reactions. Their luminescent properties were studied, the quantum yield for $[Gd2(4,7\text{-bodbpc})_3(H_2O)_3]$ reached 25%. The luminescent response to various analytes (metal cations, anions, antibiotics, amines) was studied. Compounds demonstrate increase in luminescence intensity upon addition of gallium and aluminum solutions, which makes it possible to consider these MOFs as sensors.

Upon interaction of ligands with salts of zinc or cadmium and different N-donor ligands (dim, 4,4ʹ-bpy, 4,7-di(imidazol-1-yl)benzothiadiazole (dibtd) and 4,7-di(1,2,4-triazol-1-yl)benzothiadiazole (dtbtd)) seven different 2D-polymers were obtained. Some of them are porous, which makes it feasible to study their adsorption properties. The luminescent response to various analytes was studied for [**Zn(4,7-btdbpdc)(dibtd)**].

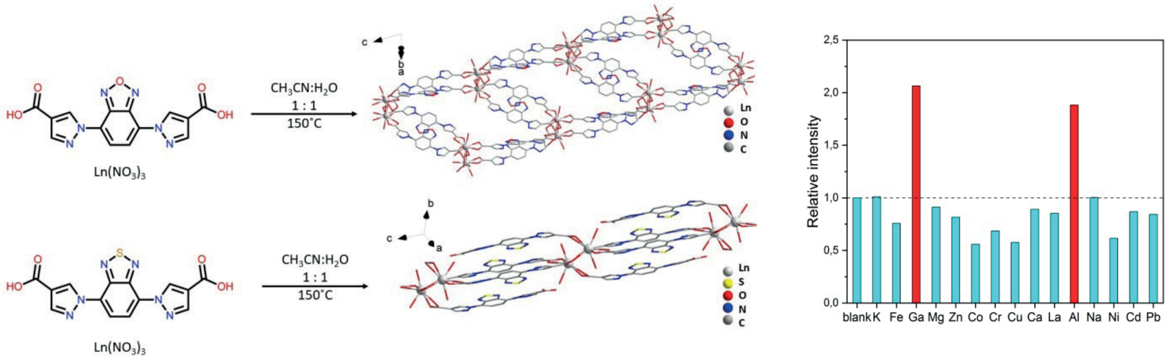

Fig. 1. Synthesis and structure of $[Ln_2(4,7\text{-bodbpc})_3(H_2O)_3]$ and $[Ln_2(4,7\text{-btdbpc})_2(4,7\text{-btdbpcH})_2(H_2O)_4]$ (left) and luminescent response of $[La_2(4,7\text{-bodbpc})_3(H_2O)_3]$ on different metal cations (right).

This work was supported by the Russian Science Foundation, grant No. 23-43-00017 “Novel metal-organic frameworks with high luminescence for the detection of biologically active substances and environmental pollutants”, https://rscf.ru/project/23-43-00017/.

N,N’-DIARYLDIHYDROPHENAZINES: A PROMISING ALTERNATIVE TO PRECIOUS METAL-BASED PHOTOREDOX CATALYSTS

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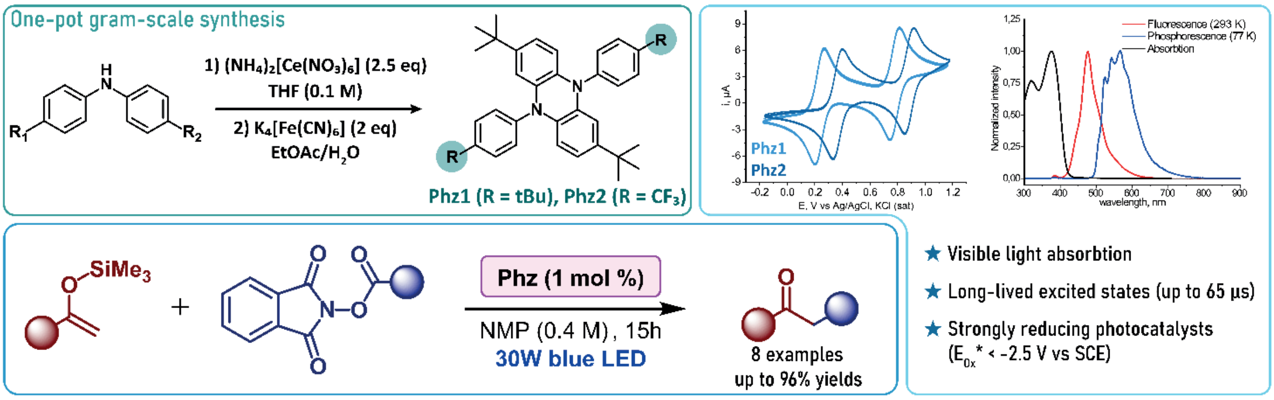
Photoredox catalysis producing short-lived highly reactive intermediates under mild conditions is one of the most powerful synthetic strategies. At present, highly efficient Ir and Ru complexes dominate in the photoredox chemistry field, despite of their toxicity, high price and low abundance. A search for metal-free purely organic photocatalysts as an affordable and effective alternative is a topical problem.

New N,N’-diaryldihydrophenazines demonstrating advanced photophysical properties were obtained. The facile, one-pot scalable synthetic approach was elaborated. The compounds absorb visible light forming long-lived excited triplet states (the τ = 65 μs at r.t. exceeds that for $Ir(ppy)_3$ (2 μs)); they are easily oxidized (EO_x = 0.2-0.4 V vs SCE) yielding persistent radical-cations. The estimated values of the excited state oxidation potential is ca. -2.5 V vs SCE. These properties allow considering new N,N’-diaryldihydrophenazines as promising strongly reducing photocatalysts.

Experimental testing of the new compounds was performed in the visible light driven alpha-alkylation of ketones, the reaction that was previously carried out with the Ir-based photocatalysts. The results obtained confirmed excellent photoredox activity of novel N,N’-diaryldihydrophenazines: the yields of alkylated ketones were comparable and in some cases exceeded that ones for the Ir counterparts. Functionalization with primary, secondary and even sterically hindered tertiary aliphatic C-radicals was successfully demonstrated.

Thus, new N,N’-diaryldihydrophenazines can serve as affordable alternative to precious metal-based photoredox catalysts.



- ★ Visible light absorbtion
- ★ Long-lived excited states (up to 65 μs)
- ★ Strongly reducing photocatalysts (E_{0x}* < -2.5 V vs SCE)

Acknowledgement: This work was supported by Russian Science Foundation (Project N 22-13-00093).

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CHEMO- AND REGIOSELECTIVITY CONTROL IN THE CONDENSATION REACTIONS OF 1,2,4-TRIKETONE ANALOGS WITH HYDRAZINES

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1,2,4-Triketones and their analogs, containing three nonequivalent electrophilic centers, serve as versatile building blocks for design of diverse heterocyclic and acyclic compounds by reactions with 1,2- and 1,3-binucleophilic agents [1]. Meanwhile, their synthetic potential is scarcely studied.

Novel 1,2,4-triketone analogs **1-3**, including fluorine-containing, were synthesized by Claisen condensation according to previous reports [2-4]. It is found that acetal-functionalized lithium β-diketonates **1** and 1,3-diketones **2**, can also be stable in a cyclic form of furan–3(2*H*)-ones **3**. Taking into account this feature, the chemical properties of 1,2,4-triketones **1-3** have been explored during acid-catalyzed condensation reactions with a range of hydrazines (Fig.).

Herewith, fluorinated diketonates **1**,**3** can lead to 3-R^F or 5-R^F pyrazoles **4**,**5** and **6**,**7**, pyridazinones **8** and **β**-diketohydrazones **9**, depending on the structure of the initial reagents and the solvent used [5]. In the case of non-fluorinated analogs, both the nature of the substituent near 1,3-dicarbonyl moiety and in hydrazine were found to be crucial for regioisomeric acetylpyrazoles **4**,**5** or pyridazinones **8** formation. Moreover, the role of the temperature and acid catalysis was determined for chemo- and regiocontrolled transformations of building blocks **2**,**3** to heterocyclic compounds.

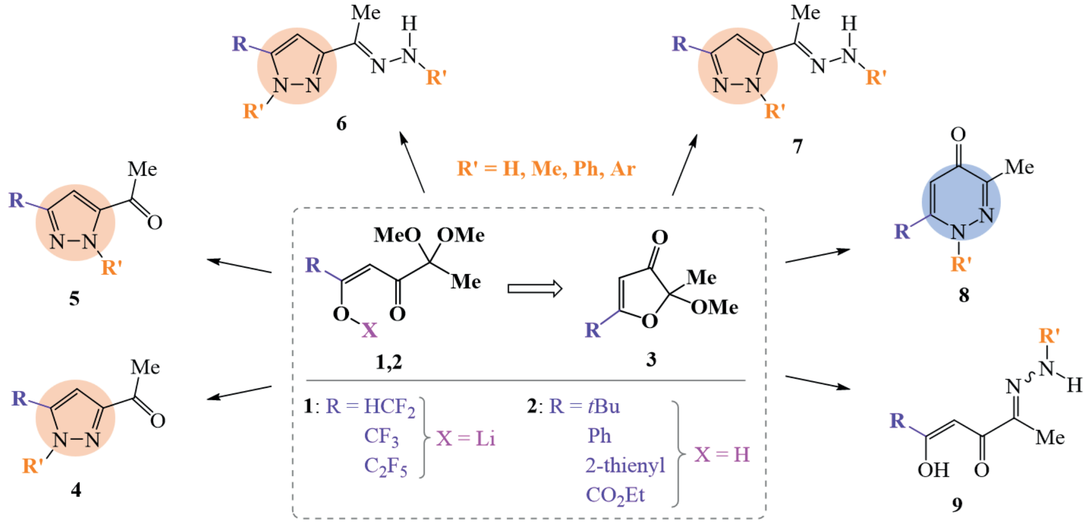

Figure.

This work was financially supported by Russian Science Foundation (project № 23-23-00425, https://rscf.ru/en/project/23-23-00425/).

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BIODEGRADABLE pH-SENSITIVE CONTAINERS BASED ON POLYMERS AND LIPOSOMES FOR BIOMEDICAL APPLICATIONS

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Increasing the efficiency of drug delivery to target cells and organs is a key task of pharmacology. Bilayer lipid vesicles (liposomes) are among the drug carriers that have been intensively used for drug immobilization. pH-sensitive liposomes have great potential for biomedical applications, in particular as nanocontainers for the delivery of biologically active compounds to specific areas of the human body, since lower pH is typical for tumors, areas of inflammation, etc. A great number of pH-sensitive liposomes have been described, but, thereby, it is still a considerable challenge to prepare liposomes that could quickly release the encapsulated substance under small changes in the pH. We suggest the new type of pH-sensitive liposomes with embedded ampholytic molecular switch (AMS) with anionic and cationic groups attached to the opposite ends of the steroid core. The AMS is able to change the orientation in the lipid membrane depending on the acidity/basicity of the external solution, which is accompanied by disordering of the bilayer and rapid release of the encapsulated substance.

To increase the therapeutic effect and efficiency of delivery, anionic liposomes are concentrated on the surface of a cationic biodegradable polymer carrier by electrostatic adsorption. This results in multi-liposomal and multi-functional core–shell carriers capable of carrying a mixture of various drugs in the desirable ratio; this is actually a way to design therapeutic agents for treatment of a particular patient. Biodegradable components (polymer and liposomes) ensure the removal of containers from the body after performing the transport function. At the same time, the composition of the lipid membrane has a significant effect on the properties of the complexes formed. The geometry of the lipids forming the membrane, the phase state of the bilayer, and the concentration of charged lipids should be taken into account. To prevent the fusion of liposome membranes, and, accordingly, premature release of the encapsulated substance, as well as to ensure prolonged circulation of the multiliposomal complexes in the bloodstream, the liposomes are modified with a hydrophilic polymer, polyethylene oxide. Liposomes recommended as drug carriers contain cholesterol, which increases the stability of liposomes in the biological environment. Information about the effect of liposome composition on the structure and properties of multi-liposomal containers is of key importance, as it determines the possible biomedical use of multi-liposomal constructions and can be used to control their properties.

UiO-66 FRAMEWORK WITH ENCAPSULATED SPIN PROBE AS PRESSURE SENSING MATERIAL

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Probes sensitive to a mechanical stress are in demand for analysis of a pressure distribution in materials. Most of promising techniques for a non-invasive detection of the mechanical stress using molecular probes employ mechanochromism, chemoluminescence or mechanofluorochromism. However, the approaches have own drawback, such as a depending on optical transparence of the material. To overcome the problem, we need a wide diversity of methods, based on different physical phenomena.

Many spin probes are sensitive to an environment and can be monitored via EPR spectroscopy. As a carrier for spin-probes metal–organic frameworks (MOFs) can be used. MOFs have virtually unlimited possibilities to adjust their properties. Pressure sensitive probes can be created by encapsulation a spin probe into a MOF cavity. The MOF will be a rigid structure, which can be changed according to mechanical stresses. At the same time, the spin probe within the MOF cavity will have a different EPR spectrum because of the different environment.

We report a new pressure-sensing material, which is based on UiO-66 framework with trace amounts of spin probes (0.03 wt.%) encapsulated in the cavities. Pressure read-out using electron paramagnetic resonance (EPR) spectroscopy allows monitoring the degradation of a defected MOF structure upon pressurization, where the full collapse of the pores occurs at as low pressure as 0.13 GPa. The changes is permanent, therefore, a read-out procedure can be performed after delay between a mechanical stress and the procedure. To obtain the material, we developed an approach to encapsulate a stable nitroxide radical TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) via it reduction form TEMPOH into a micropore of UiO-66 during its solvothermal synthesis wth followed . The developed methodology can be used *in* and *ex situ* and provides sensitive tools for non-destructive mapping of pressure effects in various materials.

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π-π INTERACTIONS IN CO-CRYSTAL OF ORGANIC AND CORRESPONDING TO THEM COORDINATION COMPOUNDS

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The study of non-covalent interactions is relevant due to their influence on the structure, chemical and physical properties of both compounds and materials. Special place in the hierarchy of non-covalent interactions is dedicated to stacking interactions, which often play a crucial role in the formation of both the crystalline and molecular structures, as well as influencing the processes of self-assembly. Their influence is especially crucial during the formation of polymeric structures in coordinative compounds with aromatic ligands [1]. Furthermore, π-π interactions can positively affect the photoluminescence of a compound [2].

This research presents a study of π-π interactions in co-crystals of 4-amino-2,3,5,6-tetrafluorobenzoic acid (Hpam) and its europium and terbium complexes with pyridine, quinoline and 1,10- Phenanthroline. For this study, the number of coordination compounds and co-crystals of organic salts of various compositions were synthesized. All compounds were obtained in the form of single crystals suitable for x-ray diffraction analysis and analysis of non-covalent interactions in them. It is shown that in addition to the classical hydrogen interactions formed with the hydrogen of the N-H group, overlapping π-systems both in coordination compounds and in organic co-crystals are the structure-forming element. The interaction parameters in organic and coordination salts were compared.

It has worth mentioning that in the case of monodentate ligands, unusual anionic compounds, $[Ln_2(pam)_8][HL]_2$ (L=Py, Quin), were being formed. While on the other hand the use of 1,10-Phenanthroline lead to formation of molecular complexes $[Ln_2(pam)_6(Phen)_2]$.

Photoluminescent properties of obtained compounds of rare-earth elements were studied. The highest quantum yield was observed for the molecular complex with 1,10-Phenanthroline and was equal to 53% respectively, while in case of ionic compounds with monodentate ligands,

There is an intensity decrease in the spectre at 370-420 nm. This fact indicates that this line belongs to the LMCT transition. Often LMCT transition takes part in the dipping of excited states of a rare-earth element with ligand.

The work was carried out with the financial support of the Russian Science Foundation, grant № 22-73-10192.

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ALLYLATION MECHANISMS OF NORBORNADIENE WITH ALLYL FORMATE IN THE PRESENCE OF PALLADIUM COMPLEXES

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Recently, papers [1] devoted to the catalytic allylation of norbornadiene (NBD) with allyl formate (AF) in the presence of Pd complexes are regularly published. The reaction in one technological stage leads to a number of diverse polycyclic compounds, among which there are monomers that are difficult to obtain for the polymer industry, figure. 1. Methods of density functional theory (DFT-PBE/L11) were used to simulate the mechanisms of interaction between NBD and AF in the presence of Pd complexes of various compositions [2, 3].

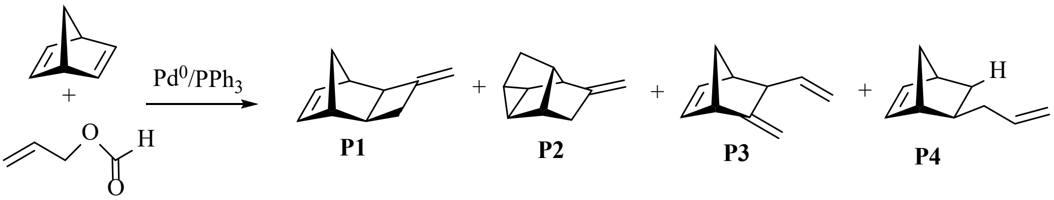

Fig. 1. The main products of Pd-catalyzed allylation of NBD with allylformate.

It has been established that the rate-determining step for all routes of allylation of NBD is the formation of the first C-C bond, since the step is characterized by the maximum activation barrier. The predominant formation of *exo*-structure products in the presence of phosphines is associated with a lower transition state energy of this step, because it is also responsible for the stereostructure of the product.

It was shown that the formation of the hydroallylation product (**P4**) proceeds along two routes with similar activation energies, which differ in the order of the steps of C–C bond formation and β-hydride elimination. In the absence of phosphine ligands, the regioselectivity of obtaining the **P4** product is mainly due to the large activation barriers of the step of formation of second C-C bonds in the routes of oxidative allylation products (**P1-P3**) formation. The introduction of PPh_3 ligands reduces the Gibbs energy of activation of this step, thereby opening the way to other products.

Representations about the course of key steps were detailed. Thus, for example, the formation of η^3-allyl complexes of Pd occurs through the formation of a five-center transition state. The cleavage of the C–C bond, leading to the product **P3**, proceeds in the methylenecyclobutane fragment by the type of β-carbon elimination. The cleavage of C–H bonds during β-hydride elimination is possible with the participation of β-agostic Pd complexes.

Based on calculations [4] using the DFT-ωB97X-D3(BJ)/ZORA-def2-TZVP/SARC-ZORA-$TZVP_{Pd}$ method, it was shown that it is possible in principle to obtain a noticeable enantiomeric excess in the reaction using chiral alkylarylphosphine ligands. In this case, the most optimal is the presence of one aryl substituent in the phosphine. In addition, chiral phosphines can affect the regioselectivity of the reaction for products of the same stereostructure (*exo* or *endo*).

This work was financially supported by the Russian Science Foundation (Project No. 23-73-00123).

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$ZnFe_2O_4$ WITH DIFFERENT NUMBER OF OXYGEN VACANCIES AS AN ANODE MATERIAL FOR LITHIUM-ION BATTERIES

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Graphite is currently used as a basic anode material in commercial lithium-ion batteries (LIBs) due to such advantages as wide availability, outstanding electronic conductivity, low cost, and favorable hierarchical structure for intercalation of lithium ions. However, disadvantages of graphite anodes, such as moderate specific capacity (theoretical value is 372 mAh/g), low performance at high current densities, low stability, and safety risks due to dendrite growth at low operating potential and sustained deposition of lithium, have prompted further development and optimization of anode materials for LIBs.

In 2004, $ZnFe_2O_4$ was first introduced as a promising anode material [1] and has since been studied due to its remarkable properties such as chemical and structural stability, high theoretical specific capacity of about 1072 mAh/g and non-toxicity. Despite these advantages, significant disadvantages are the low specific capacity at high current densities and rapid degradation of the material due to the extremely low electronic conductivity, low coulombic efficiency, as well as volume expansion of the order of 100% due to the conversion mechanism of the electrochemical reaction.

$ZnFe_2O_4$ was synthesized via simple and widely used method co-precipitation of aqueous salt solutions followed by calcination of the samples for 2 or 6 hours at temperatures of 300, 500, 700 °C. Physicochemical characterization was carried out by X-ray diffraction and X-ray photoelectron spectroscopy, the morphology was studied by scanning electron microscopy.

An increase of the calcination temperature expectedly leads to raise of samples crystallinity. The size of zinc ferrite crystallites was also estimated using the Williamson-Hall method; the crystallites size enlarges with increasing processing temperature and holding time. The lattice parameters decrease with increasing the processing temperature. As expected, the number of oxygen vacancies declines with the growth of temperature and synthesis time.

Electrochemical properties of electrode materials based on synthesized $ZnFe_2O_4$ were studied using the galvanostatic charge-discharge technique and cyclic voltammetry. Analysis of the capacity data on the 1st charge cycle revealed its almost linear dependence on the number of oxygen vacancies; the spinel with the lowest concentration of defects in the crystal structure has the highest initial specific capacity and, conversely, the material with the highest number of defects has the lowest specific capacity.

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CYTOTOXIC COMPLEXES OF ESSENTIAL METALS WITH 1H-TETRAZOLE-5-ACETIC ACID AND DERIVATIVES OF 1,10-PHENANTHROLINE, 2,2´-BIPYRIDINE

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Recently, the possibility of using transition metal coordination compounds as potential therapeutic agents has attracted increasing interest. The growth of publications on cytotoxic transition metal complexes is due to the success of cisplatin, which is widely used in medicine due to its high efficiency. At the same time, there are certain disadvantages, such as serious side effects and the emergence of resistance in patients to platinum-based drugs, which limits their clinical use. This stimulates the search for biologically active complexes that exhibit an alternative mechanism of action compared to applied drugs with a reduction in side effects of treatment and an improvement in clinical efficacy.

As part of our work, mixed-ligand manganese(II), nickel(II), copper(II) and zinc(II) complexes with 1Htetrazole5acetic acid (H_2L) and derivatives of 1,10-phenanthroline, 2,2´-bipyridine (1,10-phenanthroline (phen), 1,10-phenanthroline-5,6-dione (phendione), 4,7-dimethyl-1,10-phenanthroline (dmphen), 5-chloro-1,10-phenanthroline (Cl-phen), 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'- bipyridine (dmbipy)) were synthesized. These compounds were characterized by elemental, thermogravimetric and powder X-ray diffraction analyzes, IR spectroscopy.

Crystal structures have been obtained from the mother liquor for some complexes. Zinc(II) and copper(II) complexes are characterized by the formation of polymer chains due to the bridging function of the tetrazole ring. L^{2-} is coordinated by N1 and N4 atoms in $\{[Zn(dmbipy)L]\cdot H_2O\}n$ (Fig. 1). In a similar complex of copper(II) with dmbipy, the oxygen of the carboxyl group participates in coordination in addition to the N1 and N4 atoms of the tetrazole ring. The nickel(II) complex with the same additional ligand (dmbipy) has a mononuclear structure. L^{2-} shows bidentate coordination mode *via* N1 atom and O atom of the carboxyl group.

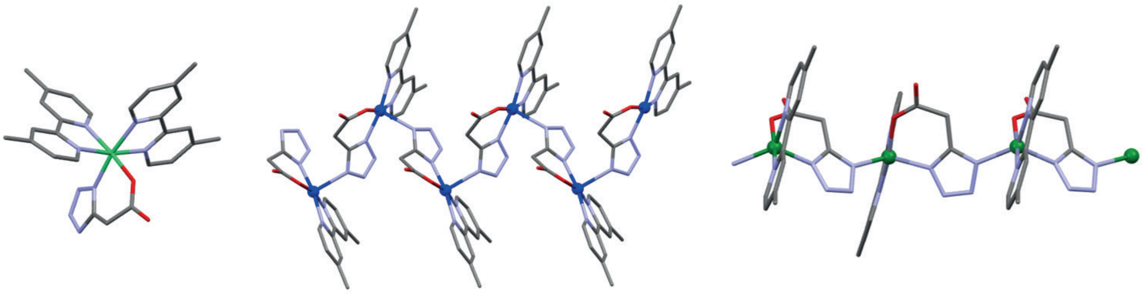

Figure 1. The structures of $[Ni(dmbipy)_2L]\cdot C_2H_5OH$ (on the left), $[Cu(dmbipy)L]_n$ (on the center) and $\{[Zn(dmbipy)L]\cdot H_2O\}_n$ (on the right).

Cytotoxicity of ligands, metal acetates and complexes was studied on HepG2 (hepatocellular carcinoma cells) and MCF-7 (breast carcinoma cells) cell lines using an IN Cell Analyzer 2200 (GE Healthcare, UK). Among the series of compounds, the most cytotoxic are copper(II) complexes, in which IC_{50} values are in the range of 0.9-4.5 μM for all tested cell lines. Complexes of manganese(II), nickel(II) and zinc(II) with phendione have cytotoxic activity (IC_{50} values are in the range of 0.926.0 μM). Zinc(II) complexes are characterized by pronounced cytostatic properties. In addition, all copper(II) complexes and manganese(II), nickel(II), zinc(II) complexes with phendione were studied on a non-cancerous cell line MRC-5, and then the selectivity indexes were calculated.

This work has been supported by the Russian Science Foundation (project №20-73-10207).

ELECTRONIC FORCE FIELD BASED BINDING APPROACH: APPEL’S SALT

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We present a binding approach based on the electrostatic and kinetic force density fields, which is proposed to elucidate interatomic interactions, structures, and chemical reactions. It consists in the understanding of (i) the arrangement of pseudoatomic zero-flux surfaces (ZFSs), (ii) the mutual compression of force-field pseudoatoms of the same type, (iii) the penetration of a bonded atom into neighboring force-field pseudoatoms, (iv) the distortion of the force fields, and (v) the occurrence of a binding path connecting two force-field attractors as the inherent consequences of the emergence and existence of any many-electron multinuclear system. Herein, the interatomic charge transfer and the reciprocal quantum-chemical response accompanying the covalent and noncovalent bond formation were studied using the abovementioned penetration, exemplified by Appel’s salt. It was found that the three-center chalcogen bonding $Cl^{-}\cdots S–S$ and tetrel bonding $Cl^{-}\cdots C\cdots Cl^{-}$ in the crystal of Appel’s salt resemble the initial and transition states of bimolecular nucleophilic substitution reactions, respectively. Being extracted from the crystal structure, the corresponding ion pairs undergo chemical rearrangement: forming the covalent bonds Cl–S and Cl–C leads to the collapse of the pseudoatomic ZFSs and the alignment of the bond and binding paths in the internuclear regions.

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RARE EARTH METAL IONS SORPTION ON THE Co-MOF SURFACE

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Sorption is one of the most promising processes for the rare earth metal ions extraction. Organometallic framework structures (MOF) should be considered preferred sorbents for the rare earth elements extraction. MOFs are coordination polymers consisting of mono- or multicore clusters and organic multifunctional linkers. These compounds have a large specific surface area, have the ability to fine-tune the structure and pores volume together with high thermal and chemical stability. The MOFs using in the rare earth elements extraction and purification is a promising and more environmentally friendly method to meet the growing demand for rare earth elements in industry.

The paper proposes an optimized method for the synthesis of a zeolite imidazolate framework based on Co(II), presented in [1]. It is established that the particles have a hexagonal structure and are the micro heterogenic system with an average particle size of 0.05 - 0.1 microns. Nitrogen adsorption isotherms in Co-MOF pores were obtained, and the parameters of the porous structure of Co-MOF were found in the result of their processing.

Pr^{3+}, Nd^{3+}, Sm^{3+}, Er^{3+} and Yb^{3+} ions adsorption from the aqueous solutions at temperatures of 298 and 313K has been studied. Sorption was carried out under static conditions; the method of constant samples and variable concentrations was used in the work. It is established that equality in the “Co-MOF - metal ion” system is achieved at a contact time of no more than 60 minutes. The results of experimental studies allowed us to determine the values of the sorption capacity. The character of the obtained sorption isotherms is identical for all ions, they have a pronounced linear section in the Henry region. The obtained dependences correspond to the isotherms of monomolecular adsorption. The results of ion adsorption isotherms formal processing made it possible to calculate the thermodynamic characteristics of sorption processes – limiting adsorption, adsorption coefficients, distribution constants and Gibbs energies, as well as sorption activation energy.

A high degree of extraction of rare-earth metal ions from solutions of their salts is shown. The adsorption process is spontaneous in all cases. Linearization of experimental data on ion adsorption in the coordinates of the Langmuir and Dubinin-Radushkevich isotherm ($n = 2$) confirms the course of adsorption in the volume of an energetically homogeneous porous adsorbent and the predominance of 2-ethylimidazolate cobalt (II) micropores in the structure. The values of the characteristic sorption constants are obtained from the linear coordinates of the Freundlich isotherm. It is established that the adsorption of rare earth metal ions has an ion-exchange nature of the process.

The work was carried out with the financial support of the Russian Science Foundation (project No. 22-73-10158).

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TYPE, VOLUME AND POSITION OF SUBSTITUENTS ON THE CHARACTERISTICS OF THE CRYSTAL PACKING OF BODIPY DERIVATIVES

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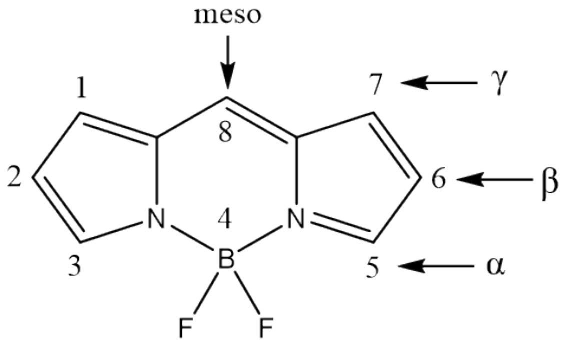
Phosphors of the family of dipyrromethene boron fluoride complexes (BODIPY) have a whole range of important physicochemical properties: intense absorption and fluorescence in the visible region of the spectrum, biocompatibility and non-toxicity, high photo- and thermal stability. As a rule, organic phosphors are used in the form of thin films and crystals, the way the molecules within which are associated plays an important role in the manifestation of their valuable properties. The extended π-system of the indacene backbone makes BODIPY molecules capable of efficient π–π-stacking, which is the main driving force behind the self-association of BODIPY molecules. The main method for varying the properties of such molecules is the introduction of substituents of different nature into different positions of the indacene backbone, which determine the type of the supramolecular associate. The only direct method for establishing both the structure of the molecule and the type of supramolecular associate is X-ray diffraction analysis; therefore, in the framework of this work, **11** crystals of new members of the BODIPY family were analyzed for stacking interactions and types of supramolecular associates controlled by substituents of different types at different positions of the indacene backbone.



Pic. 1. Structure of BODIPY

It has been established that π–π interactions with varying degrees of overlap of π systems are realized in all the studied crystal structures with the formation of associates of three types: infinite columns, symmetric dimers, pseudosymmetric dimers [1].

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CONFORMATIONAL AND VIBRATIONAL ANALYSIS OF DIPROPYL SULFONE BY DENSITY FUNCTIONAL THEORY METHODS

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The methods of computational chemistry are a powerful tool for predicting various properties of molecules. The choice of the quantum chemical method and the basis set is essential for reliable calculation. Among quantum chemical methods, density functional theory methods (DFT), in combination with appropriate basis sets, are in some respects so reliable that can be compared with experimental ones. Depending on the computational purpose there are various DFT functionals available: the local density approximation (LDA), pure, hybrid, double-hybrid and dispersion-corrected etc. In the present work, several DFT methods and basis sets were tested for performing the conformational and vibrational analysis of dipropyl sulfone (DPSO2). Sulfones are dipolar aprotic solvents widely used in chemical technologies. The main goal of this study was to elaborate a methodology for predicting the structural and spectral parameters of DPSO2 based only on quantum chemical calculations on the model compounds. All quantum chemical calculations were performed using Gaussian 09 computational package. Among the DFT methods and basis sets tested, wB97XD/6-311++G(2df,2pd) method/basis set combination was the best choice for performing the conformational and vibrational analysis of DPSO2. It is worthy to note that several DFT methods also B3LYP was unable to predict correct structural and spectral parameters. A complete analysis of potential energy surfaces (PES) of DPSO2 exhibited the coexistence of 28 unique conformers with different degeneracy states, for which absolute energies, relative populations, degeneracies, structural parameters, and IR spectra were calculated. To conduct a full data analysis and build a simulated IR spectrum of DPSO2, taking into account the calculated results of all stable conformers, the appropriate scripts were written in LabTalk and C Programming languages in Origin 8.5 program. Figure 1 represents PES (one of four) of DPSO2 and its simulated IR spectrum, which is in good agreement with the experimental spectra of its homologues [1].

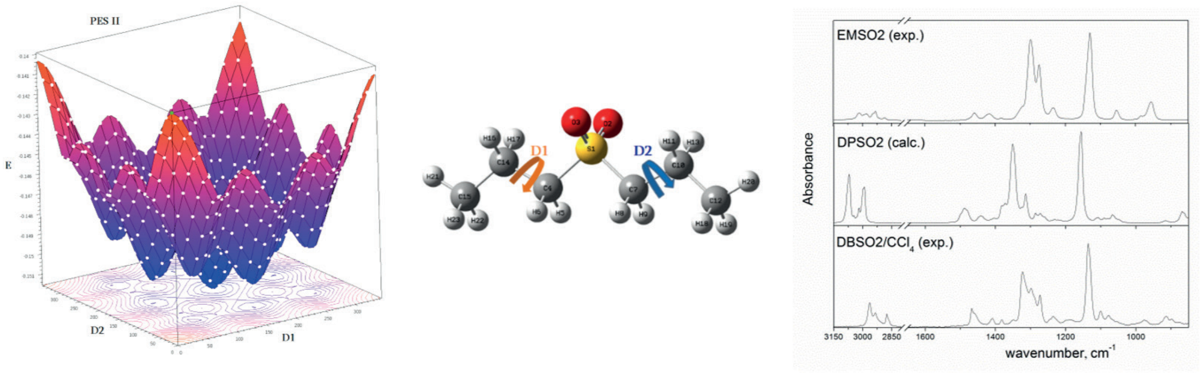

Fig. 1. Potential energy surface of DPSO2, its simulated IR spectrum and experimental FTIR spectra of some homologues.

This work was supported by Science Committee of the MESCS RA, in the frame of financing of Chemistry Research Center, Laboratory of Physical Chemistry.

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SYNTHESIS OF POTENTIAL ASYMMETRIC ORGANOCATALYTIC SYSTEMS ON THE BASE OF AZOLES

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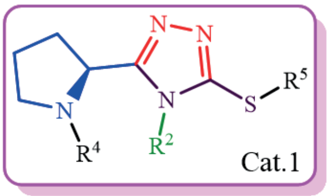
Among the different approaches used to access enantiomerically pure compounds, chiral transition metal complexes and organocatalysts evolved as essential instruments in the toolbox of organic chemists.

It should be noted that a special place in all this is occupied by various catalysts synthesized on the basis of proline, which demonstrate a high selectivity and have a wide range of applications.

Synthesized of the new derivatives of azoles containing amino acid residues based on 1,2,4- and 1,2,3-triazoles which can be used in asymmetric synthesis as Brønsted bases and/or as ligands in catalytic reactions with transition series metals.



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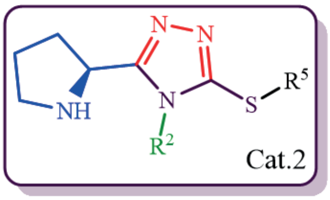

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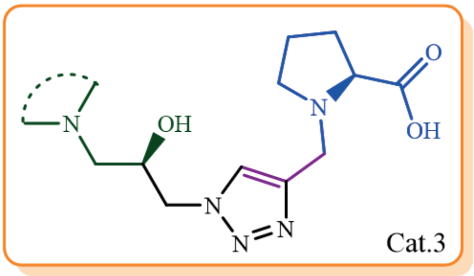

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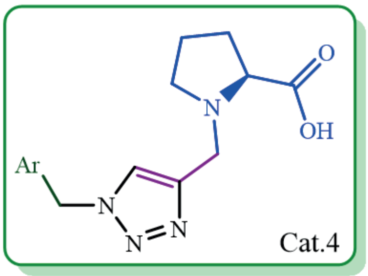

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The structure of compounds was determined by the methods of ^{1}H, ^{13}C NMR, mass spectrometry and X-ray diffraction analysis (XRD).

The research was supported by Committee of Science of MESCS RA in frames of projects 21SCG-1D005, 21T-1D320, 22AA-1D005 and 22YSSPD-005.

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SYNTHESIS AND ANTIOXIDANT ACTIVITY OF SULFURCONTAINING 3,7-DIAZABICYCLONONANE DERIVATIVES

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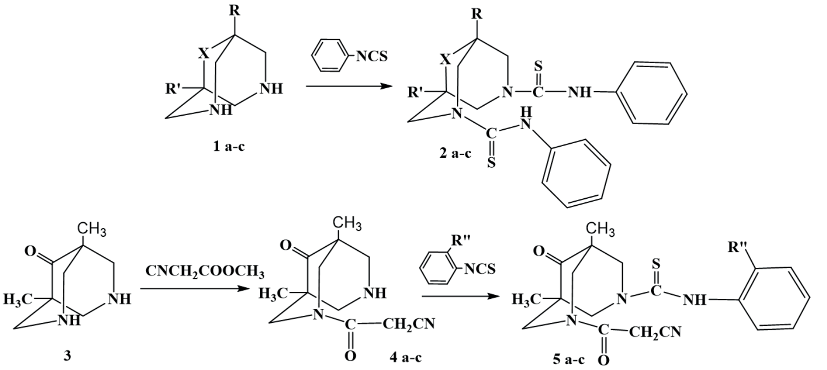
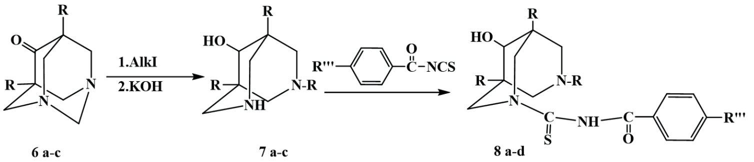
By reaction of 1,5-dialkyl-9-oxo-3,7-diazabicyclo/3.3.1/nonanes **1 a-c** with phenylisothiocyanate were synthesized the corresponding 3,7-disubstituted phenylisothiocyanates **2 a**-c. 1,5-Dimethyl-9-oxo-3,7-diazabicyclo/3.3.1/nonane (**3**) converted with cyanoacetic acid methyl ester to a monocyan derivative **4**, which with substituted phenylisothiocyanates forms 3,7-disubstituted 1,5-dialkyl-9-oxo-3,7-diazabicyclo/3.3.1/nonanes **5 a-c**.



(a) X = CH_2, R = R' = CH_3 ; (b) X = C=O, R = R' = C_2H_5; (c) X = C=O, R = CH_3, R'=C_3H_7, R'' = H, CH_3, OCH_3

From 5,7-dialkyl-6-oxo-1,3-diazaadamantanes **6 a-c** were synthesized 1,5-dialkyl-3-methyl-9-hydroxy-3,7-diazabicyclo/3.3.1/nonanes **7 a-c**, which was converted to 3,7-disubstituted bicyclononanes **8 a**-d by reaction with substituted benzoylisothiocyanates.



(a) R = CH_3, R''' = H; (b) R = CH_3, R''' = Cl; (c) R = C_2H_5, R''' = H; (d) R = C_3H_7, R''' = H.

Some derivatives of this series have moderate antioxidant activity, especially compounds, containing hydroxyl group in 9-th position of diazabicyclononane ring [1].

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RELATIONSHIP BETWEEN THE CONFIGURATION LABILITY OF NITROGEN AND SULFUR ATOMS OF SULFONAMIDES OF THE THIAZINE SERIES DURING THE FORMATION OF CRYSTAL-FORMING MOTIFS

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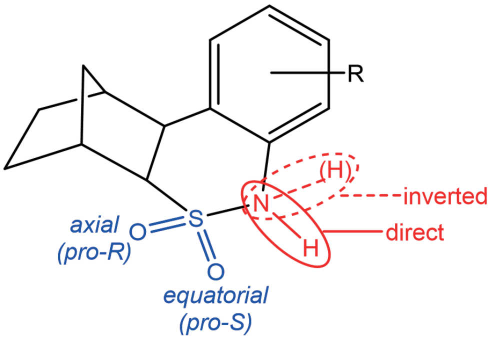
The crystal structure of thiazine sulfonamides contains two interesting stereochemical moments: firstly, the nitrogen atom in such a system usually acquires a pyramidal configuration, either conditionally direct or conditionally inverted. Secondly, the presence of two oxygen atoms in the sulfone group, carrying a close charge value and having approximately equal steric accessibility, but having different stereochemical identifiers (*pro-S* and *pro-R*), can lead to the participation of both one and the other oxygen atom in hydrogen bonding, which corresponds to different relative supramolecular configurations of the sulfur atom.

In the crystals of sulfonamides **1–5**, various packing motifs were identified, formed by classical N–H···O=S hydrogen bonds involving various diastereomeric forms.



R:
(1) *meta*-CH_3
(2) H
(3) *para*-CH_3
(4) *meta*-CF_3
(5) *para*-F

Figure 1. The general scheme of the studied of sulfonamides **1–5**.

The work was supported by the Russian Science Foundation (grant No 22-13-00284).

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EXCESS MOLAR VOLUMES IN HOMOGENEOUS REGION OF PROPIONITRILE+DMSO+WATER TERNARY LIQUID MIXTURES AT TEMPERATURES FROM (298.15 TO 323.15)K

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The ternary mixtures exhibit peculiar solvation properties thanks to simultaneously possessing a few functional groups. The preparation of such systems opens a wide avenue to fine-tune the physicochemical properties of the medium and, therefore, obtain designer solvents to match specific problems in applications. Regarding ternary systems, such as alkyl nitriles/sulfoxide/water mixtures, the volumetric properties beyond those for the water/acetonitrile/dimethylsulfoxide mixtures have not been investigated [1]. The main reason is that alkyl nitriles with longer alkyl chains are practically insoluble in water. Subsequently, the whole range of homogeneous contents for these ternary mixtures is considered inaccessible.

Propionitrile (PN), dimethylsulfoxide (DMSO), and water all represent quite polar molecules yet to different extents and capable to form both homo- and heteromolecular associates [2]. By using densitometric measurements (Anton Parr DMA 4500 vibrating-tube densitometer) over wide ranges of compositions, we have identified that $x_{DMSO}/x_{water} \geq 1$ is sufficient for the ternary homogeneous mixture incorporating any contents of PN from 298.15 to 323.15 K.

This observation can be readily rationalized because the molecule of water is smaller than that of DMSO and creates up to four hydrogen bonds both with DMSO, the cyano group of PN, and neighboring water molecules. In turn, the larger fractions of DMSO favor DMSO-DMSO dipole-dipole coupling and DMSO-PN coupling both of which are predictably weaker as compared to the hydrogen bonds.

Acknowledgments. The work was carried out in the Laboratory of Physical Chemistry of the YSU Chemistry Research Center with the financial support of the Science Committee of the RA MESCS.

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SYNTHESIS OF PLATINUM-BASED POLYSILOXANE FOR HETEROGENEOUS Si—O DEHYDROCOUPLING

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Polymer-metal complexes of the transition metals are one of the most promising catalysts for the production of organoelement and macromolecular compounds[1]. Among many transition metals, platinum metal complexes are crucial for synthesis low and high molecular compounds in organosilicon chemistry[2]. Nowadays, many platinum group metal complexes are well known as homogeneous catalysts in hydrosililation[2] and dehydrocoupling[3] reactions. However, the main problem of homogeneous catalysts is their regeneration, purification and reuse due to the high cost of the platinum-based complexes. While heterogenous catalyst can be easily and effectively recovered[4]. Just a few studies report about heterogeneous platinum-containing catalysts for hydrosililation reaction and no data about catalysts for catalytical dehydrocoupling reactions for organosilicon compounds preparation[5].

The aim of this work is to synthesize platinum based polysiloxane (Pt-PDMS) for heterogeneous Si—O dehydrocoupling. The Pt-PDMS was synthesized using Cu(I)-catalized azide-alkyne cycloaddition between platinum C,N-cyclometalated complex and (3-azidopropyl)polysiloxane (Fig. 1). The structure of Pt-PDMS was investigated by ^{1}H and ^{195}Pt NMR spectroscopy. Additionally, concentration of Pt (atomic %) in Pt-PDMS was investigated by X-ray photoelectron spectroscopy (XPS). In catalytic tests the obtained Pt-PDMS is easily separated from reaction mixture and can be used up to five times without loss of catalytic activity.

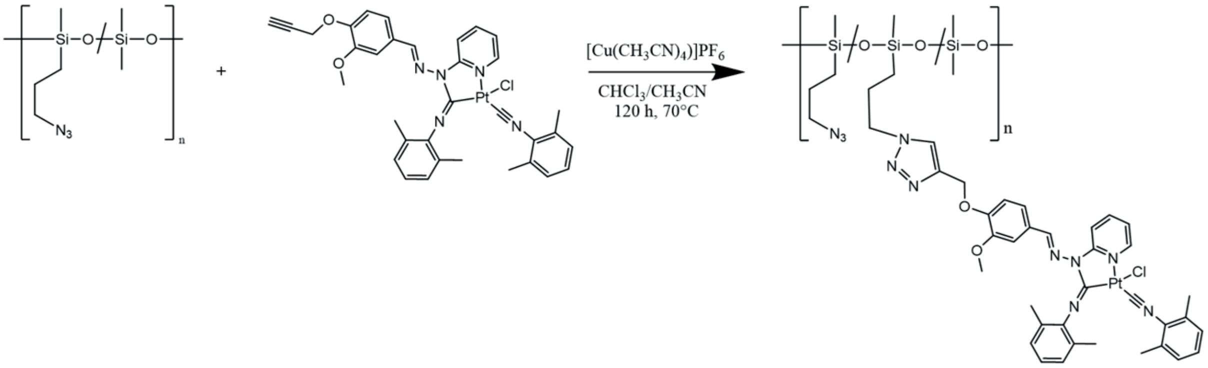

Figure 1. Pt-PDMS synthesis.

This study was supported by Saint Petersburg State University (project no. 94124215).

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CRYSTAL STRUCTURE DETERMINATION OF ACTIVE PHARMACEUTICAL SUBSTANCES FROM SYNCHROTRON POWDER X-RAY DIFFRACTION DATA

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Evolution of many research areas in chemistry, biology, pharmacology requires accurate data about the atomic and molecular structure of the corresponding objects. Determination of crystalline structure of various bioactive compounds is of great importance in pharmaceutical chemistry. However, growth of single crystal for these substances might be difficult or impossible. In this case, powder X-ray diffraction (PXRD) can be an efficient alternative to obtain accurate data about the crystalline structure of pharmaceutical compositions.

PXRD demonstrated a high potential to determine different crystal structures of lanthanide complexes, siloxanes, layered materials [1] and various organic compounds, including a new polymorph of Favipiravir (therapeutic agent for the treatment of COVID-19) [2]. In current work we applied Kurchatov source of synchrotron radiation and cooling powder samples to low temperatures to obtain high-resolution diffraction data. We achieved an increase in the intensity of high-angle reflexes and a corresponding decrease in thermal displacement of atoms.

The objects of research were the solid forms of active pharmaceutical substances, such as ticagrelor (form III), palbociclib, nilotinib hydrochloride hydrate (Fig. 1). Using periodic quantum chemical calculations based on the obtained diffraction data, the molecular and crystalline structure of these compounds were solved, refined and optimized. The features of the structure and packaging of molecules in a crystal were noted.

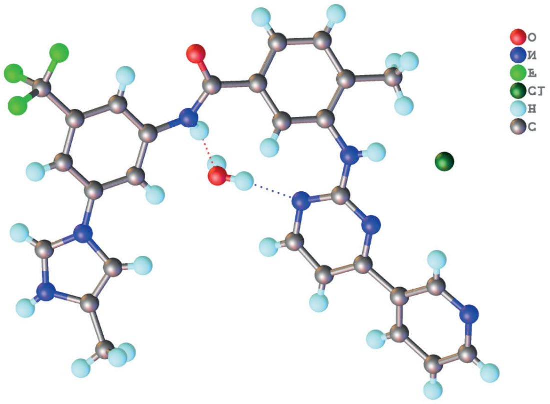

Figure 1. Crystal structure of nilotinib hydrochloride hydrate

This work was supported by the Russian Science Foundation (grant № 23-73-00027).

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COPPER(II) COMPLEXES BASED ON 2,2'-BIPYRIDINE / 1,10-PHENANTHROLINE AND 5-PHENYLTETRAZOLE: SYNTHESIS, STRUCTURAL AND BIOLOGICAL ASPECTS

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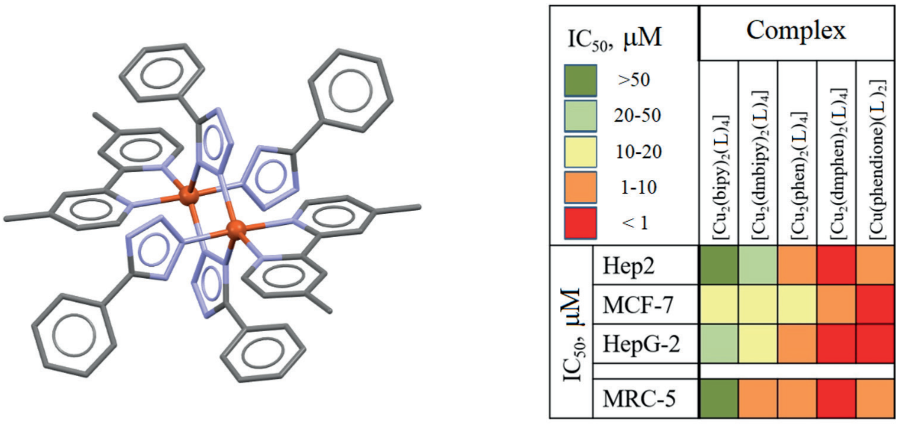
Nowadays chemotherapy is one of the main ways to treat various types of cancer, therefore a huge number of studies are carried out worldwide to develop new improved antitumor drugs. Due to the successful completion of preclinical trials for one copper(II) complex from the Casiopeinas series, 1,10-phenanthroline / 2,2'-bipyridine based copper(II) complexes as anticancer drugs are of particular interest to scientists.

Within the framework of this work, mixed-ligand copper(II) complexes with 5-phenyltetrazole (HL) and 1,10-phenanthroline, 2,2´-bipyridine ligands (1,10-phenanthroline (phen), 1,10-phenanthroline-5,6-dione (phendione), 4,7-dimethyl-1,10-phenanthroline (dmphen), 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'- bipyridine (dmbipy)) have been synthesized. These compounds have been characterized by elemental and powder X-ray diffraction analyzes, EPR and IR spectroscopy. According to single-crystal X-ray diffraction analysis, obtained compounds (with the exception of [Cu(phendione)$(L)_2$]) possess centrosymmetric binuclear structure, in which copper atoms are connected to each other by two bridging phenyltetrazole anions (Fig. 1).



IC$_{50}$, μM
🟩 >50
🟢 20-50
🟨 10-20
🟧 1-10
🟥 < 1

IC$_{50}$, μM	[Cu_2(bipy)$_2$(L)$_4$]	[Cu_2(dmbipy)$_2$(L)$_4$]	[Cu_2(phen)$_2$(L)$_4$]	[Cu_2(dmphen)$_2$(L)$_4$]	[Cu(phendione)(L)$_2$]
Hep2	🟩	🟢	🟧	🟥	🟧
MCF-7	🟨	🟨	🟨	🟧	🟥
HepG-2	🟢	🟨	🟧	🟥	🟥
MRC-5	🟩	🟧	🟧	🟥	🟧

Figure 1. The structure of [Cu_2(dmbipy)$_2$(L)$_4$] (on the left) and heat map indicating cytotoxic effect of complexes on different cell lines (on the right).

Cytotoxic activity of complexes and ligands has been evaluated on cancer (Hep2 (larynx carcinoma), MCF-7 (breast adenocarcinoma), HepG2 (hepatocellular carcinoma)) and non-cancerous (MRC-5 cells (normal lung fibroblast)) cell lines. Copper(II) complexes exhibit significant dose-dependent cytotoxic effect. 1,10-Phenanthroline based compounds are much more cytotoxic than complexes containing 2,2'-bipyridine (Fig. 1). Based on the cytotoxicity data on MRC-5 cells, the selectivity indexes were calculated. [Cu_2(bipy)$_2$(L)$_4$] and [Cu(phendione)(L)$_2$] have been shown to be the most selective. Cytotoxicity of this compounds was further investigated on 3D model of HepG2 cells and on cisplatin-resistant Hep2C cell line. Moreover, complexes were evaluated on the ability to influence the transport activity of P-glycoprotein (key ABC transporter responsible for multidrug resistance) by absorption of Calcein-AM. *In vivo* studies have been conducted for the most promising complex – [Cu(phendione)(L)$_2$]. The LD$_{50}$ value was estimated as 145 mg/kg by different doses administrated intraperitoneally in mice.

This work has been supported by the Russian Science Foundation (project №20-73-10207).

SYNTHESIS OF NOVEL ARYLBITETRAZOLE-BASED ENERGETIC MATERIALS

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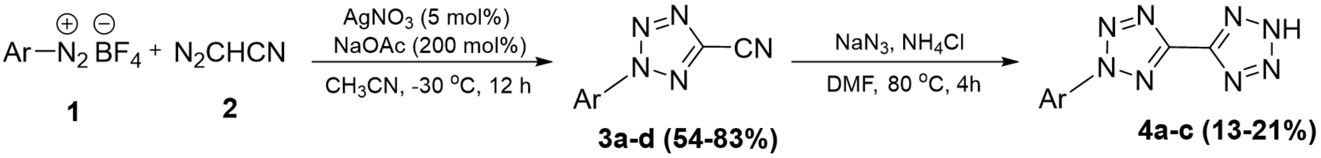
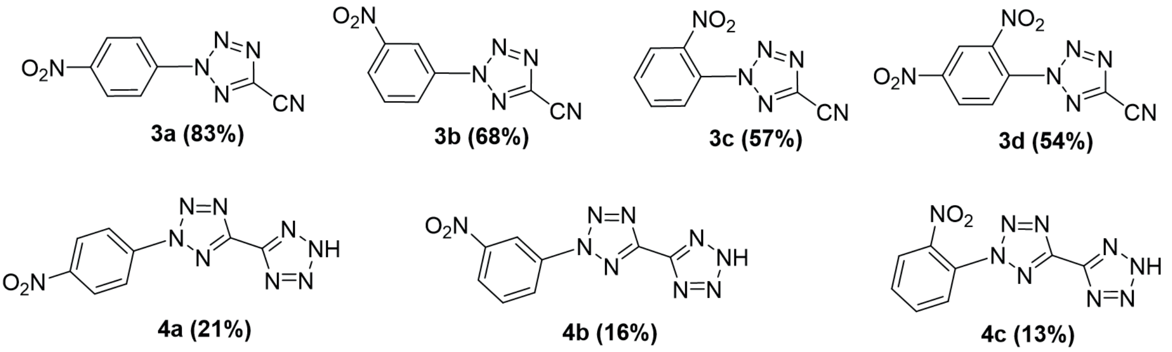
One of the leading directions in organic chemistry is the synthesis of heterocyclic compounds, study of their reactivity and determination of practically useful properties. Nitrogen-rich systems are of particular interest because of their valuable properties that find application in a number of high-tech industries.

The aim of this work is the synthesis of polynitrogen heterocyclic systems based on formal tandem [3+2] cycloaddition reactions. Aryldiazonium salts **(1)** used as initial substrates undergo [3+2] cycloaddition [1] with diazoacetonitrile **(2)** resulting in a formation of cyanotetrazoles **(3)**, which are introduced into the second [3+2] cycloaddition reaction with sodium azide to form bitetrazoles **(4)** [2].



Currently, a set of cyanotetrazoles (**3a-d**) and three target compounds (**4a-c**) were prepared (Fig. 1). Experimental density of the bitetrazole **4a** is 1.58 g cm^{-3}.


3a (83%) **3b (68%)** **3c (57%)** **3d (54%)**

4a (21%) **4b (16%)** **4c (13%)**

Fig. 1. Obtained substances

Attempts to obtain cyanotetrazoles from diamino-1,2,5-oxadiazole and 3-amino-1,2,4-triazole diazonium salts were unsuccessful. In these cases, the preparation of cyanotetrazoles is complicated because of the formation of two cyanotetrazole isomers (Fig. 2) having similar R_f values, making their separation quite difficult. Optimization of this protocol in regard to heterocyclic-based diazonium salts is currently undertaken in our group.

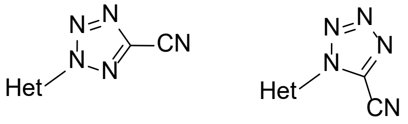


Fig. 2. Cyano-tetrazole isomers

Acknowledgement: This work was supported by the Russian Science Foundation, grant 21-73-10109.

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GUANIDINIUM POLYAMPHOLYTES FOR DRUG DELIVERY

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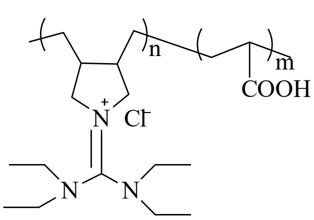
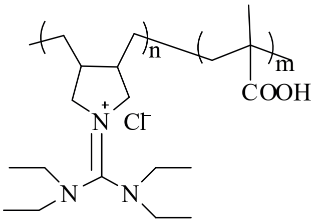
Polyfunctional water-soluble copolymers, whose molecules contain cationic and anionic groups, have amphoteric properties and are considered as being one of the most interesting and promising classes of polymers. By varying the total charge of the copolymers, it is possible to significantly change the properties of the target macromolecule, such as molecular weight, solubility, reactivity, etc [1,2]. Compounds containing a guanidine group have a high bactericidal activity and are widely used as fungicides and broad-spectrum bactericides [3].

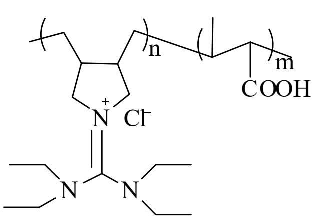
In an attempt to create new polyampholytes, the radical copolymerization of 2,2-diallyl-1,1,3,3-tetraethylguanidinium chloride (AGC) with acrylic (AA), methacrylic (MAA), vinylacetic (VAA) and crotonic (CA) acids in bulk and in organic solvents has been studied. According to their activity in the reaction of radical copolymerization with AGC, the unsaturated acids can be arranged in the following sequence: MAA > AA > CA > VAA. It is shown that the copolymerization of AGC with unsaturated carboxylic acids proceeds with the formation of symmetrical stereoisomeric pyrrolidinium cycles in the polymer chain.



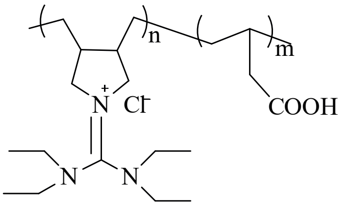
AGC-AA



AGC-MAA



AGC-CA



AGC-VAA

In recent years, polymer systems of drug carriers have attracted increasing attention owing to their various properties such as biocompatibility, biodegradability, mechanical properties and high surface area. Among these compounds, drug-conjugated polymers are very promising. From this point of view, the presence of carboxyl groups in our polyampholytes offers opportunities for the introducing various drugs via polymer-analogous transformations.

Here the possibility and prospects of chemical modifications of copolymers by drugs bearing an amino group are considered. By functionalizing polyampholyte macromolecule with isoniazid and ampicillin, there were obtained new water-soluble physiologically active drug forms of prolonged action. These modified polyampholytes are effective against both Gram positive and Gram negative microflora. The results illustrate the broad application prospects of modified polyampholytes as scaffolds for drug carriers.

Financial support by the Russian Science Foundation (research project No. 23-23-00073) is gratefully acknowledged.
Analytical, spectroscopic, and biological studies were carried out using the equipment of the Core Facilities Center "Research of materials and matter" at the PFRC UB RAS.

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ANTIPROLIFERATIVE ACTIVITY OF NOVEL COPPER, COBALT AND ZINC COMPLEXES WITH ABIRATERONE ACETATE

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In the treatment of neoplastic diseases, platinum preparations (cisplatin, carboplatin, oxaliplatin) are widely used, but their clinical efficacy is significantly limited by high toxicity, significant side effects and accumulation in the body. Therefore, in recent years, close attention has been paid to the search for drugs based on compounds of other metals. Cu(II), Co(II), Zn(II) complexes are known to exhibit anti-inflammatory, antimicrobial, and antitumor activity [1]. Thus, compounds of Cu (II) and Zn (II) are able to increase life expectancy, reduce the average weight of Ehrlich ascitic carcinoma, and inhibit the growth of tumor cells in mice. Abiraterone acetate (AbAc) is a medicine used to treat prostate cancer. AbAc is converted *in vivo* to abiraterone, which is an inhibitor of androgen biosynthesis. In addition, abiraterone has been found to act as a direct estrogen receptor agonist and induce the proliferation of human breast cancer cells *in vitro* [2].

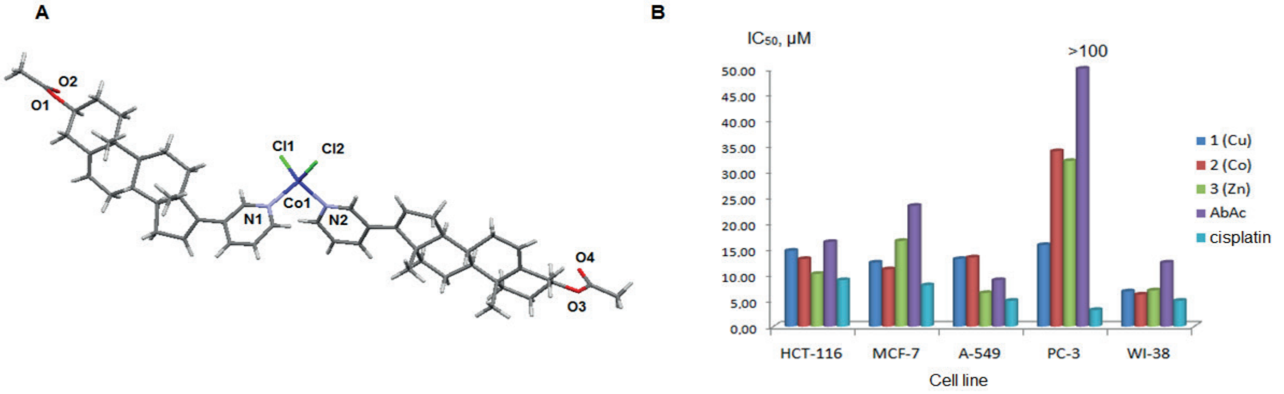

Fig. 1. Molecular structure of complex **2** (A); MTT-test results (B).

Novel complexes **1-3** of the general formula $CuCl_2(AbAc)_2$, $CoCl_2(AbAc)_2$ and $ZnCl_2(AbAc)_2$ respectively have been synthesized. The structure of compound **2** was confirmed by X-ray diffraction (Fig. 1A). The ability of the compounds to inhibit cell proliferation was examined using the MTT test. It was found that the activity of the obtained compounds against cancer HCT-116, MCF-7, A-549, PC-3 and normal WI-38 cells is comparable to the activity of cisplatin (Fig. 1B). It should be noted that in relation to prostate cancer PC-3 cells, complexes **1-3** exhibit a higher activity compared to AbAc, which indicates the effect of the metal on the antiproliferative properties.

In addition, compound **2** causes cell cycle arrest in the G0/G1 phase of RNA protein synthesis. The results obtained open up possibilities for further investigation of complexes **1-3** as potential antitumor agents.

The financial support of RSF (grant № 22-23-00295) is gratefully acknowledged.

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ANTIMONOAMINE OXIDASE PROPERTIES OF NEW DERIVATIVES OF CONDENSED PYRIDINE-5-CARBONITRILES

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It is known that MAO inhibitors prevent the destruction of various monoamines (serotonin, norepinephrine, dopamine, phenylethylamine, tryptamine, etc.), and thereby increase their concentration in the synaptic cleft, inhibiting the occurrence of depressive processes in the body. MAO inhibitors also inhibit the reuptake of monoamines in the presynaptic membrane, increasing the content of free neurotransmitters [1].

The purpose of this study is to study the antimonoamine oxidase properties of the new 14 pyridine derivatives [2]. The source of monoamine oxidase (MAO) was a 50% bovine brain homogenate, which was obtained by homogenizing the brain in a glass homogenizer with an equal (by weight) volume of a 2.5% Arkopal solution. The substrate used was serotonin (5-OT), creatinine sulfate monohydrate, which was added to the samples after a 30-minute preincubation of the enzyme with the test substance at room temperature. The technique for studying the antimonoamine oxidase activity of compounds was reported by us earlier [3]. The obtained 50% homogenate was determined by the activity of MAO. Each compound was tested in 3 experiments, from which average data were derived using the GraphPad Instat method. The results were compared with the known drug, the antidepressant Indopan [4].

It has been established that the studied pyridine derivatives exhibit moderate anti-MAO properties. Compounds D011-07, D011-08, D011-035 were relatively active in this series, significantly inhibiting serotonin dezamination by 88% (D011-07), 75% (D011-08), 75% (D011-035), respectively by 1mkmol/ml concentration. Under the same conditions, indopan inhibits the dezamination of serotonin by 86%.

Thus, the study of the antimonoamine oxidase activity of some new pyridines has shown that the active compounds can be considered in the future as a potential antidepressant. At the same time, when studying the structure-biological activity relationship, it turns out that isoquinoline derivatives have a higher activity than their pyranopyridine counterparts.

The work was supported by the Science Committee of RA, in the frames of the research project № 20TTSG-1D011

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STUDY ON SOLVENT- MEDIATED RADICAL SCAVENGING ACTIVITY OF MORIN TOWARDS 2, 2-DIPHENYL-1-PICRYLHYDRAZYL

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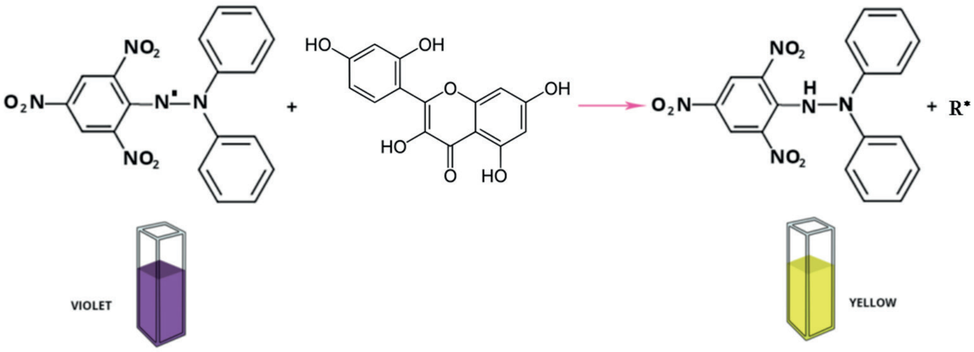
The hydroxyl hydrogen removal from phenolic compounds in radical scavenging processes is of great chemical and biological importance. The efficiency of these processes depends on the polarity of the environment. This work presents the results of solvent-mediated radical scavenging properties of morin (3, 5, 7, 2′, 4′pentahydroxyflavone) towards 2, 2-diphenyl-1-picrylhydrazyl radical (DPPH$^\cdot$).



Interaction of morin with DPPH$^\cdot$

The reaction of morin with DPPH$^\cdot$ was studied in polar protic (water, methanol, and ethanol) and polar aprotic solvents (dimethylsulfoxide - DMSO, dimethylformamide - DMF, and dimethylacetamide DMA) using UV/Vis spectroscopy. The scavenging capacity (Rs), effective concentration (*EC*50), antioxidant reducing power (*ARP*), stoichiometry (*EC100*), and the number of reduced DPPH$^\cdot$(*n*) were determined using the DPPH$^\cdot$ assay [1]. Morin can demonstrate radical scavenging activity due to 3-OH, 2′-OH, and 4′-OH groups, which are the main reactive sites of morin. Antioxidants react with free radicals by different mechanisms-hydrogen atom transfer (HAT), single electron transfer mechanism (SET), or the combination of both HAT and SET mechanisms. On the bases of obtained results, morin demonstrates considerably more reactive and effective radical scavenging activity in polar protic solvents than in polar aprotic solvents according to the following series $H_2O > CH_3OH > C_2H_5OH >$ DMSO > DMF > DMA. This can be explained by the effect of solvent structure and properties on the mechanism of the reaction between the antioxidant and radical.

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A NEW METHOD FOR THE SYNTHESIS OF QUINAZOLINE 3-OXIDES FROM ANILIDES AND NITROALKANES ELECTROPHILICALLY ACTIVATED WITH POLYPHOSPHORIC ACID

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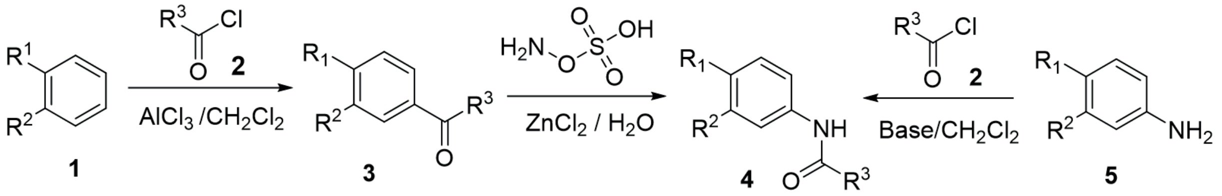
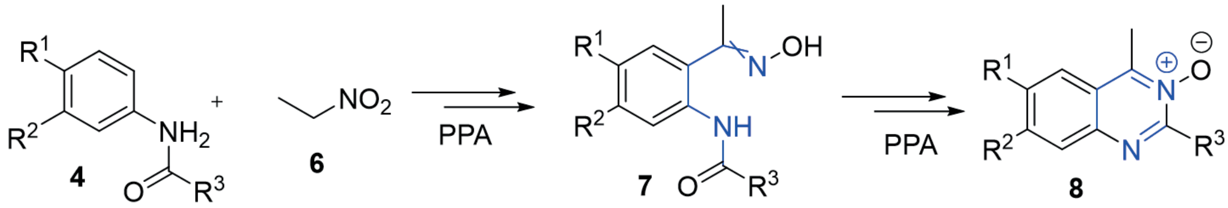
In this study, revealing the synthetic capabilities of nitroalkanes activated by polyphosphoric acid (PPA), nitroethane **6** and π-excess anilides **4** were selected as building blocks for the assembly of the framework of quinazoline 3-oxides.

The initial anilides **4** were obtained either by C-acylation of arenes **1** by Friedel-Crafts chlorohydrides **2** followed by amination ketones **3**. The yield of acyl derivatives **3** was 87-98%, the yield of products **4** at the amination stage was 64-90%. According to another variant, anilides **4** (R^1=H, R^2=OCH_3) were obtained by direct N-acylation of substituted anilines **5**, namely, m-anisidine with carboxylic acid chlorohydrides **2** (or their anhydrides). The yield of anilides **4** in this case was 91-97%.



The target quinazoline **3**-oxides were obtained by the interaction of anilides **4** with nitroethanoam **6** in a PPA medium. Thus, at the first stage of cascade transformations, an oxime **7** is formed, prone to subsequent 6-*exo-trig* cyclization with elimination of the water molecule and aromatization leading to *N*-oxide 8. In some cases, intermediate oximes (**7a, c, d**) were isolated in an isolated form with a yield of 10-30%.



7a: R^1=H, R^2=OCH_3, R^3=Me; **7c**: R^1=H, R^2=OCH_3, R^3=CF_3; **7d**: R^1=H, R^2=OCH_3, R^3= 4-fluorophenyl; **8a**: R^1=H, R^2=OCH_3, R^3=Me; **8b**: R^1=H, R^2=OCH_3, R^3=Et; **8c**: R^1=H, R^2=OCH_3, R^3=CF_3; **8d**: R^1=H, R^2=OCH_3, R^3= 4-fluorophenyl; **8e**: R^1+R^2=OCH_2CH_2O, R^3=*n*-Pr; **8f:** R^1+R^2=OCH_2CH_2O, R^3=Bn; **8g:** R^1+R^2= OCH_2CH_2O, R^3=Et; **8h**: R^1+R^2=OCH_2CH_2O, R^3=Me; **8i**: R^1=R^2=OCH_3, R^3=*n*-Pr; **8k**: R^1=R^2=OCH_3, R^3=Et.

In the presence of two EDG substituents, the yield of quinazoline 3-oxides (**8 e-h**) was 52-64%.

The developed protocol, which allows the assembly of quinazoline derivatives of 3-oxides containing alkyl, aryl, benzyl and trifluoromethyl substituents in the position 2 of quinazoline, is heating with intensive stirring of a mixture of an anilide derivative (1 mmol) and nitroethane (2 mmol) in 86% PFC (2g/1 mmol anilide) at 85 °C for 5-10 minutes, then for 1-1.5 hours at 105 °C and, at the end, for 2-3 hours at 115 °C.

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SYNTHESIS, ANTITUMOR AND ANTIBACTERIAL ACTIVITY OF ISOPIMARIC ACID DERIVATIVES

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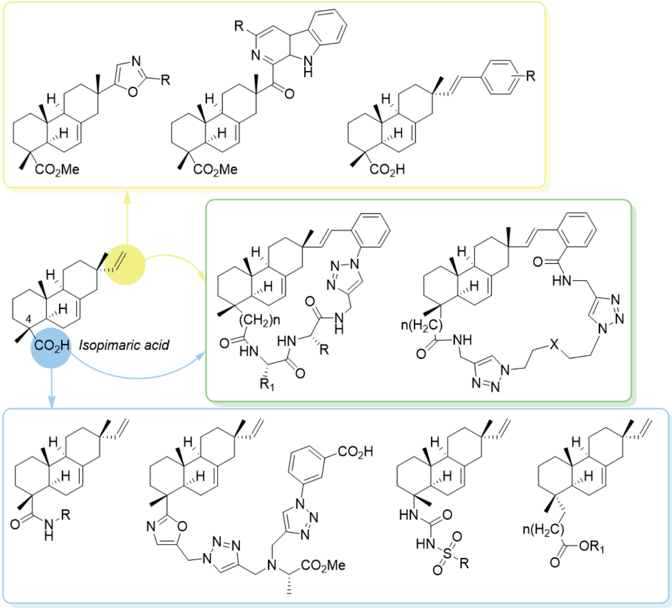
Isopimaric acid, an available metabolite of *Pinus sibirica*, has a wide range of biological effects [1]. Isopimaranes substituted at the terminal alkene and carboxyl group represent a relatively small group of substances and are mainly limited to natural compounds. However, modifications at these positions of the tricyclic skeleton are of interest in connection with the available data on the antitumor activity of some synthesized derivatives [2-4].

We have carried out selective transformations of isopimaric acid at the double bond. As a result of the Waker process 15-oxo-16-formylisopimarate was synthesized, on the basis of which 4-(oxazol-2-yl)- and β-carboline-18-norisopimaranes were obtained. (*E*)-16-Arylisopimaranes have been synthesized by palladium-catalyzed arylation of isopimaric acid or its methyl ester in the presence of silver carbonate. Carboxamides, 2,5-disubstituted-1,3-oxazoles, 4-(arylsulfonylureido)-substituted derivatives of tricyclic diterpenoids were first synthesized as a result of derivatization of the 4th position of the isopimaran core. Synthetic methods for isopimaric acid derivatives, the terminal carboxylic acid of which was separated by two or three methylenes from the tricyclic skeleton were developed. 1,2,3-Triazole macrocyclic diterpenoids linked to a terpene backbone via a terminal alkene and a carboxyl group were synthesized by CuAAC-based macrocyclization.

Among the synthesized compounds, selective antibacterial compounds against gram-positive bacteria *Staphylococcus aureus* and *Bacillus cereus* and cytotoxic agents were found.



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PLATINIZED ORGANO-INORGANIC HYBRID PHOTOCATALYSTS BASED ON LAYERED TITANATE $H_2La_2Ti_3O_{10}$

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In recent years, environmental problems caused by using fossil fuel have become particularly acute. Hydrogen produced by the photocatalytic splitting of water and organic substrates under the action of sunlight can be a promising replacement for hydrocarbon fuel. Of particular interest among heterogeneous photocatalysts is a class of layered perovskite-like oxides, in the structure of which there is an alternation of negatively charged perovskite blocks with blocks of a different structure, called interlayer space, which can act as a separate reaction zone in the photocatalytic process[1]. The introduction of organic molecules, for example amines, into interlayer space contributes to an increase in the photocatalytic activity of samples in the reaction of obtaining hydrogen from a 1% (mol.) aqueous solution of methanol under the action of ultraviolet irradiation [2]. In this case, samples additionally modified with photo-deposited platinum particles exhibit particularly high activity. It was assumed that this effect is caused by the expansion of the interlayer space, which led to an increase in the accessibility of this zone for water and methanol molecules. The organic components undergo various transformations due to irradiation with ultraviolet light [3]. At the same time the activity of the photocatalyst remains constant throughout the experiment. A possible reason for the immutability of the activity of organo-inorganic hybrids may also be the deposition of platinum particles in the interlayer space expanded by the introduction of organic matter. In this instance, the activity of the samples would be preserved even after the decomposition of the organic modifiers.

This work focuses on the study of the effect of organic modifiers on the process of photo-deposition of platinum particles and the relationship of this process with the observed photocatalytic activity of hybrid samples. It was found that the sequence of procedures for modifying layered oxide $H_2La_2Ti_3O_{10}$ by intercalation of alkylamines RNH_2 (R = Me, Oc) and platination significantly affects the stability of the formed platinum particles to the action of aqua regia. The photocatalytic activity of organic platinized derivatives in the reaction of hydrogen extraction from a 1% (mol.) aqueous methanol solution under UV irradiation was also compared. It was shown that all modified samples exceed the initial $H_2La_2Ti_3O_{10}$/Pt in terms of photocatalytic activity by 3 times or more, but they did not differ so markedly from each other. As the result it was found that intercalation of organic molecules can affect the deposition of platinum particles in layered oxide. At the same time, the stable photocatalytic activity of the samples is not due to the different spatial distribution of Pt nanoparticles. Thus, the increased activity of photocatalysts is rather associated with the modification of oxides by organic molecules.

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INTERACTIONS OF 6-AMINO-2-METHYLQUINOLIN-4-OL WITH SUBSTITUTED BENZALDEHYDES: A STUDY ON THE BIOPHYSICAL PROPERTIES OF THE RESULTING COMPOUNDS

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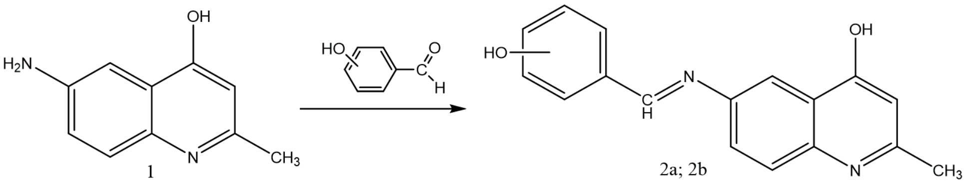
Quinoline derivatives have been widely utilized in the field ofbioimagingand pharmaceutical agents [1,2]. In this study, we present an affordable and cost-effective approach for synthesizing quinoline derivatives using 2-methyl-4-hydroxy-6-aminoquinoline as a starting material. This method involves the condensation of the amino group in quinoline with the aldehyde groups of hydroxyphenylaldehydes, resulting in good yields of the desired compounds. The design concepts have been drawn in Scheme 1.



Shceme 1

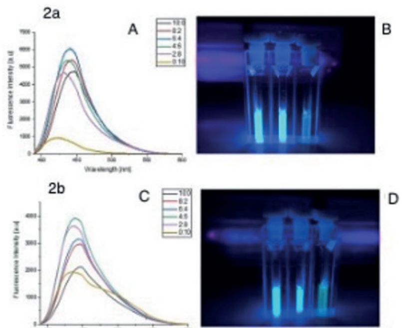


Figure 1

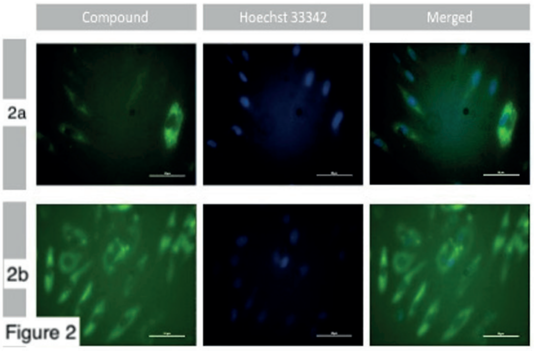


Figure 2

Interestingly, the synthesized quinoline-based Schiff bases exhibit strong intramolecular charge-transfer fluorescence with significant Stokes shifts. We investigate the emission behavior of sterically hindered compounds in various mixtures of water and DMSO. The emission spectra showed an interesting response in DMSO/water mixtures. The fluorescence intensity at 445 nm continuously increased as the water fraction in the solvent increased up to 60% (for 2a) or 40 (for 2b)%. The emission peaks of one compound red-shifted from 435 to 445 nm when the water fraction increased from 0 to 60(or 40)%, possibly due to the combined effect of increased water polarity and self-assembled agglomerates [1, 56]. With the addition of more water, the emission intensity decreased slightly with a blue shift. This was attributed to the formation of uniform nanoscale aggregates, enhancing the fluorescence intensity. However, at higher water fractions (>60%), the compound molecules agglomerated randomly, resulting in a decrease in fluorescenceintensity[1, 57].The increase in blue emission with the increasing volume fraction of water in the water-DMSO mixture clearly indicates the occurrence of the aggregation-induced emission effect, as shown in the inset of Figure 1B and 1D.Furthermore, we have successfully applied these quinolines in live-cell imaging experiments.Two quinoline derivatives (2a,b),effectively act as bioimaging agents in aquatic environments, exhibiting bright green emission specifically in the cytoplasm of fibroblast cells. The fluorescence images shown in Figure 2 indicate that these dyes selectively stain the cytoplasmic regions of the cells without interacting with the nucleic portions.

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PREPARATION OF NEW DERIVATIVES OF QUINOLINES FUSED WITH 1,2,4-TRIAZOLE-3-THIONES AND 1,3,4-THIADIAZOLES.

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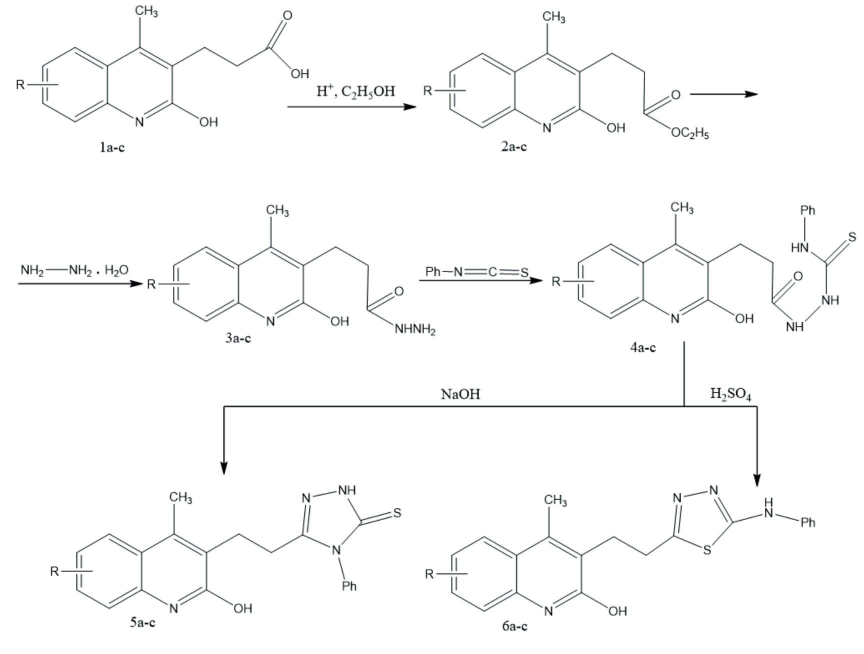
Quinoline fragment constitutes an important structural unit of many synthetic and natural biologically active molecules [1,2] and is an important scaffold for the development of new drugs [3,4]. Keeping this in view, we have designed two new series of quinoline derivatives with possibly a new mode of action. The design concepts have been drawn in Scheme 1. New series of quinoline derivatives were synthesized starting from 3-(2-hydroxy-4-methylquinolin-3-yl)propanoic acids (1a-c) through multi-step reactions. In the reaction sequence, substituted 3-(2-hydroxy-4-methylquinolin-3-yl)propanoic acids (1a-c) was underwent esterification to benz-substituted ethyl 3-(2-hydroxy-4-methylquinolin-3-yl)propanoates (2a-c), the hydrazinolysis of compound 2a-c was carried out with hydrazine hydrate resulting in the to 3-(2-hydroxy-4-methylquinolin-3-yl)propanehydrazides (3a-c), which was then transformed to 2-(3-(2-hydroxy-4-methylquinolin-3-yl)propanoyl)-N-phenylhydrazine-1-carbothio¬amides (4a-c). The key scaffolds 5-(2-(2-hydroxy-4-methylquinolin-3-yl)ethyl)-4-phenyl-2,4-dihydro-3H-1,2,4-triazole-3-thiones (5a-c) and 4-methyl-3-(2-(5-(phenylamino)-1,3,4-thiadiazol-2-yl)ethyl)¬quino¬lin-2-ols (6a-c) obtained from the compounds 4a-c, which were successfully converted to target quinoline derivatives, by cyclization using 5% NaOH solution to form 5a-c and with conc. H_2SO_4 to give 6a-d [5], in good yields .

Scheme 1



R = H(a), 6-CH_3(b), 8-CH_3(c)

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A GREEN CHEMICAL APPROACH: SYNTHESIS OF 2-AMINOTHIOPHENE DERIVATIVES VIA GEWALD REACTION IN IL

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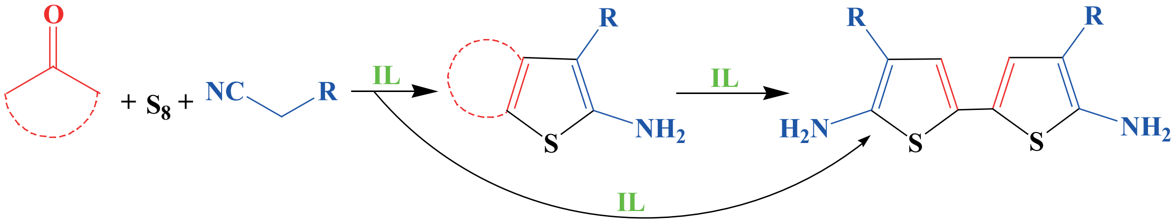
Thiophene derivatives - bithiophenes, oligo thiophenes, alkil/aryl thiophenes and bithiophenes [1] have attracted the attention of many researchers to synthesize donor-acceptor substituted π-conjugated systems, such as formyl π-conjugated systems, through cross-coupling/metalation followed by DMF quenching and Vilsmeier-Haack-Arnold formylation reactions.

The synthesis procedures are carried out using the version of Gewald strategy to achieve the final products starting from preparation of the 2-amino-4-thiophene compounds [2]. The approach was investigated in the synthesis of 2-aminothiophene derivatives [3] via a three-component cyclocondensation of ketones with activated nitriles and elemental sulfur catalyzed by ionic liquids.



Deuterated ketones were used to study activity, reaction process and conditions.

The used catalytic approach has a number of advantages, such as its eco-friendliness, ease of set up, reusability, and simple procedures of separation and purification of products in high yields at short period without using chromatography.

The study was carried out with the financial support of the Science Committee of the Republic of Armenia within the framework of scientific projects No. 20TTSG-1D011 and 20TTWS-1D049.

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THE PHYSICOCHEMICAL AND ANTIMICROBIAL PROPERTIES OF SILVER NANOPARTICLES SYNTHESIZED BY *Spirulina* BIOMASS

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The biosynthesis of nanoparticles (NPs) is an emerging research field enabling the production of stable NPs with various biological activities [1]. The "green" synthesis of NPs by plants, microorganisms, and algae has been shown to be highly efficient. In this perspective, the high protein, essential fatty acid, carotenoids, phycocyanin, and vitamin content of cyanobacteria *Spirulina platensis*, make it an excellent candidate for synthesizing NPs [2].

In the current study, we examined the physicochemical and antimicrobial properties of AgNPs synthesized by using the biomass of *S. platensis*. UV-Vis and Fourier Transform Infrared spectroscopic investigations of biosynthesized AgNPs revealed an absorption peak at ~425 nm and the involvement of some functional groups in their formation (Fig. 1). Further physicochemical characterization by the advanced dynamic light scattering and transmission electron microscopy showed that AgNPs have an average hydrodynamic radius of ~28.7 ± 5.4 nm with a polydispersity index of ~36.5 % and spherical morphology. "Green" AgNPs demonstrated concentration-dependent antimicrobial activity against selected conditionally pathogenic Gram-positive (*Staphylococcus aureus* and *Enterococcus hirae*) and Gram-negative (*Pseudomonas aeruginosa* and *Salmonella typhimurium*) bacteria associated with nosocomial diseases and multidrug resistance (Fig. 1). Moreover, Gram-negative bacteria demonstrated greater sensitivity against "green" AgNPs, compared to Gram-positive ones, which can be related to the bacterial cell wall structure. Hence, *Spirulina* biomass can be utilized for the development of biomedically relevant stable NPs with high antimicrobial activity.

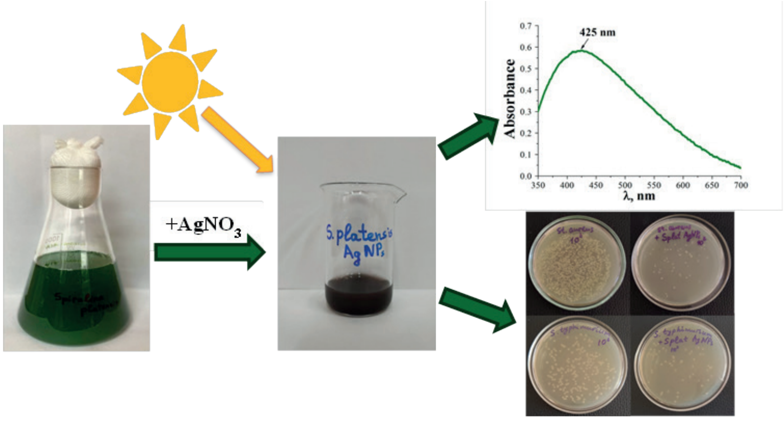

Fig. 1. *Spirulina*-mediated "green" synthesis of AgNPs and their characteristics.

The work was supported by the Science Committee of RA, in the frames of the research project №21T-F179.

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EFFECT OF MICROWAVE IRRADIATION ON SOLUBILITY OF HARDLY SOLUBLE SUBSTANCES IN WATER

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The Microwave irradiation (MWI) is largely carried out in different spheres of technique, industry and everyday life. In scientific view the study of the efficiency of the MWI on increasing of solubility of hardly soluble substances as the model for solving the problem of solubility increasing of hardly soluble drugs in water has practical importance for pharmaceutical industry.

The objects of studies have been chosen both inorganic $CaCO_3$, $NiCO_3$, $CaSO_4$ and organic compounds tyrosine and ketoprofen (pharmaceutical drug). The irradiation was carried out by using microwave brand "Ethos Touch Control Microwave Labistation SK10". The amount of solved inorganic compounds was obtained by atomic absorption Varian AA 240 FS spectrophotometer, and the amount of solved organic compounds- by UV-Vis spectrometer T60.

During the experiment the samples irradiated from 5 to 40 min at constant conditions (power 800 W, pressure 1 atmosphere, t=25 ^{0}C). It was obtained that the MWI effect on solubility of studied compounds only during the first 5 min and then the solubility stays unchanged. Moreover, it has been established that the MWI differently acts on solubility of organic and inorganic compounds. The influence of MWI on solubility of organic compounds is negligible: thus, after 5 min of irradiation the solubility of tyrosine rises up to 5, $21\cdot10^{-3}$ mol/l from $2{,}76\cdot10^{-3}$ and solubility of practically insoluble ketoprofen increases from $2.0\ .10^{-5}$ mol/l to $1{,}1\cdot10^{-3}$ mol/l. It is important to note that due to the MWI the characteristic adsorption wavelength of tyrosine (275 nm) and ketoprofen (259 nm) doesn't change and the new adsorption wavelength does not appear which helps to make a conclusion that under the MWI tyrosine and ketoprofen do not undergo structural changes or destruction.

Quite other solubility behavior has been obtained for inorganic compounds studies. Under the MWI the studied inorganic compounds in aqueous mixture transfer to stable suspension state in which the amount of studied inorganic salts hundreds of times exceeds the amount of their real solubility. In mixture with water the studied salts form suspension in aqueous phase where the content of inorganic salts is higher than their true solubility values. The amount of solved $CaSO_4$ in suspension was been obtained $1{,}3\cdot10^{-1}$ mol/l, while the true solubility of $CaSO_4$ is $1{,}5\cdot10^{-2}$ mol/l. The obtained amounts of solved $CaCO_3$ and $NiCO_3$ in suspension were $1{,}5\cdot10^{-3}$ mol/l and $7{,}7\ 10^{-3}$ mol/l respectively, while their true solubility is $1{,}4\cdot10^{-4}$ mol/l and $7{,}8\ 10^{-4}$ mol/l, respectively. It is very important to note that the MWI increases the stability of suspension: after 5 min of irradiation the suspension saves stability about 2 days while without irradiation the aqueous phase is separated about after 10 min.

Thus, it can be concluded from studies that the MWI is not directly acting on solubility of hardly soluble compounds. The mechanism of the MWI action is the increasing stable state duration time of suspensions in which the amount of hardly soluble compound is much higher than it is in real aqueous solution.

NEW PREPARATIVE FORMS BASED ON PHEROMONE OF THE ORIENTAL FRUIT MOTH

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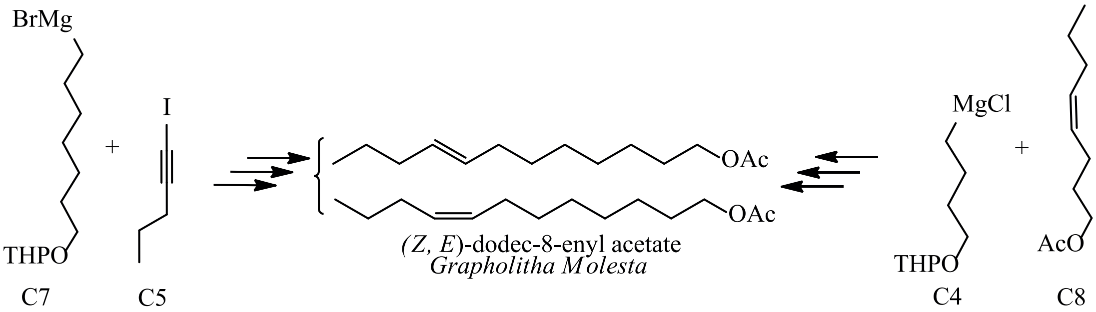
The synthesis of natural compounds such as pheromones, is one of the most promising part of contemporary organic chemistry. The realization of these tasks requires developing the methods, which will allow creating biologically active substances with certain structure [1]. The most promising is the use of pheromones in extermination and disorientation of male insects, which will essentially decrease the quantity of the pesticides now in use.

For this purpose, we have developed two ways for obtaining the sex pheromone of the oriental fruit moth *(Grapholitha molesta)*. The key step of the first scheme, based on the C7 + C5 two-synton strategy, were the preparation of 1-iodopent-1-yne (C5) from pent-1-yne using cadmium(II) acetate and condensation with the C7 component, obtained by analogy with the method described earlier [2].



However, the condensation stage (C5+ C7) had low yields (up to 20%) and turned out to be inexpedient. Therefore, the target pheromone Grapholitha Molesta with a predominant content of (Z)-dodec-8-enyl acetate was synthesized according to the C8 + C4 two-synthon scheme developed earlier on the basis of furfuryl alcohol and tetrahydrofuran [3].

On the basis of this pheromone, dispensers made of polyamide fiber coated with a polymeric material were obtained. These preparative forms make it possible to more effectively control the rate of active substance isolation and provide relatively slow diffusion from the fibers. The preparative forms successfully tested in the apple gardens of the Zhytomyr region of Ukraine and the apricot gardens of the Armavir region of the Republic of Armenia (project №21T-1D270).

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DIRECT SYNTHESIS OF SIX-COORDINATE NITROSYL COMPLEXES OF MANGANESE-PORPHYRINATE WITH *Trans*-P-DONOR LIGANDS

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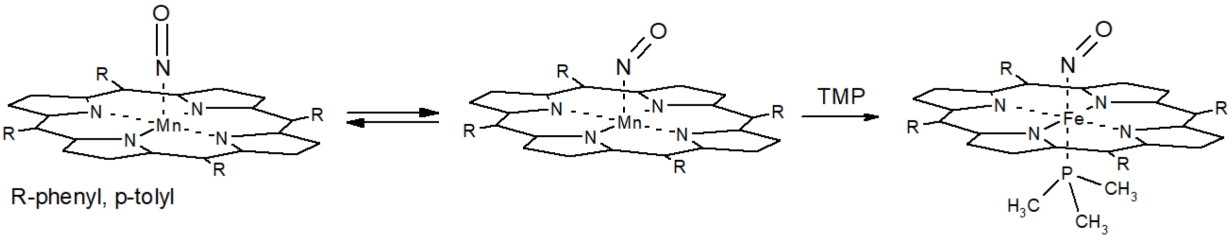
Nitric oxide (NO) is widely accepted bioregulatory molecule playing an important role in a variety of physiological processes. The main targets of NO in vivo are heme-iron containing enzymes. For example, the binding of NO to the heme iron in soluble guanylyl cyclase (sGC) led to the activation of this enzyme, resulting eventually in vasodilation. NO binds to both ferrous Fe(II) and ferric Fe(III) hemes, although NO binding to ferric hemes is weaker than that for ferrous hemes. The coordination chemistry of Mn nitrosyl porphyrins remain less investigated by comparison to the iron analogs [1]. At the same time Mn(II) nitrosyl porphyrins are isoelectronic with the ferric porphyrin nitrosyls and may be used us suitable model. To date, there are only few structurally and spectroscopically studied six–coordinate manganese(II) nitrosyl porphyrins, namely those of (TPP)Mn(NO)(4-Mepip) [2], (TTP)Mn(NO)(CH_3OH), (TTP)Mn(NO)(1-MeIm) and (TTP)Mn(NO)(pip) (TTP is meso-tetra-p-tolylporphyrinatodianion) [3], that were obtained and revealed the linearity of Mn-NO units in these complexes. Five coordinate manganese(II) porphyrin nitrosyls, in its sublimed layers, show two ν(NO) bands in room temperature IR spectra, assigned earlier to the linear and bent Mn-NO isomers[4]. Resently we have investigate 6-coordinated nitrosyl comples with DMSO (TPP)Mn(NO)(DMSO) [5], where DMSO coordinated through O-atom.



The interaction of the trimethylphospine (TMP) donor ligand with the sublimed layers of manganese(II) porphyrin nitrosyl complex Mn(TPP)(NO) was studied using electronic and infrared absorption spectroscopy. Upon TMP interaction with Mn(TPP)(NO), the bent isomer is disappeared while the ν(NO) band of linear one shifted and increased in intensity. This IR spectral changes, as well as the changes observed by UV-Vis spectroscopy are consistent with the ligand binding at the axial position trans to the NO and formation of the six-coordinate adduct. This six-coordinated adduct in the solid state is quite stable at room temperature and reported for the first time.

Acknowledgements: The financial support from SCS of the Republic of Armenia (Project 21AG-1D040) is gratefully acknowledged.

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SYNTHESIS AND ANTIMICROBIAL ACTIVITY OF QUATERNARY AMMONIUM SALTS CONTAINING UNSATURATED GROUPS WITH ALKYL OR ALKYL OXYCARBONYL METHYL GROUPS

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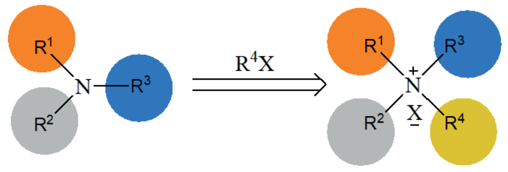
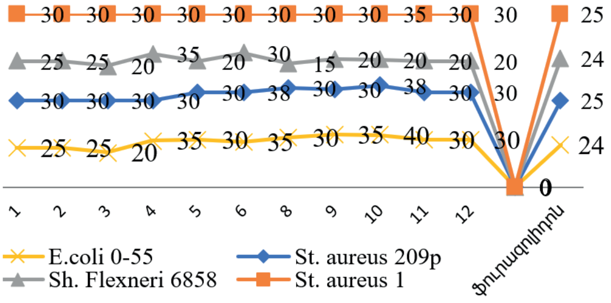
In terms of the discovery of new antimicrobial drugs, cationic surfactants, particularly quaternary ammonium compounds, which have a broad spectrum of antimicrobial activity, are promising. It has been confirmed that ammonium salts containing a propargyl group have a bactericidal effect on gram-positive and gram-negative microorganisms [1]. The aim of this work is the synthesis and study of the antimicrobial activity of quaternary ammonium salts containing alkyl or alkoxycarbonylmethyl groups with unsaturated groups. Salts (**a**) were synthesized based on the interaction of 1-(diethylamino)-3-(prop-2-ynyloxy)propan-2-ol and alkyl bromides and iodides (C7-C10). The interaction of N-methyl-N-(prop-2-ynyl)prop-2-yn-1-amine with halogen derivatives (C8-C12) also gives the corresponding quaternary ammonium salts (**b**). The study of the antimicrobial activity of the synthesized quaternary ammonium salts was carried out against gram-positive (Staphylococcus aureus 209p, 1) and gram-negative microorganisms (Shigella Flexneri 6858, Esherichia coli 0-55). Furazolidone was used as a control drug under similar experimental conditions [2].

All synthesized compounds have high bactericidal activity against gram-positive microorganisms, suppressing their growth (30-40mm) in diameter. Most compounds show similar activity against Esherichia coli 0-55 strain, and their activity against Shigella Flexneri 6858 strain is slightly lower (20-25 mm). The introduction of alkyl or alkyloxycarbonylmethyl groups along with propargyl groups improves the antimicrobial properties of the investigated substances. Compounds containing propargyl and hydroxyl groups along with various alkyl groups, also show high activity against the tested strains.



a $R^1 = R^2 = C_2H_5, R^3 = CH_2\text{-}CH(OH)CH_2OCH_2C\equiv CH$
$R^4 = C_7H_{15}, C_8H_{17}, C_9H_{19}, C_{10}H_{21}, CH_2\text{-}C\equiv CH, X = Br, I$
b $R^1 = CH_3, R^2 = R^3 = CH_2C\equiv CH, R^4 = C_8H_{17}, C_9H_{19}, C_{10}H_{21}, CH_2COOC_8H_{17}, CH_2COOC_9H_{19}, CH_2COOC_{10}H_{21}, CH_2COOC_{12}H_{25}, X = Cl, Br, I$



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TRANSFORMATIONS OF 6-(4-METHYLTHIOPHENYL)-3-(2-PYRIDYL)-1,2,4-TRIAZINES UNDER THE ACTION OF ARYNE INTERMEDIATE

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Aryne compounds are known to be of special interest due to their remarkable versatility in various synthetic strategies. The reactivity of various 6-(4-methylthiophenyl)-3-(2-pyridyl)-1,2,4-triazines with the aryne intermediate was studied in this work. It has been shown that 5-unsubstituted 1,2,4-triazine reacts with aryne to give the S-arylation product in the absence of transformations of the pyridyl-triazine moiety. Incorporation of the pentafluorophenyl moiety into the C(6) position can affect the nature of the interaction with aryne, which occurs simultaneously at two reaction centers. In particular, one can observe the rearrangement of the 3-(2-pyridyl)-1,2,4-triazine system into 10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-a]indole, as well as the S-arylation process. The synthesized product of double functionalization, 10-(5-(perfluorophenyl)-4-(4-(phenylthio)phenyl)-1*H*-1,2,3-triazol-1-yl)pyrido[1,2-a]indole, has been found to be characterized by blue emission with λ_{em} = 395 nm, with the fluorescence quantum yield in this case being commensurable with ones for the previously obtained analogues.

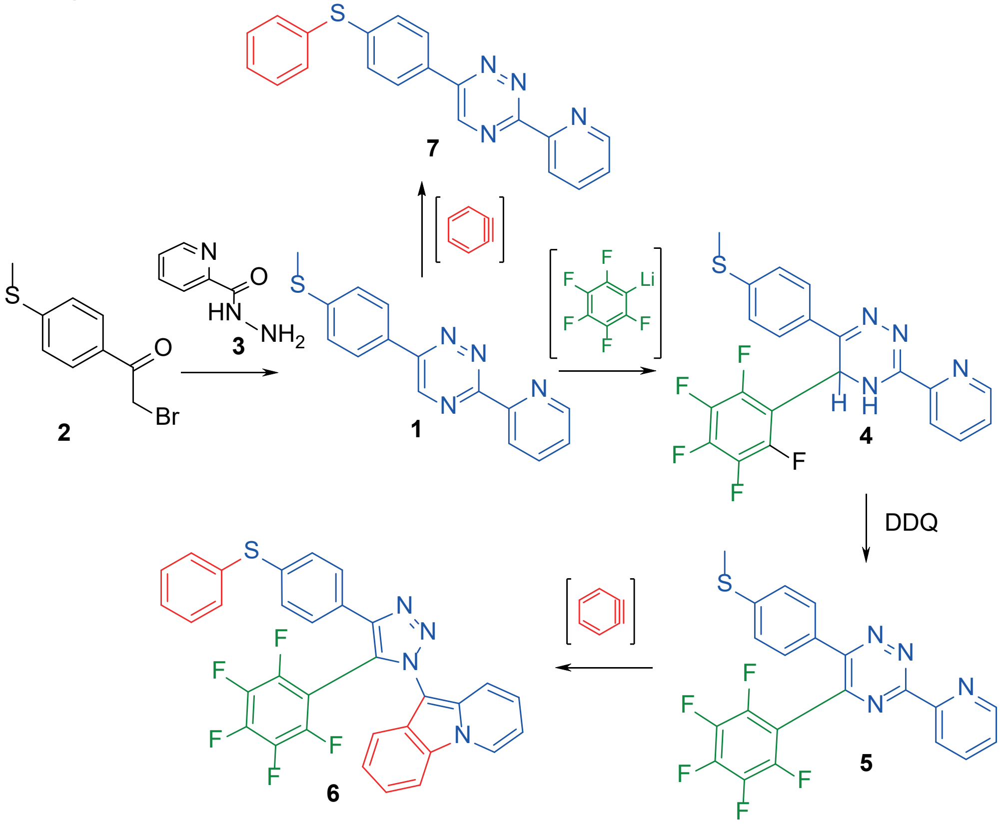

Figure 1. Transformations of 6-(4-methylthiophenyl)-3-(2-pyridyl)-1,2,4-triazines

This research was funded by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-1118)

CASCADE SYNTHESIS LOGIC REVISITED: CASE OF ELECTRON-DEFICIENT CARBOCYCLES

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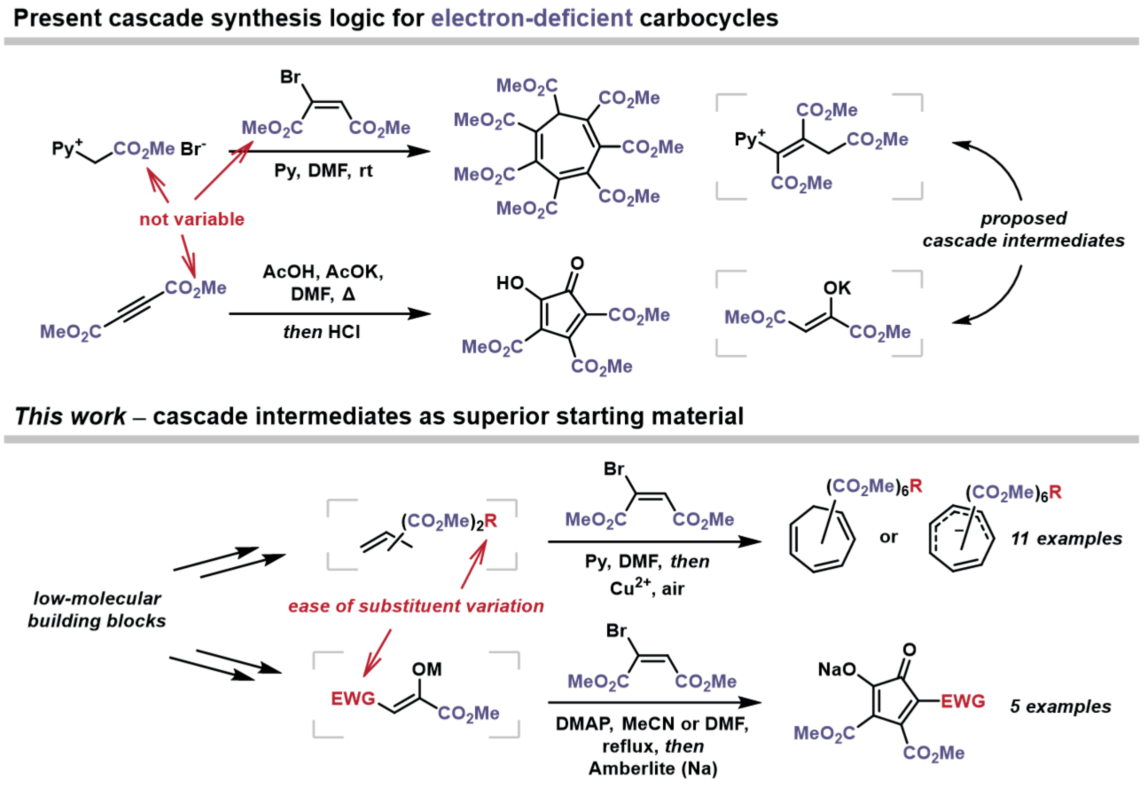
The nature of hyperfunctionalized organic compounds is inextricably linked with their nontrivial reactivity and unique set of physicochemical properties. Despite the synthetic value of these compounds, known approaches to their synthesis do not make it possible to obtain products with a variable substitution pattern due to either unavailability of the required building blocks or the restrictions on the substituent nature dictated by the reaction itself. Overall, present methodology of the synthesis of these systems significantly inhibits further development of both fundamental knowledge about their nature and the practical application of functional materials based on them.

Similar "symptoms" are characteristic of the families of polysubstituted electron-deficient cycloheptatrienes and cyclopentadienones. During our research of these systems, we have developed methodology for their synthesis based on cascade sequences. Imposed limitations on the substituents can be overcome if synthetic equivalents of intermediates are employed in cascade reactions as initial reagents. Thus, the procedure for the synthesis of cycloheptatrienes using CH-acid propenes and a vinylating agent with subsequent oxidation made it possible not only to obtain a number of products with new substitution patterns, but also to discover a previously unknown class of zwitteriones with a cycloheptatrienyl anion [1]. The combination of the nucleophilic oxosuccinate enolate and analogs with the same vinylating agent results in the formation of various 2-hydroxycyclopentadienone derivatives.



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SYNTHESIS AND LUMINESCENT PROPERTIES OF NEW PYRAZOLINE AND PYRIMIDINE DERIVATIVES OF 1-BIPHENYL-4-YLETHANONE

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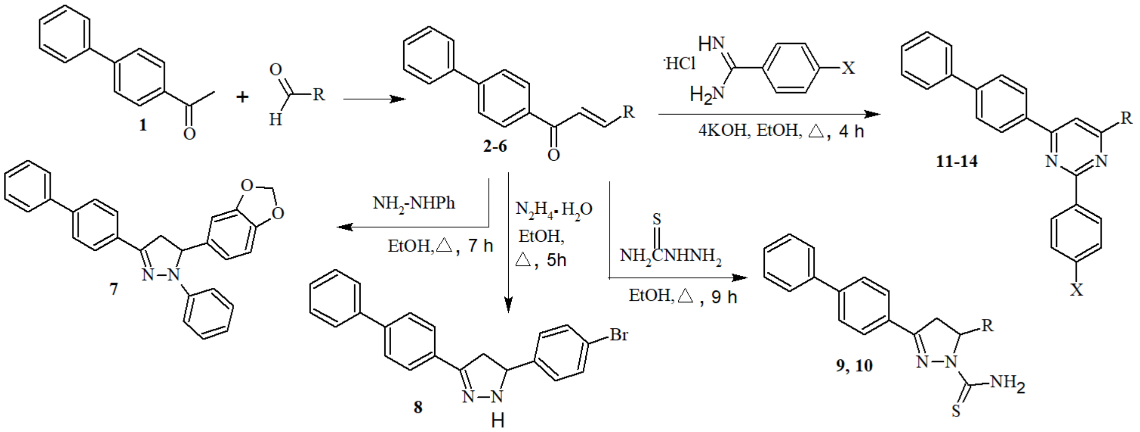
Currently, the creation of materials with high luminescence efficiency finds its application in the creation of new materials for optoelectronics and chemical photonics (such as light emitting diodes (OLED), luminescent sensors, sensors for toxicants, etc. Promising among luminescent materials are pyrazoline and pyrimidine derivatives [1-3].

Chalcones **2-6** were obtained by the condensation reaction of 1-biphenyl-4-yl ethanone **1** with aromatic aldehydes in the presence of sodium hydroxide in an aqueous ethanol solution. Subsequent cyclization of the latter with hydrazine hydrate, phenylhydrazine, and thiosemicarbazide with a catalytic amount of sulfuric acid (no sulfuric acid is added in the case of hydrazine hydrate) leads to pyrazolines **7-10**. The reaction of benzamidine and 4-methylbenzamidine hydrochlorides with chalcones **4-6** in the KOH–ethanol system gave pyrimidines **11-14**.



R=4-N(CH_3)$_2$-Ph (**2, 9**), R= 4-Br-Ph (**3**), R= thiophen-2-yl (**4, 10**), R= benzo-[1,3]-dioxol-5-ylmethyl (**5**), R= 4-OCH_3-Ph (**6**); R= benzo-[1,3]-dioxol-5-ylmethyl, X=H (11), R= benzo-[1,3]-dioxol-5-ylmethyl, X=CH_3 (**12**), R= 4-OCH_3-Ph, X=H (**13**), R= thiophen-2-yl, X=CH_3 (**14**).

The structure of the synthesized compounds was established on the basis of IR, ^{1}H NMR, and ^{13}C NMR spectrometry data. The luminescent properties of the obtained systems are studied in a DMF solution using fluorescence spectroscopy method. The dependence of the luminescent properties on the structure of the fluorophore has been established.

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SYNTHESIS OF 2,4-DIARYL-6-(4-ALKOXYPHENYL)-PYRIMIDINES BASED ON NEW (E)-3-ARYL-1-(4-ALKOXYPHENYL)PROP-2-EN-1-ONES

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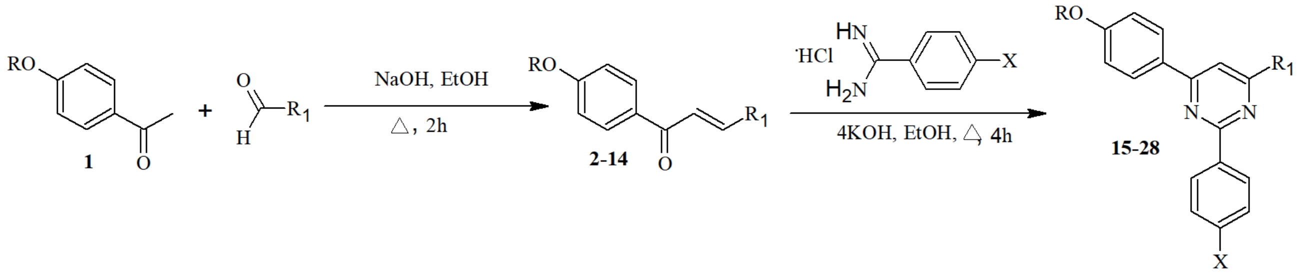
Pyrimidine derivatives have a wide range of pharmacological activity (antiviral, psychotropic, antimicrobial, antitumor, and anabolic), which allows us to consider the core of pyrimidine as a promising scaffold for the development of new biologically active compounds [1-3].

The condensation reaction of 1-(4-alkoxyphenyl)ethanones **1** with aromatic aldehydes in the presence of sodium hydroxide in an aqueous ethanol solution gave (E)-3-aryl-1-(4-alkoxyphenyl)prop-2-en-1-ones (**2-14**). By reacting benzamidine and 4-methylbenzamidine hydrochlorides with substituted prop-2-en-1-ones in ethanol in the presence of KOH, 2,4-diaryl-6-(4-alkoxyphenyl)pyrimidines were synthesized (**15-28**).



R=Et, X=H: R_1=4-Br-Ph (**2, 15**), R_1=4-MeO-Ph (**3, 16**), R_1=4-NMe_2-Ph (**4, 17**), R_1= benzo-[1,3]¬dioxol-5-ylmethyl (**5, 18**); R=Pr, X=H: R_1=4-Br-Ph (**6, 19**), R_1=4-MeO-Ph (**7, 20**), R_1=4-NMe_2-Ph (**8, 21**), R_1= benzo-[1,3]¬dioxol-5-ylmethyl (**9, 22**); R=Bu, X=H: R_1=4-Br-Ph (**10, 23**), R_1=4-MeO-Ph (**11, 24**), R_1=4-NMe_2-Ph (**12, 25**), R_1= benzo-[1,3]¬dioxol-5-ylmethyl (**13, 26**), R_1=4-*iso*-PrO-Ph (**14, 27**), R=Bu, X=CH_3, R_1=benzo-[1,3]¬dioxol-5-ylmethyl (**28**).

The structure of the synthesized compounds was established on the basis of IR, ^{1}H NMR, and ^{13}C NMR spectrometry data. The luminescent and anti-MAO properties of the synthesized compounds will be studied.

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IONIC LIQUIDS GLASSES STUDIED VIA EPR

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Ionic liquids (ILs) show a variety of unusual and intriguing properties on a molecular level. In our group we discovered unprecedented suppression of molecular mobility near the glass transition (T_g), which is assigned to unusual structural rearrangements of glassy ILs on the nanometer scale [1-3]. In particular, the coexistence of two types of IL environments was observed, one of which progressively suppresses the molecular mobility upon temperature increase between (T_g-60 K) and T_g. This is a highly uncommon behavior, since most of known substances, including the same ILs in bulk, become less dense upon temperature increase, so it was termed "structural anomaly". We used several independent electron paramagnetic resonance (EPR) approaches (continuous wave, pulse and time-resolved) that helpfully complement each other [4]. Recently, we implemented the developed complex EPR approach to investigate the influence of water content [5], IL cation alkyl chain length [6] and metal-organic frameworks embedding [7] on the structural anomaly in IL glasses and disclose its origins.

This work was supported by the Russian Science Foundation (No. 19-13-00071).

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LANTHANIDE(III) COMPLEXES WITH ISOTHIAZOLE DERIVATIVES: SYNTHESIS, STRUCTURE, AND PHOTOLUMINESCENT PROPERTIES

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Rare-earth element coordination compounds have unique photoluminescent properties: intense emission, high quantum yields, and long lifetimes of excited states. Therefore, the synthesis of new lanthanide(III) complexes remains a widespread field in chemistry.

The present work is devoted to new lanthanides(III) coordination compounds with isothiazole derivatives, namely 4,5-dichloroisothiazole-3-carboxylic acid (HL^1) and 3,4-dichloroisothiazole-5-carboxylic acid (HL^2). The obtained lanthanides(III) complexes with isothiazole derivatives have been detailed characterized by physicochemical methods of analysis (IR-spectroscopy, elemental, single-crystal and powder X-ray diffraction analysis). According to single-crystal X-ray diffraction analysis, acetate-ions serve as bridge leading to the formation of polymeric chains (Fig. 1). The ligand HL^1 also exhibits bidentate-bridging coordination *via* two oxygen atoms of the carboxyl group, as well as chelating coordination by oxygen atom of the carboxyl group and nitrogen one of isothiazole ring. In contrast to HL^1, the ligand HL^2 demonstrates both chelating and monodentate coordination by oxygen atom of the carboxyl group.

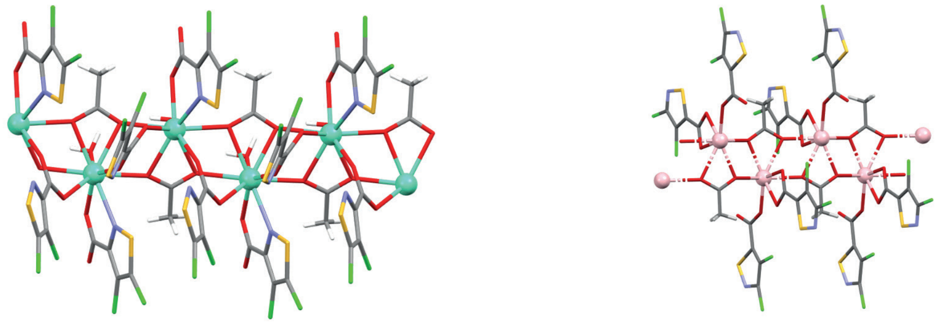

Figure 1. The structure of $[Eu(H_2O)L^1_2(OAc)]_n$ (on the left) and $[EuL^2_2(OAc)]_n$ (on the right).

The photoluminescent properties of polycrystalline samples have been studied at room temperature, also the quantum yields and lifetimes of the excited state have been measured. There are narrow characteristic bands of lanthanide ions in the emission spectra of all complexes, indicating energy transfer from a ligand excited triplet state to the central atom (Fig. 2).

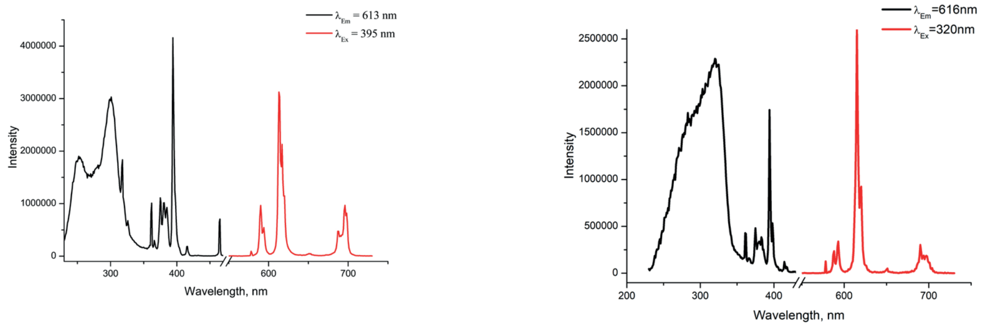

Figure 2. Excitation and emission spectra of $[EuL^1_2(OAc)(H_2O)]_n$ (on the left) and $[EuL^2_2(OAc)]_n$ (on the right).

The reported research has been funded by Russian Science Foundation and the government of the Novosibirsk region of the Russian Federation, project № 23-23-10028.

REGULATION OF THE PI3K/Akt PATHWAY IN THE FIGHT AGAINST CANCER AS AN ALTERNATIVE APPROACH

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Lung cancer is one of the most common cancers among men worldwide. Chemotherapeutic agents promise positive effects in anticancer therapy, however, they have many undesirable side outcomes, among them short-term effects, drug resistance, as well as the relapse of the original tumor and formation of new ones. Science is attempting to fill this gap by combining chemotherapeutic agents with plant-derived compounds. The effect of the latter in most NSCLC (non-small cell lung cancers) is not clear, and the mechanisms by which these combinations work are also unknown. This study aims to clarify the anti-cancer combined effect of *Rumex obtusifolius* extract (RO) and 5-FU on A549 non-small lung adenocarcinoma. We consider the TNF-a/PI3K/Akt/COX-2 /NOS/Caspase-3 pathway to reveal metabolic alterations in it in cancer.

The plant materials were harvested from the Tavush region of Armenia. Plants were deposited to the Herbarium of Yerevan State University Voucher specimen serial numbers were given. The plant extract (0.25 mg/ml) and chemotherapeutic drug (40 µM) were performed to assess the influence on A549 cells for 24 h. Quantitative changes in individual components of the above-mentioned pathway were determined by ELISA and colorimetric assay kits in cell culture medium and cell lysates.

The results show a reducing effect of the combination of 5-FU and RO on TNF-a, which was not different from the separate effect of RO. We determine total and phosphorylated PI3K and Akt and observe the modulatory effect of the herb during combination, which decreases both phosphorylated and total amounts of these proteins. As a promoter of inflammatory processes COX-2 being in direct contact with TNF-a, did not respond to the separate effects of 5-FU and RO, however, it decreased by about 70% observed during the combined treatment compared to the control. The activity of NOS was decreased both by combined and separate treatment with the herb extract and 5-FU. Since suppression of the COX2/NOS and PI3K/Akt pathway can trigger apoptosis, we observe the change in Caspase-3 activity likewise. Results show that the combination stimulate Caspase-3 activity by 2,5 times compared to the separate treatment.

Thus, 5-FU and RO promote apoptosis through the regulation of the PI3K/Akt pathway, and such approaches may open a new door in antitumor therapy. Particularly, these hallmarks of cancer can be targeted with the individual active components of the herbs, which could lead to potential therapeutic benefits for cancer patients in the clinical setting.

A NEW APPROACH TO THE REACTION OF THIOUREAS WITH GLYOXAL

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Heterocyclic compounds based on imidazolidine-2-thiones are used in pharmaceutical chemistry. In particular, substituted imidazolidine-2-thiones exhibit various types of biological activity – antifungal, antimicrobial and antioxidant. The presence of hydroxyl and thioamide groups in its structure allows using these compounds as ligands with different types of metals [1].

4,5-dihydroxyimidazolidine-2-thione (DHIT) and its derivatives are obtained by the interaction of the corresponding thioureas and glyoxal, while a racemic mixture of cis- and trans-isomers is formed as the target product, where the predominance of the trans-form is observed. However, the ways of formation of target and by-products are not given in the literature [2]. The reactions of the interaction of benzil with substituted thioureas have been studied, and the reactions of the interaction of diphenylthiourea with glyoxal are also given [3]. Therefore, the aim of this work is to identify the target and by-products of the interaction of thiourea and its N,N'-dimethyl derivative with glyoxal, as well as the proposed mechanism for their formation.

The reaction of thiourea with glyoxal was investigated using HPLC on the consumption of thiourea and the formation of DHIT. It has been established that thiourea is completely consumed, however, but the yield of DHIT is approximately 60%, which indicates on the formation of by-products. Using 1D (^{1}H, ^{13}C) NMR spectroscopy and 2D NMR (HMQC, HSQC) it was found that the by-products in the reaction are a racemic mixture of cis- and trans-4,5-dihydroxyimidazolidin-2-one (1, 2) and 1,3-dihydro-2H-imidazole-2-thione (3).

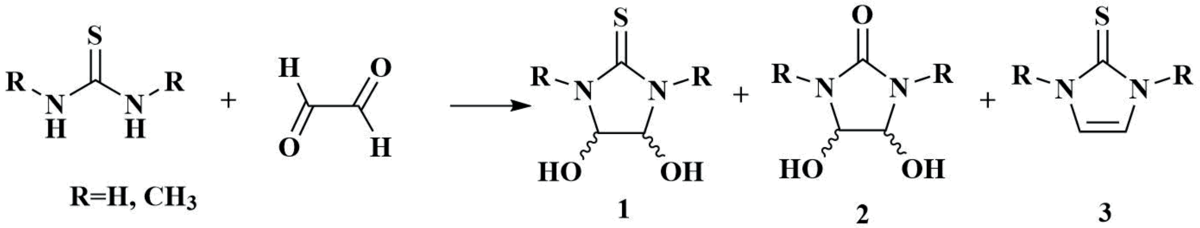

Figure. Scheme reaction between glyoxal and thiourea

While calculating the kinetic parameters of the reaction and comparing the results of the analysis obtained by NMR and HPLC, it was found that compound **3** is obtained by the reaction of the initial thiourea and the formed DHIT. We observed the same results for N,N'-disubstituted thiourea.

It has to be noted that the proposed mechanism of the reaction between thiourea and glyoxal suggests a new strategy for the synthesis of compound **3** from available reagents (the corresponding DHIT and thiourea). At the moment, the literature describes a method for obtaining 1,3-dimethyl-1,3-dihydro-2H-imidazole-2-thione through the sulfonation of a salt of 1,3-dimethylimidazolium iodide in an alkaline medium in methanol [4]. 1,3-dimethyl-1,3-dihydroimidazole-2-thione have shown remarkable effect in detoxification of various organomercurials including methylmercury by producing insoluble HgS [5].

This study was supported by the Tomsk State University Development Programme (Priority2030).

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CRYSTAL STRUCTURES AND THERMAL BEHAVIOR OF POTASSIUM, CALCIUM AND AMMONIUM SORBATES

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Sorbic acid and its potassium and calcium salts are well known food preservatives (E200, E202, E203). They possess antimicrobial and fungistatic properties and in low doses have no impact onto human health.

Since most foods are exposed to heat during manufacturing or cooking, the thermal behavior of additives should be studied comprehensively. Nevertheless, there is poor data concerning the thermal and even structural properties of these substances [1].

In this work, potassium, calcium and ammonium sorbates were synthesized or recrystallized from water. The crystal structures of the three sorbates were determined for the first time by X-ray single crystal diffraction. Potassium and calcium salts were found to be 2D coordination polymers while the ammonium salt showed similar pattern *via* hydrogen bonds. The consideration of their crystal packings proved some common patterns in their structures. In particular, the crystals consist of two distinguished alternating zones – the hydrocarbon chains and the cation-oxygen cores. In the structure of ammonium sorbate, the double bonds are preorganized in a way making the [2+2] photocycloaddition reaction possible. The UV-irradiation of the crystals leads to the formation of cyclobutane-fragments (confirmed by X-ray structure analysis) and to the further amorphization. The other salts do not change upon irradiation by UV light.

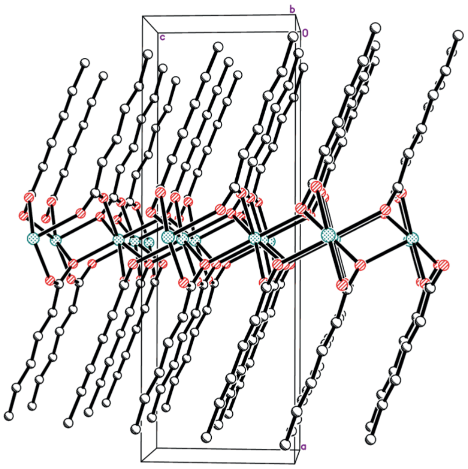

Fig. 1. Crystal packing of calcium sorbate.

The thermal properties of the compounds were studied the temperature range typical for cooking (r. t. – 250°C) or manufacturing. Differential scanning calorimetry combined with thermomicroscopy were used to get a complete picture of the thermal processes. It was found that potassium sorbate undergoes a phase transition at ca. 161°C without loss of crystallinity, whereas calcium sorbate stays unchanged in the investigated temperature range. In contrast, the ammonium sorbate releases a gas (ammonia) and decomposes to sorbic acid when exposed to heat. Together with its photoreactivity and tendency to form cocrystals with sorbic acid it makes ammonium sorbate unsuitable for use in food chemistry.

Thus, this study reveals the structures and thermal behavior of potassium, calcium and ammonium sorbates, offering inspirations for future comprehensive investigations of seemingly simple yet very important and overlooked food ingredients.

This work was supported by Russian Science Foundation (project № 23-23-00208, https://rscf.ru/en/project/23-23-00208/).

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SYNTHESIS OF NEW POLYCONJUGATED SYSTEMS CONTAINING IMINODIHYDROFURAN AND BENZENE RINGS

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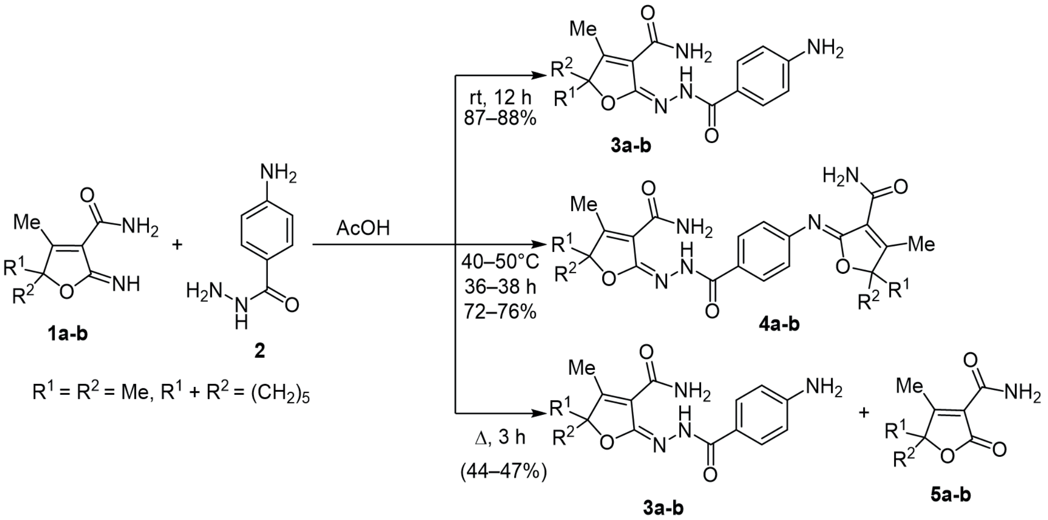
Both natural and synthetic 2-oxo- and 2-imino-2,5-dihydrofuran derivatives exhibit a broad spectrum of biological activities and are used in medicine, agriculture, perfumery, etc. [1–5]. On the other hand, derivatives of 2-oxo- and 2-imino-2,5-dihydrofurans attract much interest as intermediate products for organic synthesis due to their high synthetic potential.

Synthesis of new derivatives of 2-imino-2,5-dihydrofuran has been of continuous interest in the development of efficient and convenient methods for preparation of various 2,5-dihydrofuran derivatives and in their synthetic applications.



Polyconjugated systems containing 2-imino-2,5-dihydrofuran and aromatic rings were synthesized by the reaction of 2-imino-2,5-dihydrofuran-3-carboxamides [6] **1a-b** with 4-aminobenzohydrazide **2** in glacical acid. When the reaction was carried out with an equimolar amount of 4-aminobenzohydrazide **2** in glacical acid at room temperature for 12 h, the corresponding *N*-substituted 2-iminodihydrofurans **3a-b** were obtained in high yields. When half the amount of 4-aminobenzohydrazide **2** was used, the corresponding bisiminodihydrofurans **4a-b** were formed upon heating at 40–50°C for 36–38 h. When the reaction mixture of compound **1a-b** with 0.5 equivalents of 4-aminobenzohydrazide **2** was heated under reflux for 3 h, instead of the expected bisiminodihydrofurans **4a-b**, 2-*N*-substituted iminodihydrofurans **3a-b** and 2-oxo-2,5-dihydrofurans **5a-b** were obtained.

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SYNTHESIS OF POTENTIALLY BIOACTIVE 1,4-DISUBSTITUTED 3-CYANOPYRIDIN-2(1H)-ONES

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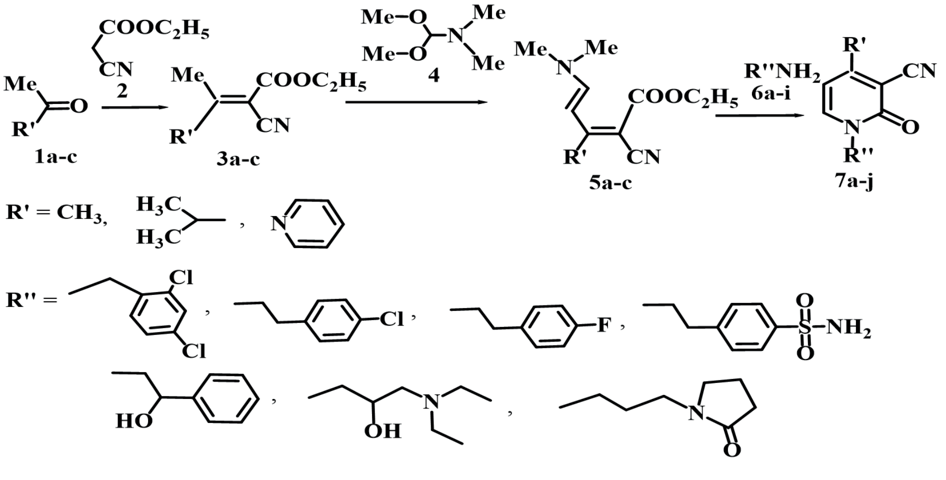
The demand of new effective, selectively acting and low-toxic drugs of natural and synthetic origin is growing every year. Most of the currently used drugs are mono- and polycyclic, especially *N*-containing, heterocyclic compounds.

Compounds containing pyridinone-2 moiety as a precursor have proven to possess several biological properties (Pyridone L-697, 661, Milrinone WIN 47203, Amrinone WIN 40680, Pirfendone PFD) [1-7]. The 3-cyanopyridinone-2 nucleus is also the structural basis of the alkaloid ricinine – the first known alkaloid containing a cyano-group.

New 1,4-disubstituted-3-cyanopyridine-2-ons with predicted substituents were synthesized. The interaction of alkyl and heterocyclic ketones **1a-d** with cyanoacetic ether **2** was carried out in absolute ethanol in the presence of sodium ethylate under reflux for 20-25 hours, which afforded various ylidenecyanoacetic acid ethyl esters **2a-d**. The latest were condensed with dimethylformamide dimethyl acetal **4** in anhydrous xylene under reflux for 3-4 hours. The intermediate dimethylamino derivatives **5a-d** so formed were treated with primary amines **6a-i** in xylene under reflux for 13-15 hours to yield the targeted 1,4-disubstituted-3-cyanopyrinedin-2-ons **7a-j** in good yields.

The proposed method is available and universal, it allows one to obtain a wide range of target products with various substituents at positions N-1 and C-4 by varying the starting ketones (aliphatic and heterocyclic) and amines (aromatic and heterocyclic).



This work was supported by the ANSEF-2022: NS-microbio-2744

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PREPARATION AND TRANSFORMATION REACTIONS OF NEW DERIVATIVES OF 9(10)-THIOXOPYRIDO[3’,2’:4,5] THIENO[3,2-D]PYRIMIDINES

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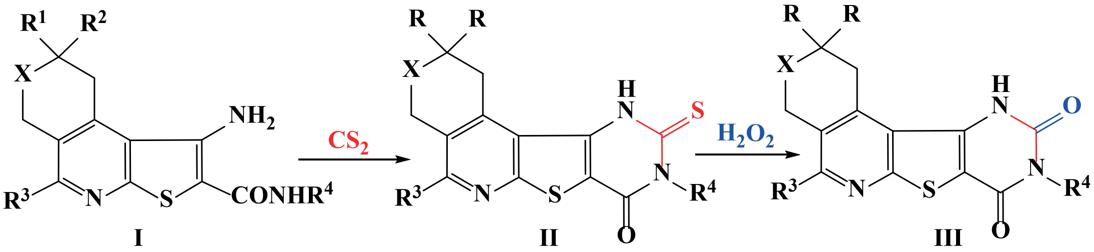
Many synthetic pyrimidine derivatives are successfully used in medicine as depressants, sedatives, anti-inflammatory, antihypertensive agents, and in agriculture as pesticides and fungicides [1]. Thienopyrimidines are also of theoretical interest from the point of view of organic chemistry, since they simultaneously contain π-deficient pyrimidine and π-excessive thiophene rings in the molecule, which makes it possible to obtain various derivatives and study the mutual influence of heterocycles and heteroatoms on the reactivity and biological activity of the system in in general.

To obtain 2,3-substituted derivatives of thieno[3,2-d]pyrimidines, we used 1-amino-2-amidocarbonylpyrano[4,3-d]thieno[2,3-b]pyridines and thieno[2,3-b]isoquinolines (**I**). The presence of NH_2 and CONH groups made it possible to carry out further transformations with treatment with carbon disulfide were obtained N-alkyl-4-oxothieno[3,2-d]pyrimidine-2-thiones (II).



To obtain fused 8,10-dioxo-thieno[3,2-d]pyrimidines, we tried several methods, but the only productive method was the synthesis from the corresponding 10-thio derivatives (II). The reaction proceeds using a concentrated solution of hydrogen peroxide. In the IR spectrum of compound III there are no characteristic absorption bands of the C=S group, and in the region of 1680, 1710 cm^{-1} there are characteristic absorption bands of two amide C=O groups.

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ANTIGLYCEMIC AND ENERGY-REGULATORY EFFECTS OF STEVIA REBAUDIANA BERTONI UNDER CONDITIONS OF IMMOBILIZATION STRESS

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In modern medical practice, herbs and phytopreparations prepared from them are used to prevent and treat various diseases. *Stevia rebaudiana* Bertoni is distinguished by its medicinal properties and composition of physiologically active ingredients, which contain natural antioxidants, including flavonoids and glycosides, thanks to which it can increase the body's resistance to adverse environmental conditions and stress factors [1.3]. With prolonged action of one or more stress factors, the general and specific resistance of the organism decreases and the stage of exhaustion develops. In the metabolism processes of disintegration are intensified. All the signs characteristic of the shock phase of the stress reaction reappear. Immobilization stress is one of the risk factors for the development of pathological processes in the body, which may be the cause of the disruption of adaptation processes. As a stress factor, it causes tension in regulatory mechanisms, reduces the reserve capacity of the body, and inhibits energy processes.

Our study aimed to investigate the hypoglycemic and energy-regulatory role of Stevia under conditions of exposure to prolonged immobilization stress. The research was done with 2 stress models. In the first version, the animals were immobilized in appropriate conditions for 30 days, 5 hours a day. In the second version, stevia grass dry powder was added to the animal's diet at the rate of 0.5g/kg of animal weight.

It has been shown that at the initial stage of immobilization stress, an increase in the amount of glucose in the blood plasma is found up to 34%, after which, along with the prolongation of the stress, pronounced hypoglycemia is recorded, which is apparently due to the intensive use of glucose as an energy source. On the other hand, as the duration of stress increases, the amount of glycogen in the liver and skeletal muscles gradually decreases by 64% and 68%, respectively.

The summary of the research results of the 2nd model showed that the glucose content in the blood starting from the 10th day was within the range of the physiological norm, and a gradual increase in the glycogen content was observed in the liver, which is due to the steviosides contained in the stevia grass leaves [2]. The obtained data give reason to believe that the glycosides contained in the leaves of stevia can be a means of regulating carbohydrate metabolism under stress conditions.

The given data do not exhaust the entire range of possible uses of stevia, but they indicate the prospect of creating new functional food products for various groups of the population, especially for people suffering from metabolic disorders and diabetes mellitus.

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ELECTRONIC AND CRYSTAL PACKING EFFECTS WITHIN BINDING APPROACH: PICOLINIC ACID N-OXIDE AND METHIMAZOLE

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We experimentally obtained and studied the inner-crystal scalar potential fields and the respective vector force fields of kinetic and static nature in picolinic acid N-oxide and methimazole. The “through-bond” and “through-space” electronic effects were defined and distinguished via the vector fields and concurred with the penetration of the electron contributor’s electrostatic and kinetic force field pseudoatoms into the occupier’s chemical atom. The experimental electric and kinetic force fields in the molecular crystals were compared to the theoretical ones for the free molecules and hydrogen-bonded associates, which helped figure out the natural consequences of the crystal packing effect. As expected, the appearance of neighboring attractors in a dense crystal packing requires zero-flux surfaces emerging in the vector fields and the compression of the outer force field pseudoatoms of a molecule. We proposed to consider a zero-flux surface in the kinetic force field to be a turning surface for electrons in the sense that an electron passed through the boundary is immediately affected by the redirected force attributed to another attractor.

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AZA-MICHAEL REACTION AS A PATHWAY THE SYNTHESIS OF EXOCYCLIC AZOLYLTETRAZOLIC SYSTEMS

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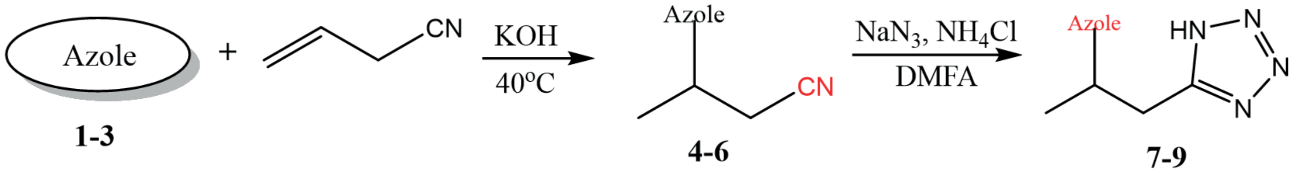
The development of efficient and operationally simple protocols for C-C and C-N[1] bonds formation, aimed at the construction of valuable molecules. The aza-Michael reaction is considered a very efficient and versatile method for synthesize compounds above mentioned requirements. The preparation of derivatives of pyrazole, 1,2,4 triazole and tetrazole via aza-Michael reaction are considered biological active compounds[2,3] and can be applied in the medicine[4]**.**

The preparation of nitriles **(4-6)** in the presence of catalytic amount of KOH water/acetone system via aza-Michael reaction have been implemented[5] **(Scheme 1)**. The synthesis exocyclic azolyltetrazolic systems **(7-9)** based on nitriles **(4-6)** have been completed[6] **(Scheme 1)**. The final products structure were confirmed by IR, NMR ^{1}H, ^{13}C data.

Scheme 1



Azole= Pyr, Im, Try

The work supported by “PhosAgro/UNESCO/IUPAC 058 project research grant in green chemistry for young scientists”.

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SYNTHESIS OF NORBORNENYLPIPERAZINE COMPOUNDS AND IN SILICO STUDY OF THEIR PROPERTIES

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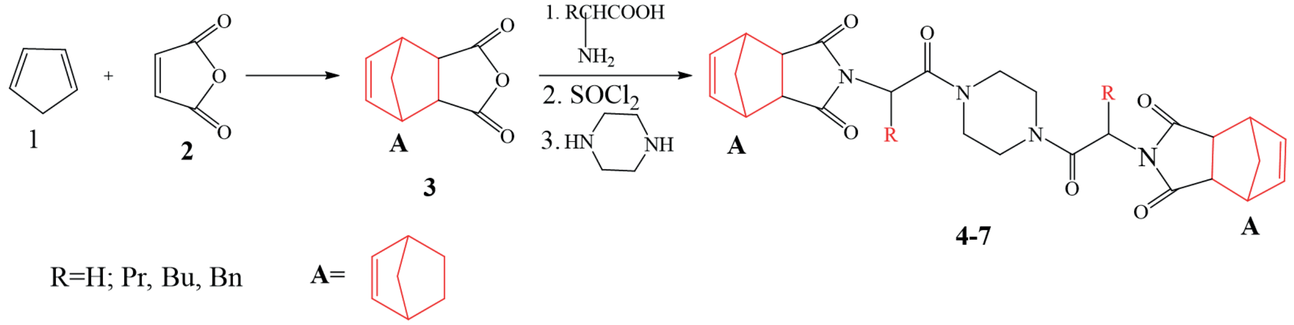
Norbornenyl compounds can most of the structures displayed by natural products and therefore have a good chance of interacting with biological targets, because this is what natural products are for, biological activities have already been demonstrated for some compounds, [1] by application of a multidisciplinary approach combining synthetic chemistry, molecular docking and NMR screening [2].

Due to the biological properties of piperazine [3], first time we have been implemented the synthesis of piperazine derivatives containing the norbornenyl fragment **(A) (scheme 1).**

Scheme 1



The prepared products **(4-7)** have been obtained known pathway providing 50-80% yields. The structures of the synthesized products were confirmed by IR, 1H, 13C MMR data, and possible biological targets were determined using the MolScreen virtual ligand screening method of the ICM-PRO 3.9.3 software package [4]. The virtual ligand screening was performed against 1200 biological targets, from which theoretically the best targets were selected based on the analysis of the screening results (R=H Molpkd=7.308672, R=Bu Molpkd=8.121005).

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SYNTHESIS OF NORBORNENYLPIPERAZINE COMPOUNDS AND IN SILICO STUDY OF THEIR PROPERTIES

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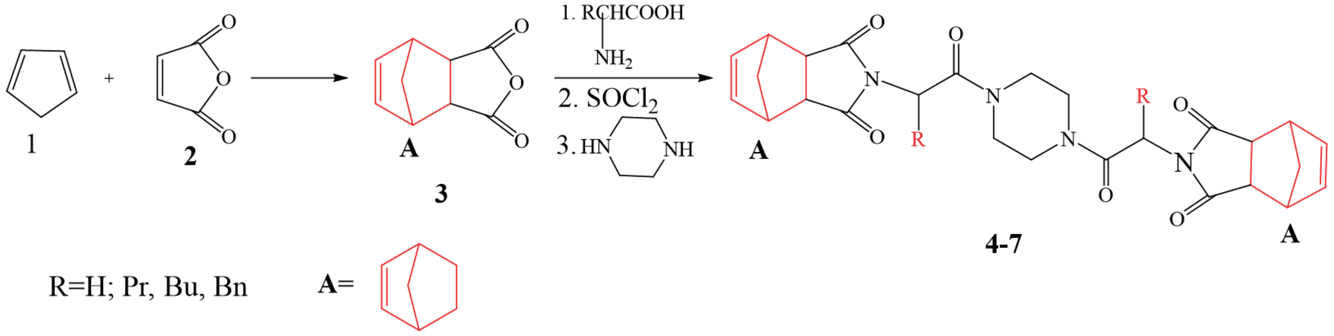

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Ni-PCP AND Ni-PCN CATALYSTS FOR DEOXYGENATIVE HYDROBORATION AND TRANSFER HYDROGENATION REACTIONS

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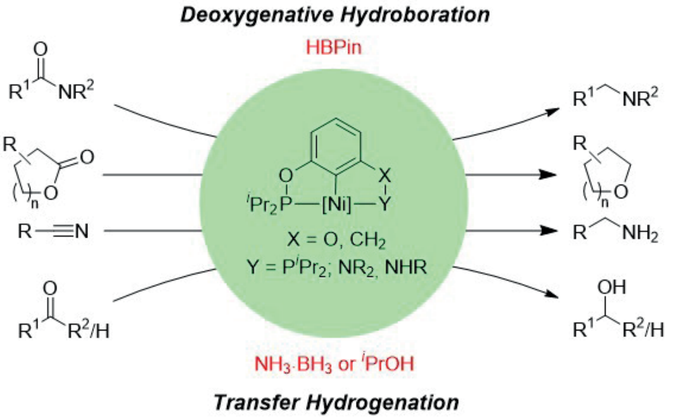
The reduction of unsaturated carbon-heteroatom bonds (C=O, C=N, and C≡N) remains a fundamental approach to producing synthetically important saturated functionalities in organic chemistry in both laboratory and industrial settings [1]. Although conventional stoichiometric metal hydride reagents are known to mediate such transformations, they typically generate large amounts of metallic salt by-products and suffer from a lack of control, selectivity, and functional group tolerance. In contrast, catalytic reductions present more appealing, selective, and atom-economical alternatives. Despite direct hydrogenations with compressed hydrogen gas are considered the most atom-economical transformations, the reactions typically require rather harsh conditions (high temperatures and pressures) [2]. This causes safety and selectivity concerns and requires the use of rather expensive high-pressure reactors. Compared to direct hydrogenations, catalytic transfer hydrogenation and hydroelementation reactions generally proceed under relatively mild conditions, allowing for operational simplicity, reduced cost, enhanced safety, and improved selectivity of transformations. The conventional catalysts developed for such reactions are mostly based on precious metals (Ru, Rh, Ir, etc.), which are limited in supply and expensive [3,4]. Therefore, during the past decades, an important venue of research in this area has been the design of more economical and efficient catalytic systems employing abundant and generally less toxic 1st row transition metals. Despite numerous reports on the use of such systems in the reduction of aldehydes and ketones being disclosed [1,3,4], examples of applications of the 1st row transition metal catalysts in the reduction of more challenging substrates (amides, esters, nitriles, etc.) are still scarce [5]. Herein we report the preparation of a series of phosphinite PCN and PCP pincer complexes of Ni(II) and the evaluation of their catalytic activity in deoxygenative hydroboration of amides and lactones with HBPin and transfer hydrogenation of carbonyl compounds and nitriles using 2-propanol and ammonia borane as hydrogen donors. The developed systems proved highly selective and operate under mild reaction conditions, representing rare examples of nickel catalysts for the above transformations.



This work was supported by the Ministry of Science and Higher Education of the Republic of Kazakhstan (project No. AP14870723).

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SYNTHESIS OF 2-METHYL-1,5-DINITRO-3-(TRIFLUOROMETHYL)BENZENE AND ITS TRANSFORMATION INTO 6-AMINO-4-(TRIFLUOROMETHYL)-*1H*-INDOL

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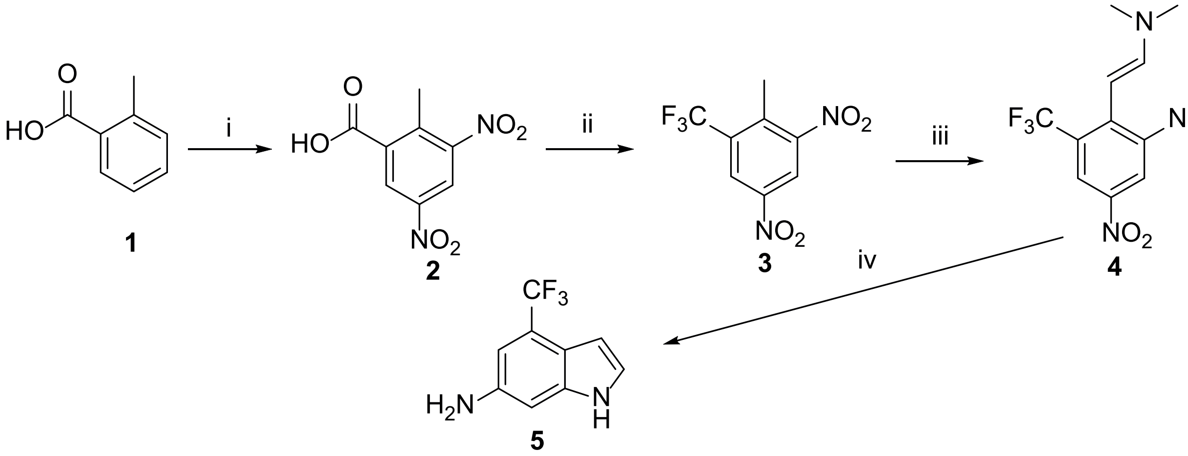
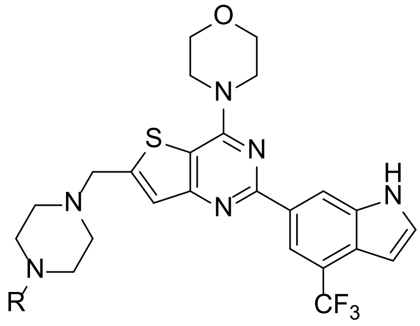
A facile two-step synthesis of 2-methyl-1,5-dinitro-3-(trifluoromethyl)benzene is described. The first step is the nitration of *otho*-methylbenzoic acids to furnish the corresponding dinitroacid. The dinitroacid then react with sulfur tetrafluoride to provide the corresponding trifluoromethylated product. The latter are easily transformed into 6-amino-4-(trifluoromethyl)-*1H*-indol by applying the Batcho–Leimgruber synthetic protocol (**Scheme 1**)



Scheme 1. Reagents and conditions: (*i*) HNO_3 (100%) – H_2SO_4 (conc.) (50 :50), 10 – 15 °C; (*ii*) SF_4, 90 °C;(*iii*) DMF DMA, 80 °C, toluene; (*iv*) Pd/C (10%), EtOAc, rt.

Indol **5** was used as a coupling reagent for the synthesis of pyrimidine derivatives as Pi3k inhibitors (**Scheme 2**).



R = different substituents

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MECHANOSYNTHESIS OF PROBES FOR THE DETECTION OF FLUORINE AND CYANIDE ANIONS

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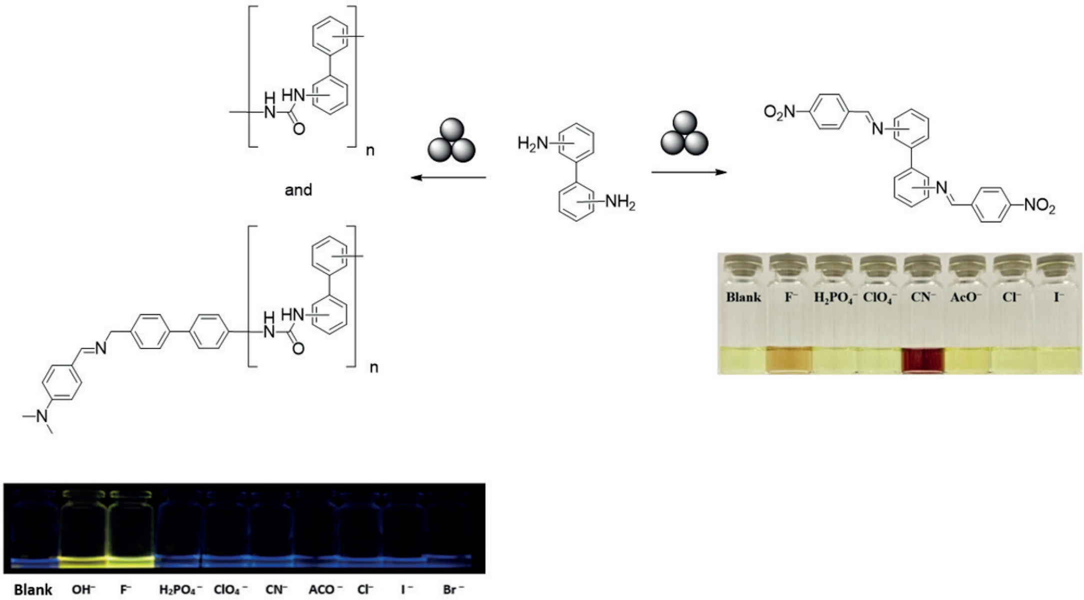
Mechanochemistry is a fast-growing area in chemistry. It possesses undeniable advantages like solvent-free approach, reduced reaction time, mild reaction conditions accompanied by high yields of the products. Numerous reviews and researches are devoted to mechanosynthesis.

We applied mechanosynthesis method to obtain two types of molecules - diaminobiphenyls-based Schiff's bases and polyureas with high yields (up to 95% for both interactions). Reaction conditions included solvent-free ball-milling at room temperature for 4 hours.

Synthesized diaminobiphenyls-based Schiff's bases demonstrated naked-eye visible response towards CN$^-$ ion, while polyureas demonstrated luminescence responses towards F$^-$ and OH$^-$ ions.



The research was financially supported by the Council for Grants of the President of the Russian Federation, Grant # NSh-1223.2022.1.3 and Ministry of Science and Higher Education of the Russian Federation, Reference # 075-15-2022-1118

SILICA-BASED AEROGELS WITH TUNABLE PROPERTIES: THE HIGHLY EFFICIENT AMPHOTERIC F-CONTAINING CATALYSTS FOR AEROGELS PREPARATION AND LOOK INSIDE THEIR STRUCTURE

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

There are several successive stages that are carried out when obtaining SA (Fig.1): (1) sol-gel synthesis, (2) aging, (3) workup, and (4) drying of gel.

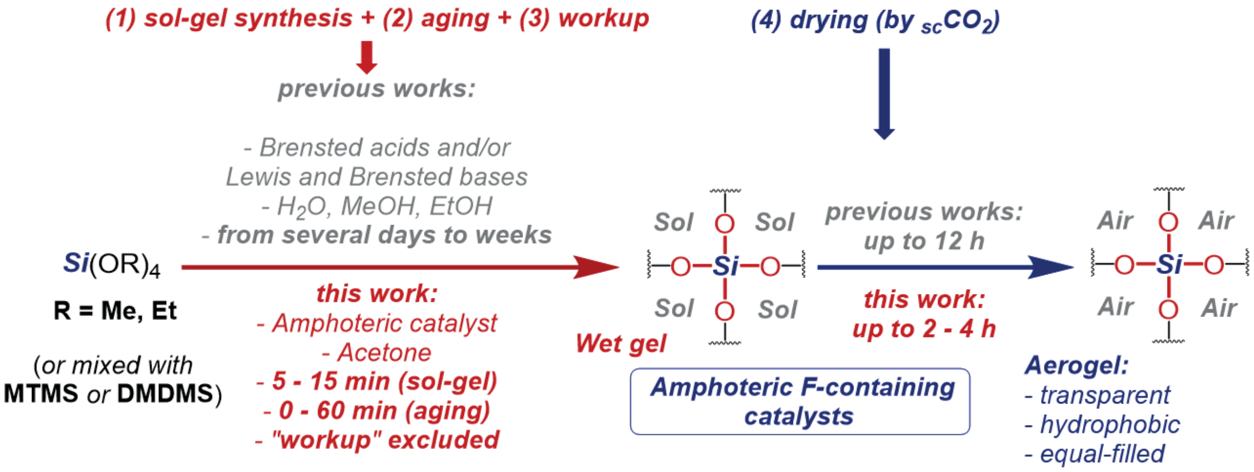

Figure 1. Silica-based aerogels production

This work presents a solution to one of the most fundamentally and practically important challenges in the production of SA, time consumption and expensiveness of these processes, with the main focus on the sol-gel process.[1] We suggested a highly efficient catalyzed by amphoteric Fcontaining compounds method for the production of aerogels, which allows one to shorten the stage of the formation of a (wet) gel to 5 min, the stage of gel aging to 0, while the stage of gel workup is not required; the duration of these stages, according to the literature, ranges from days to weeks. The process is performed using commercially available, simple, and inexpensive reagents and under mild reaction conditions: amphoteric F-containing compounds as the catalyst, acetone as the solvent, room temperature, and at atmospheric pressure. This approach allows one to quickly obtain both classic opaque and transparent SA from $Si(OMe)_4$ or $Si(OEt)_4$ as well as transparent superhydrophobic ones from their mixtures with $MeSi(OMe)_3$ or $Me_2Si(OMe)_2$. Also, the effect of the method for producing SA on their (supra)molecular structure and morphology was thoroughly studied by a set of physicochemical methods of analysis mostly with using NMR experiments. These findings allow to tune the properties SA depending on the need by choosing the right technique synthesis.

Acknowledgements. This work was supported by a grant of the Russian Science Foundation (RSF grant 19-73-10172-П)

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SYNTHESIS AND STRUCTURE OF NEW COMPLEXES OF METHYL AROYLPYRUVATES, 1,10-PHENANTHROLINE AND EUROPIUM(III)

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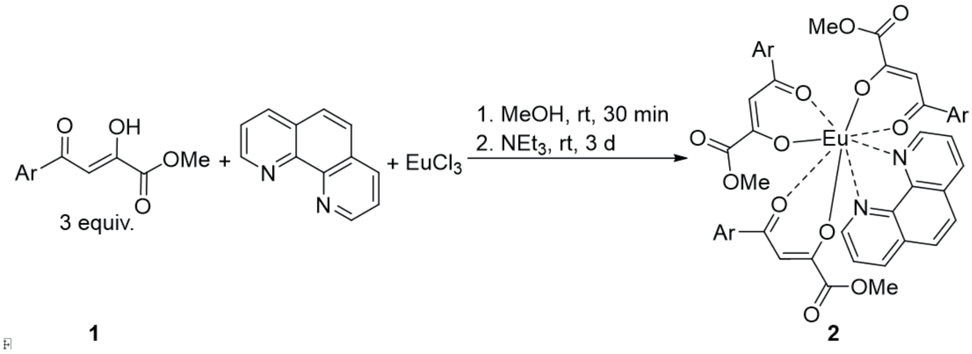
Derivatives of aroylpyruvates are valuable building blocks in organic chemistry, precursors for drug discovery, and interesting objects for creating new functional materials [1-3]. Moreover, aroylpyruvates **1** bear a β-diketone moiety, which is well known as a sensitizer to be utilized for the development of luminescent lanthanide complexes [4].

This work presents data on the synthesis (Scheme 1), structure (Figure 1) and spectral properties of new complexes **2** of methyl aroylpyruvates **1** (L), 1,10-phenanthroline (phen) and europium(III) – [Eu(L)$_3$(phen)] 2.



Scheme 1. Synthesis of complexes **2** of methyl aroylpyruvates **1**, 1,10-phenanthroline and europium(III).

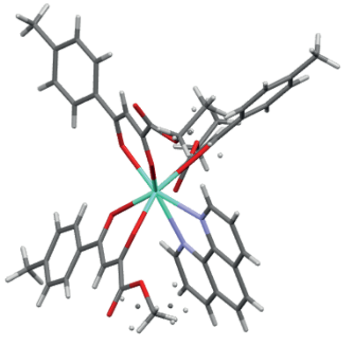


Figure 1. Structure of compounds **2** according to single crystal XRD.

The structure and composition of the studied compounds were confirmed by modern physicochemical methods: ^{1}H and ^{13}C NMR, IR spectroscopy, elemental analysis, TLC.

The resulting complexes **2** are pale yellow powdery substances with a good solubility in non-polar organic solvents (chloroform, DCM, 1,2-dichloroethane).

Compounds **2** have stable fluorescence in the solid state (Figure 2) when irradiated with a UV lamp of λ = 365 nm (intense stable radiation is observed in the red region (λ = 630-760 nm)), and when irradiated with a UV lamp of λ = 254 nm (weak stable radiation is observed in the yellow region (λ = 550-590 nm)).

Currently, complexes **2** are under investigations at Laboratory of Cellular Immunology and Nanobiotechnology of Institute of Ecology and Genetics of Microorganisms of the Ural Branch of the Russian Academy of Sciences (IEGM UB RAS) (Russia, Perm, www.lei-lab.com) to develop new protein nano- and microparticles based diagnostics tools for immunoassays.

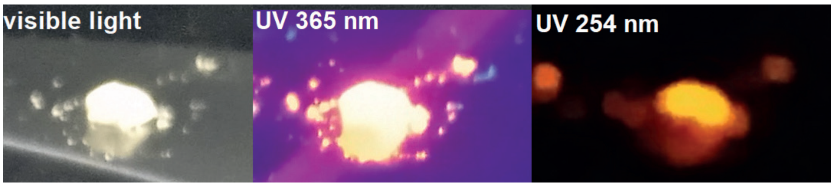


Figure 2. Solid state fluorescence of compounds **2**.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project no. FSNF-2023-0004) and the Scholarship of the President of the Russian Federation for young scientists and graduate students (project no. SP-838.2022.4).

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METAL COMPLEXES WITH N_4-ACENAPHTHENE-BASED LIGAND: STRUCTURE, REDOX PROPERTIES AND SMALL MOLECULES ACTIVATION

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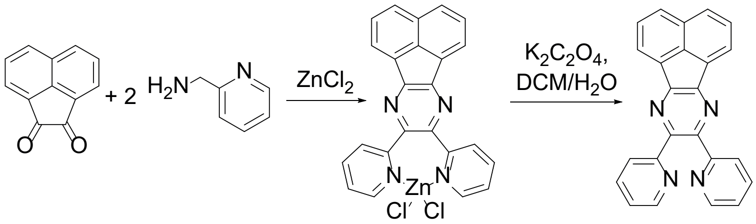
Redox-active diimine ligands in combination with redox-active transition metals, are still top in coordination chemistry, and widely used in many areas of chemistry due to their unique electronic structure, such as ability of redox-active to accept/donate electrons while remaining bonded to the metal ion. Taken together with a transition metal that can also change its oxidation degree, this redox activity provides complexes having impressive electronic structures and properties. Their utilization in small molecule activation reactions and energy storage devices contributes to protecting our planet against the greenhouse effect.

In this study we demonstrate coordination diversity of the new N4-acenaphthene based ligand (Scheme 1) toward nickel, manganese and cobalt ions. The polydentate ability of the ligand makes it possible to obtain mono-, dinuclear, and polymeric metal complexes (Figure 1). We studied redox properties of complexes by different electrochemical techniques and found their electrocatalytic activity for hydrogen evolution and carbon dioxide reduction reactions. The dependence of catalytic activity from metal ion, coordination type and catalyst structure will be discussed.



Scheme 1 The synthetic pathway to the new N4-acenaphthene based ligand

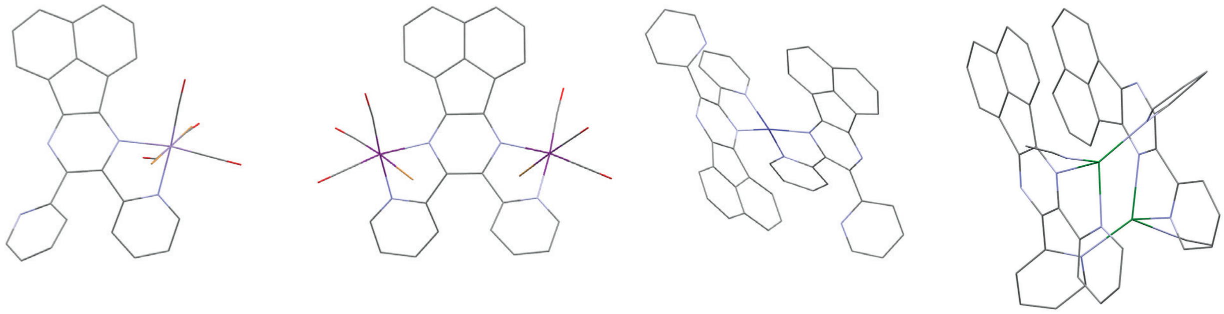


Figure 1 Metal complexes with polydentate N_4-acenaphthene based ligand (from left to right: $LMn(I)Br(CO)_3$, $L(Mn(I)Br(CO)_3)_2$, $L_2Co(0)$, $L_2(Ni(0))_2$)

The work was supported by the Russian Science Foundation, project № 21-73-10186.

SiC BASED COMPOSITE WHISKERS PREPARATION BY COMBINING SOLUTION COMBUSTION SYNTHESIS AND SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS

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Silicon carbide whiskers and fiber-like structures are of keen interest because of their useful mechanical properties at high temperatures, as well as their reinforcing ability in metal and ceramic matrix composites. Whisker reinforcements are intensively used to enhance the fracture toughness and the flexural strength of the composite at high temperatures [1]. Different studies already disclosed the mechanism of whisker formation from various precursors. Moreover, recent works on ceramics and ceramic based composites [2] have demonstrated the significance of sol-gel and solution combustion processes for the preparation of high reactivity precursors aimed at decreasing the synthesis temperature and tailoring product morphology. SCS has proved to be an effective way for the synthesis of nanopowders and is adaptable to producing whiskers/rods/fibers. This work delivers a novel approach of formation of submicron-size silicon carbide powder and SiC-Al_2O_3 composite powder augmented with whiskers by combined solution combustion synthesis with the subsequent programmed heating (HSTS) of SCS products generates, using silica hydrogel and organic reducer (alanine) as starting materials. To tailor the morphology of silicon carbide and obtain SiC-Al_2O_3 composite whiskers, the homogeneous solution of the precursors (silicon dioxide gel and alanine (Ala)) was impregnated into a necessary amount of alumina fibers to promote whisker or fiber formation in silicon carbide structure. But the interaction in the initial mixture proceeds in self-sustaining mode only in the presence of ammonium nitrate. SCS proceeds can be presented according to the following scheme:

$$SiO_{2gel}\cdot nH_2O+\varphi_1C_3H_7NO_2+\ \varphi_2NH_4NO_3\rightarrow SiO_2+C+CO/CO_2+H_2O+N_2$$

In the second stage, SCS product was heated with high heating rate given path (HSTS-3 setup). According to the results obtained, starting from a temperature of 1440°C, an endothermic interaction was observed, corresponding to the interaction of SiO_2 and C, leading to the formation of SiC (fig. 1b). As a result, depending on the precursors (SiO_2/C or SiO_2/C/Al_2O_3), the SiC is characterized by very different morphologies. The silicon carbide obtained from the SiO_2/C SCS product (fig. 1a) is a fine-grained powder (100 nm), and only in some areas the formation of whisker-like structures was observed (fig.1c).

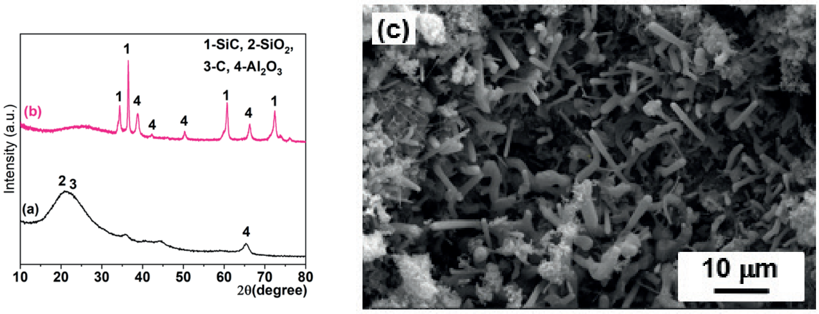

Fig. 1. (a) XRD patterns of the SCS product and (b) the quenched samples after HSTS processing, a-T=1300° C, V_h=300 ° C/min and SEM/EDS analysis of SiC-Al_2O_3 (c)

According to the resultes, it was shown that alumina fibers initiate and promote SiC whiskers growth. Highly porous composite of 40SiC-60Al_2O_3 composition was produced.

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THE FIRST DIRECT EVIDENCE FOR THE EXISTENCE OF ZWITTERIONIC PABA MOLECULES: CRYSTAL STRUCTURE OF $C_7H_7N_1O_2$•1.5(H_2O_2) PEROXOSOLVATE

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para-Aminobenzoic acid (PABA) is an intermediate in the biosynthesis of various significant natural compounds. In water solutions, PABA exhibits pH-dependent equilibria between different forms (Fig. 1).[1] On the base of spectroscopic measurements, it was considered that among two neutral (non-ionic and zwitterionic) species, non-ionic dominates in aqueous media (pK_{NZ} ~ 10).[1,2] This is due to energetic preference of non-ionic form resulting from strong π-conjugation between *para*-arranged π-acceptor $–CO_2^-$ group and π-donor amino substituent, unrealizable in zwitterionic molecule. According to CSD, in solid phases only non-ionic PABA molecules were observed (4 polymorphs and 150 cocrystals). Herein, we report the first direct evidence for the existence of zwitterionic PABA in the structure of its peroxosolvate $C_7H_7N_1O_2$•1.5(H_2O_2) (1).

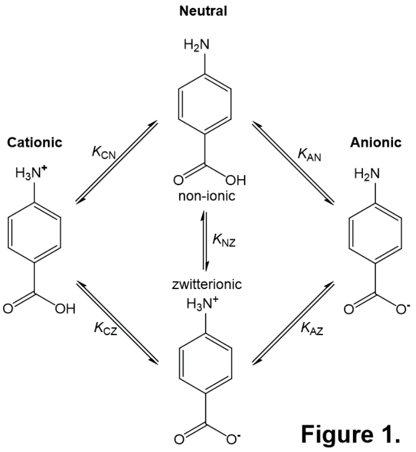
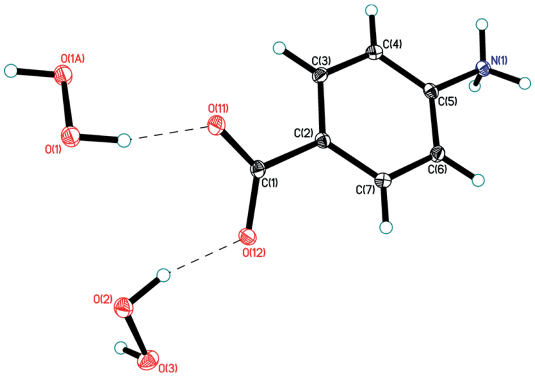


Figure 1.



The structure **1** comprises zwitterionic PABA molecule (all H atoms found from difference Fourier maps and refined isotropically) and two independent hydrogen peroxide (HP) solvents. One of them lies on an inversion center, another occupies general position with HOOH torsion angle equal to -106.4(16)° (Fig. 2). Both O–O distances demonstrate ordinary values (1.4826(16) and 1.4752(11) Å) as for other accurately determined peroxosolvate structures. All active H atoms (peroxo and amino) are involved in strong quasilinear hydrogen bonds. HP molecules form three or four donor/acceptor hydrogen bonds (Fig. 3).

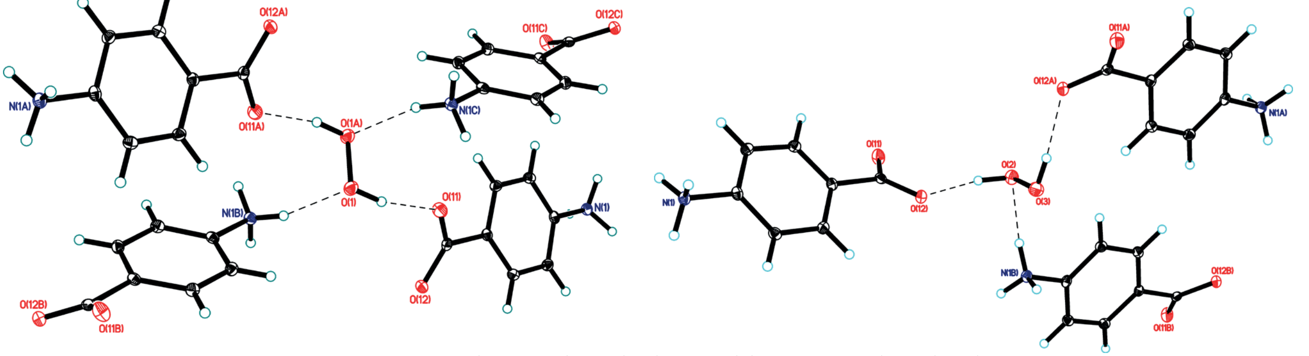


Figure 3. Hydrogen bonds formed by HP molecules in **1.**

Presumably, zwitterionic structure of **1** resulted from increased strength of charge-assisted HOOH…^-O_2C– and NH+…O_2H_2 hydrogen bonds versus $–CO_2H$…O(HO)C– and NH… O(HO)C–.[3]

Authors thank Russian Science Foundation for financial support (grant 22-23-01101).

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METAL PHTHALOCYANINES WITH NON-PLANAR STRUCTURE: EFFECT OF THE TYPE AND POSITION OF FLUORINE AND CHLORINE SUBSTITUENTS ON THE STRUCTURE AND PROPERTIES

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Metal phthalocyanines (MPc) relate to one of the most important classes of molecules that intensively studied in the field of surface science and molecular electronics [1]. The introduction of various types of central metals and the change in the type, position and number of substituents in the macrorings make it possible to widely vary their chemical and physical properties [2].

Tetrahalogen-substituted metal phthalocyanines ($MPcHal_4$) are promising materials for creating transistor structures and active layers of sensor devices [3]. Most MPc molecules have a planar structure but if the central metal atom is large or can coordinate substituents in the axial position (M = VO, Pb, Sn, Al, etc.), then molecule takes the form of a shuttlecock with the metal atom going out of the phthalocyanine macrocycle. The properties of such complexes have been studied to a much lesser extent in comparison with phthalocyanines with a planar structure.

In this work, a comparative study of the crystal structure and structural features of thin films of metal phthalocyanine $MPcHal_4$ (M = Sn, Pb, Al) with halogen substituents (Hal = F, Cl) in the peripheral ($MPcHal_4$-p) and non-peripheral ($MPcHal_4$-np) positions of the phthalocyanine ring was carried out. The influence of the position and type of the substituent as well as the central ion on the structural features of the phthalocyanine complexes and their films, as well as on their electrophysical properties was shown. For example, fluorosubstituted tin phthalocyanine $SnPcF_4$-p (triclinic) and $SnPcF_4$-p (monoclinic) have a "shuttlecock" structure but different types of molecular packing (fig.1). At the same time, in chlorosubstituted analogues synthesized by a similar method tin has valence IV, and tin phthalocyanines with Cl-substituents in the axial positions ($SnCl_2PcCl_4$) are formed. In the case of aluminum phthalocyanines, complexes of the $AlClPcHal_4$ type are formed.

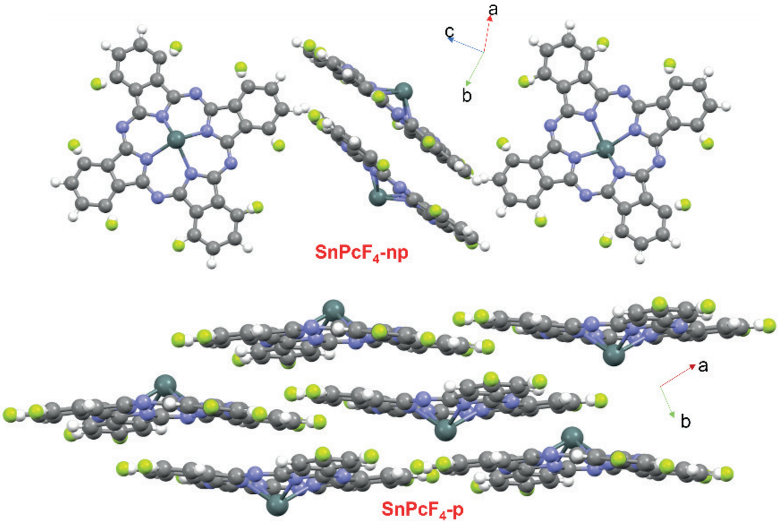

Figure 1. Molecular packing of tatrafluorosubstituted tin phthalocyanines.

Acknowledgements. *This work was supported by the Russian Science Foundation (project No 22-73-00145).*

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FAST EVALUATION OF THE SAFETY OF THE HECK AND SONOGASHIRA REACTIONS USING BIO-STRIPS

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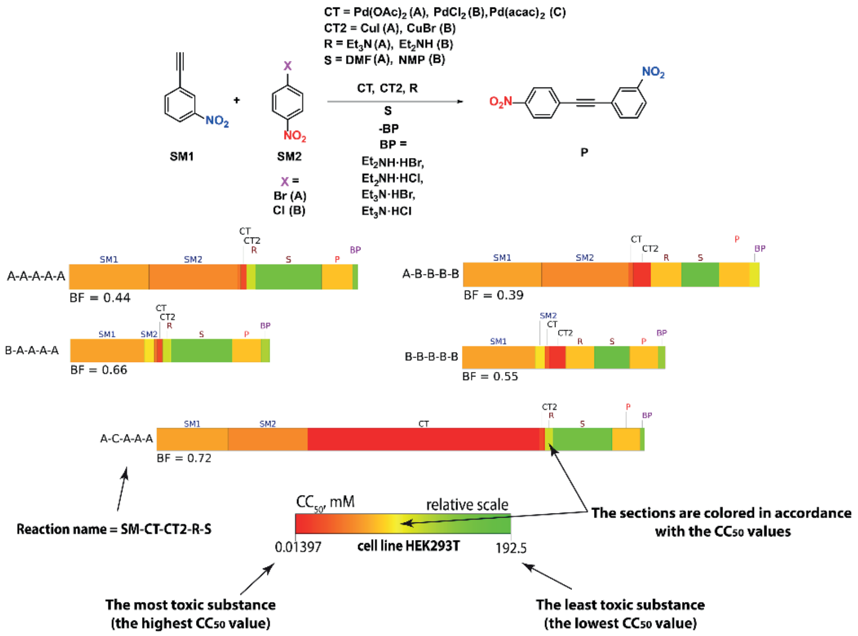
The discovery of the Heck and Sonogashira reactions has proven to be a crucial advancement in the catalytic formation of carbon-carbon bonds. Currently, these reactions find broad applications in various branches of organic synthesis. Thus, their impact on the environment can be significant. However, until recently, there has been no approach for carrying out prompt preliminary assessment of possible impact of such chemical processes on living organisms with the purpose of subsequent optimization of these processes from the viewpoint of toxicity of their components. We have proposed a novel strategy for fast assessment of potential health risks associated with chemical reactions by means of bio-Profiles and bio-Strips [1, 2]. In this study, we present preliminary evaluation of the safety of the Heck and Sonogashira reactions by using bio-Strips and the accompanying metrics calculated on the basis of cytotoxicity of all the reagents, solvents and products taking part or forming during these processes. In whole, over 150 pathways of the reactions are considered.



Reaction name = SM-CT-CT2-R-S

The sections are colored in accordance with the CC_{50} values

The most toxic substance (the highest CC_{50} value)

The least toxic substance (the lowest CC_{50} value)

Figure 1. bio-Strips: prompt preliminary assessment of the safety of chemical reactions. Adapted with modifications from [2].

This work was supported by the Russian Science Foundation (RSF Grant 21-13-00049).

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SMALL ORGANIC MOLECULES AS FUNCTIONAL MATERIALS IN THE DESIGNS OF ELECTROCHEMICAL PORTABLE MINIATURE DEVICES FOR bio-, eco- AND PHARMACEUTICAL MONITORING

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Nowadays, one of the leading directions in analytical chemistry is the development of portable miniature devices, in particular, electrochemical ones, for personalized medical diagnostics, monitoring of the human environment, and pharmaceutical analysis. Progress in this area opens up a revolutionary era in the development of point-of-care diagnostics paving the way “from the test tube to the smartphone.”

In this regard, it is especially important to use small organic molecules with unique properties. It, on the one hand, can be/are original drugs, and on the other hand, act as key components of the bio/chemical receptor layer: electrocatalysts, linkers for immobilization of bio/chemical receptors, signal-forming labels and mediators of electron transfer.

In the Scientific, Educational and Innovation Center of Chemical and Pharmaceutical Technologies of the Ural Federal University, we are conducting research in the field of studying the mechanisms of the transformation of azolo-azines and their derivatives - registered and at various stages of testing drugs, for example, Triazavirin® (sodium salt of 2-methylthio-6-nitro-1,2 ,4-triazolo[5,1-c]-1,2,4-triazin-7-one, dihydrate). The similarity of the physicochemical foundations of electrochemical and biological processes suggests parallels in the mechanisms of many redox reactions occurring both at the electrode and in the human body. Possible pathways of electroconversions of Triazavirin® and argeninium salt of 5-methyl-6-nitro-1,2,4-triazolo[1,5-α] pyrimidin-7-one, monohydrate (Triazide) have been studied, new methods for the quantitative determination of these drugs have been developed.

In addition, the studied nitrogenous heterocycles were used as agents of biomolecular recognition in the determination of some RNA viruses. The receptor properties of the molecules in this case were due to their multitarget activity, including in relation to viral proteins. Such an affinity interaction, together with a pronounced electrochemical activity, was the basis for the development of new test systems for the rapid screening of influenza and measles viruses in model suspensions and vaccine samples.

Original carbazole derivatives, such as 3,6-bis[(trimethylsilyl)ethynyl]-9H-carbazole, pentafluorophenylcarbazoles and diazinecarbazoles capable of forming supramolecular assemblies with nitrobenzene and chloramphenicol, have been studied and successfully applied as non-biological receptors in designs of portable electrochemical chemosensory devices for their quantitative determination in water bodies and honey samples.

The electrocatalytic properties of new derivatives of bipyridine and thiophene, copper(II) complexes with modified bipyridines in the bulk of dimethyl sulfoxide and on the surface of magnetic nanoparticles, as well as organometallic frameworks based on copper(II) with respect to cholesterol, glucose, urea, and creatinine have been studied. The effect of the ligand type and catalyst form on the sensitivity and selectivity of the analysis is shown. Laboratory prototypes of microfluidic portable systems have been developed for the quantitative determination of the given model substrates.

The research was supported by Russian Scientific Fund (project № 20-13-00142).

NEW CATIONIC SPIROPYRANS WITH PHOTOSWITCHABLE NIR FLUORESCENCE

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Spiropyrans (SPs) containing conjugated vinyl-3H-indolium fragment in 2H-chromene moiety are of special interest [1]. The structure of their merocyanine form (Mc) is similar to heptamethyne cyanine dyes (Cy) widely used as fluorescent markers in biology and medicine [2]. Introduction of electron-donating end-groups to Cy's usually results to bathochromic shifts of absorption and fluorescent maxima [3], which are useful for creating NIR fluorescent markers and probes. In contrast to Cy, such compounds are prone to reversible transformations between Mc and spirocyclic (Sp) forms under light exposure. This feature allows to change molecule's geometry, dipole moment and control fluorescence. Thus, two new SPs of this series (**1** and **2**) containing methoxy groups in both nitrogen heterocycles were obtained to investigate the influence of cationic fragment position on spectral and kinetic characteristics.

Compound **1** exists as a single Sp in both crystalline and non-irradiated solutions (Figure). In this case only positive photochromism is observed during UV irradiation. Thermal reverse reaction can be accelerated by visible light impact (578 nm). Photoinduced Mc form of **1** is characterized by fluorescence with maximum at 776 nm and quantum yield of 0.011.

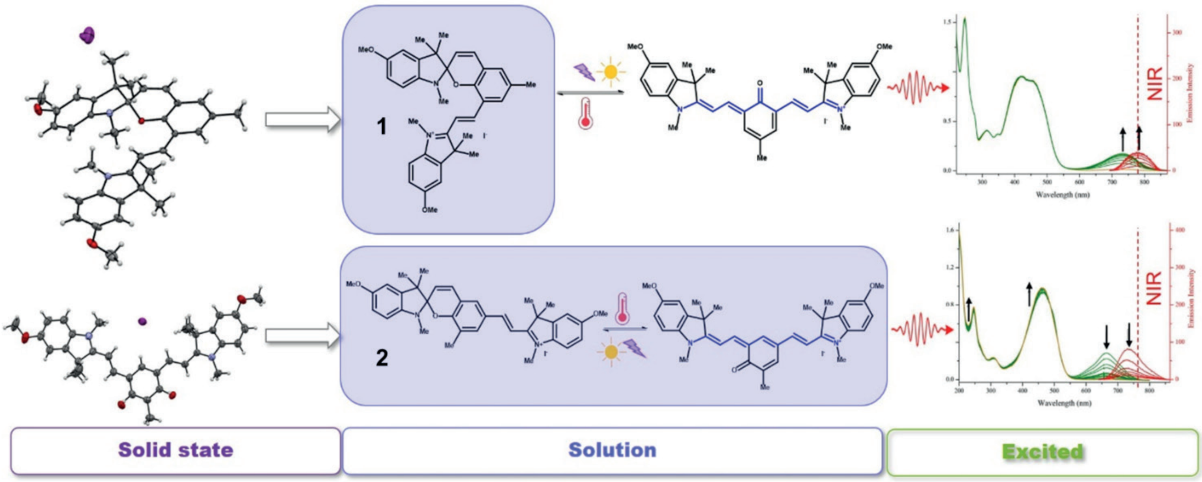

Figure. Forms of obtained SPs, observed in the solution and crystals, changes in absorption and fluorescence spectra under UV irradiation.

At the same time compound **2** in crystals exists as Mc form, while both Sp and Mc forms were observed in the solution. Due to the higher thermal stability of Mc negative photochromism is observed both under UV and visible light irradiation. Mc's fluorescence maximum is at 730 nm (quantum yield 0.017).

Thus, localization of cationic fragment at *para*-position relative to pyran oxygen atom leads to Mc stabilization and manifestation of negative photochromism in contrast to *ortho*-cationsubstituted SP **1**. Compound **1** is characterized by a bathochromic shift of fluorescence maximum in comparison with **2**.

The study was financially supported by the Russian Science Foundation grant No. 22-73-00330, https://rscf.ru/project/22-73-00330/, and carried out in Southern Federal University.

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HYDROTHERMAN SYNTHESIS OF PERFECTLY SHAPED MICRO- AND NANOSIZED CARBANATED APATITES FOR BONE SURGERY

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The development of effective synthetic materials for bone surgery is an urgent task. Hydroxyapatite (HAp) is believed to be the inorganic basis of bone tissue. That's why there is much articles on polyester/calcium phosphate composites, hydroxyapatite (HAp) and β-tricalcium phosphate (TCP) was considered as a bone materials substitute (BMS) aimed at providing specified mechanical characteristics of the composite and ensuring subsequent bone regeneration. The biomedical use of HAp is FDA approved, however, pure 'stochiometric' HAp $Ca_{10}(PO_4)_6(OH)_2$ is not quite appropriate because its high degree of crystallinity that results in reduced biodegradability, poor mechanical properties and even cytotoxicity in specific cases. The fundamental disadvantage of these phases is the unsatisfactory resorption rate, too high for TCP and too low for HAp. Among synthetic BMS, carbonated apatite (CAp) is perfectly suited for the use in composites because biomimetic HAp (bone apatite) is actually a CAp. CAp is also attractive due to its basic character, resorption rate intermediate between HAp and TCP and potential ability to neutralize acidic products of the polyesters degradation. In 2017, CAp was approved as an artificial bone substitute by the Pharmaceuticals and Medical Devices Agency (Japan) [1].

The aims of the present study were to develop a method for synthesizing morphologically homogeneous CAp, its resorption rate and biocompatibility. For the synthesis of plate-like and hexagonal carbonated apatite samples (pCAp and hCAp, respectively) we developed new synthetic approach [2]. pCAp and hCAp were prepared by hydrothermal precipitation method with the use of $CaCO_3$ as a Ca^{2+} and CO_3^{2-} source, $Na_2[EDTA]\cdot 2H_2O$ for calcite dissolution and for the control of crystallite formation, NaH_2PO_4 as a PO_4^{3-} source, and $NaHCO_3$ or Na_2CO_3 as a CO_3^{2-} source and pH support; the reactions were conducted within 5 h at 140 °C and pH 6.1 (pCAp) or at 120 °C and pH 9.2 (hCAp). The composition and structure of the obtained compounds were studied by XRD, FT-IR, EDX methods. Thermochemical properties were investigated by DSC and TGA methods. We showed that CAp-P and CAp-H exhibit in vitro and in vivo resorption rates intermediate between HAp and TCP, and excellent biocompatibility. The chemical nature of the resorption as well as the supposed reasons for the increased biocompatibility of CAp-P and CAp-H are also discussed in the report.

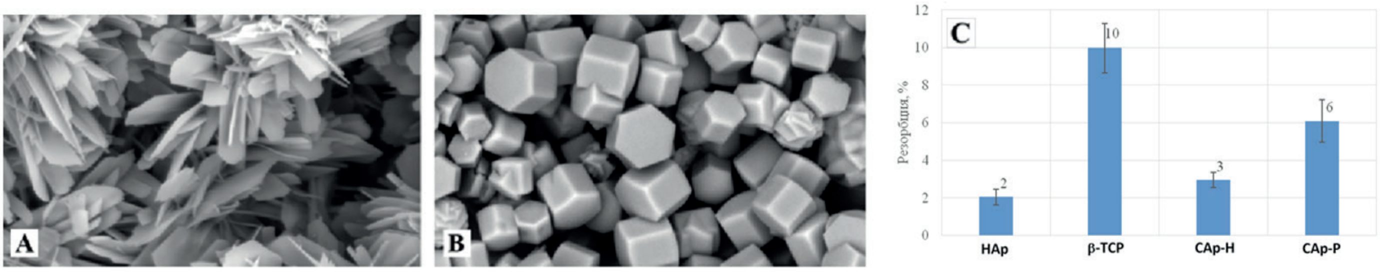

Fig. 1. **A** Plate-like carbonated apatite, CAp-P; **B** Hexagonal carbonated apatite, CAp-H;
C Comparative efficiency of resorption in vivo for HAp, β-TCP, CAp-H, CAp-P

The work was carried out with the financial support of the Russian Science Foundation, grant № 21-73-30010.

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INVESTIGATION OF THE PROCESS OF SUBSTITUTION OF POTASSIUM IONS FOR PROTONS IN A LAYERED OXIDE $K_4Nb_6O_{17}$

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The structure of the layered potassium hexaniobate oxide consists of layers of niobium-oxygen octahedrons, between which potassium cations are located (Figure 1). The niobate layers are located along the crystallographic axis b, packed in accordance with the orthorhombic type of the unit cell (Figure 1) [1]. A characteristic feature of this structure is the presence of two types of interlayer space, designated I and II. Their separation is based on the difference in the orientation of the niobate layers. Structural features of interlayer spaces lead to the appearance of various properties. Type I interlayer space easily enters into ion exchange reactions involving multivalent cations, in contrast to type II, where the replacement of K^+ ions occurs predominantly with monovalent cations, such as Li^+, Na^+. The process of substitution of alkali cations in the interlayer space for protons, which is studied in this work, is called protonation, and the resulting forms are called protonated. In general, this process can be represented by the following reaction:

$$K_4Nb_6O_{17} + xH^+ + nH_2O \rightarrow H_xK_{4-x}Nb_6O_{17}\cdot nH_2O + xK^+$$

This reaction proceeds through both interlayer spaces, which allows to obtain protonated forms both for one of them ($H_2K_2Nb_6O_{17}$) and for both at once ($H_4Nb_6O_{17}$), obtaining different protonated forms of samples is interesting for obtaining nanolayers split in one or both spaces, since these forms can have different physico-chemical properties. In the literature, one may come across conflicting data on the preparation of protonated forms $K_4Nb_6O_{17}$, as well as with insufficient information on this topic. In this regard, it was decided to investigate the process of replacing the substitution of potassium ions for protons in the layered oxide $K_4Nb_6O_{17}$ under various conditions in order to develop a procedure for the synthesis of compounds of the composition $H_2K_2Nb_6O_{17}$ and $H_4Nb_6O_{17}$.

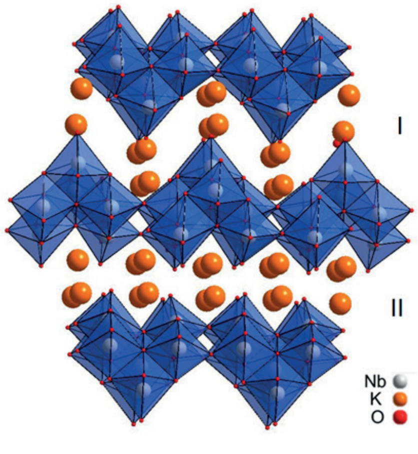

Figure 1. Structure of layered oxide $K_4Nb_6O_{17}$

Acknowledgements. The work was supported by Russian Science Foundation (grant №22-73-10110). Authors are also grateful to Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Materials Research, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics.

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CASCADE SYNTHESIS OF QUINOXALINES BASED ON THE REACTION OF 5-HYDROXYPYRROL-2-ONES WITH PHENYLENEDIAMINES

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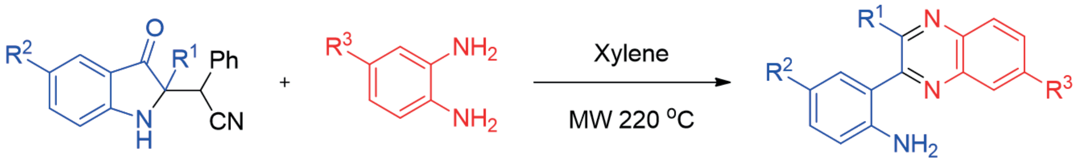
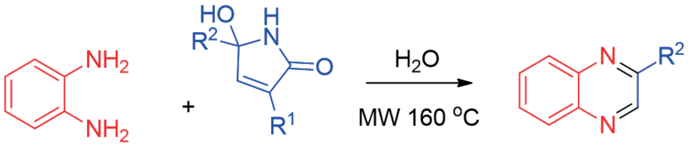
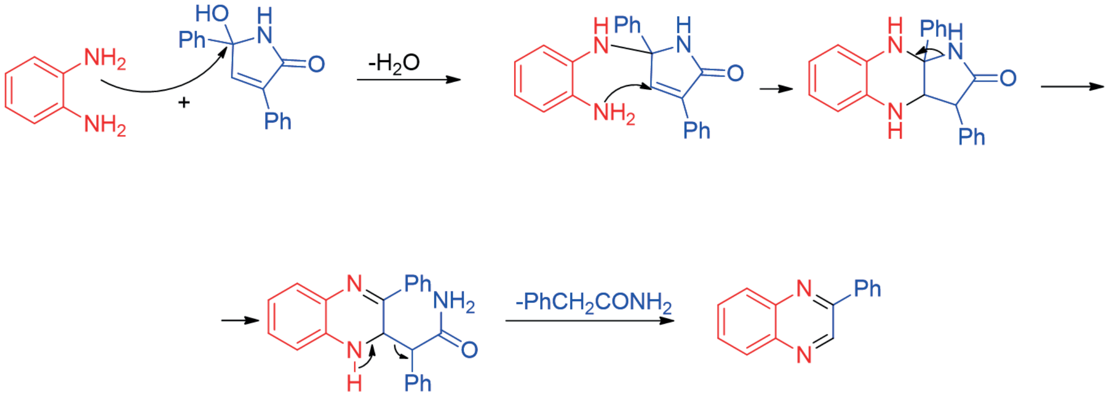
Previously, we reported the preparation of quinoxaline derivatives by microwave-assisted reaction between 2-(3-oxoindolin-2-yl)-2-phenylacetonitriles and benzene-1,2-diamines with high yields1:



Now we would like to report a new method for the preparation of quinoxaline derivatives from 5-hydroxypyrrol-2-ones and benzene-1,2-diamines via heating in water by microwave irradiation. This method meets the criteria of green chemistry, since the solvent for the reaction is water.



The proposed mechanism involves the attack of phenylenediamine on lactam with the formation of a quinoxaline ring and further elimination of phenylacetamide:



At the moment, the response scope is being developed under optimized conditions for publication in a journal.

The work was carried out with funding from the Russian Science Foundation. Project № 21-73-10029

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MOLECULAR STRUCTURE OF 5,10,15,20-TETRA(PHENYL/PERFLUOROPHENYL) PLATINUM(II) PORPHYRINATES

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Molecular structure of platinum 5,10,15,20-tetraphenylporphyrinate and 5,10,15,20-tetra(pentafluorophenyl)porphyrinate (PtTPP and PtTF$_5$PP) has been studied by a combined gas-phase electron diffraction and mass spectrometry (GED/MS) method in synchronous mode.

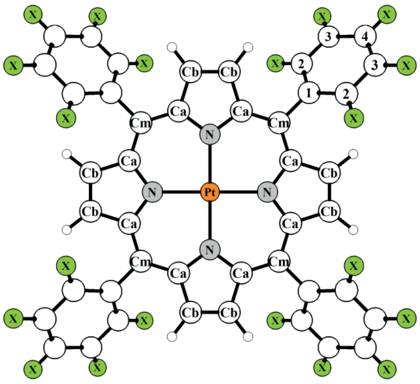

Figure 1. Molecular model of PtTPP (X=H) and PtTF$_5$PP (X=F) complexes.

The experimental geometric parameters are in good agreement with quantum chemical (QC) calculations by the DFT/B97D method. The GED identifies that the *meso*-substituents are rotated relative to the plane of the macrocycle. The angle $\Theta(C_a\text{-}C_m\text{-}C_1\text{-}C_2)$ is reasonably well-defined in the case of PtTPP - 71(4) and slightly worse for PtTF$_5$PP 79($^{-5}_{+27}$). Selected geometric parameters are given in Table 1.

Table. 1. Selected geometrical parameters of PtTPP, and PtTF$_5$PP by GED and QC calculations (bond length in Å, angles in °). QC basis functions: cc-pVTZ (C, N, H, F); aug-cc-pVTZ-PP (Pt).

	r_{h1} (GED)		B3LYP		B97D	
	PtTPP (D_{2d})	PtTF$_5$PP (D_{2d})	PtTPP (D_{2d})	PtTF$_5$PP (D_{4h})	PtTPP (D_{2d})	PtTF$_5$PP (D_{2d})
r(Pt-N)	2.025(4)	2.032(5)	2.027	2.026	2.032	2.030
$r(C_a\text{-}N)$	1.383(3)	1.378(3)	1.375	1.373	1.383	1.380
$r(C_m\text{-}C_a)$	1.398(3)	1.393(3)	1.393	1.391	1.399	1.395
$r(C\text{-}C_{Ph})_{ave}$	1.399(3)	1.396(3)	1.392	1.389	1.399	1.398
$\Theta(C_a\text{-}C_m\text{-}C_1\text{-}C_2)$	71(4)	79($^{-5}_{+27}$)	80.1	90.0	65.3	74.2
R_f, %	4.0	4.4				

The influence of the platinum atom on the geometrical structure and some physico-chemical properties of PtTPP, and PtTF$_5$PP were considered in the comparison with the 5,10,15,20-tetraphenylporphyrin molecule. The factors responsible for the C_6H_5- and C_6F_5-groups rotations were considered by NBO and F/I-SAPT0 methods.

This work was supported by the Russian Science Foundation grant 20-13-00359

SYNTHESIS OF NEW CARBAMATE DERIVATIVES OF 2-OXO-2H-CHROMENE

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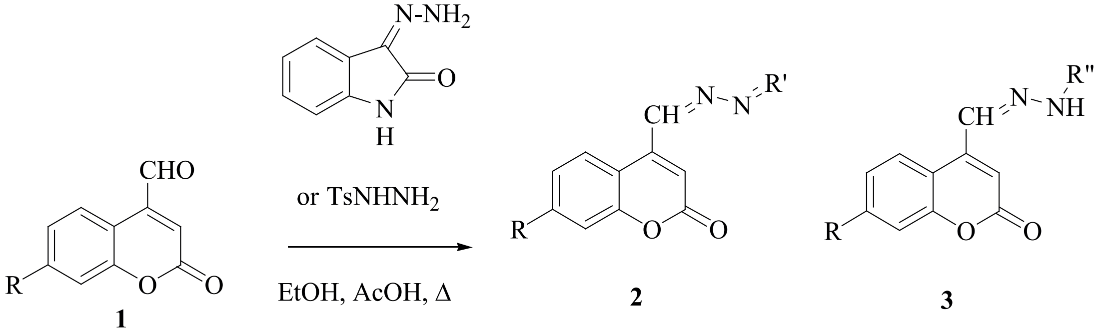
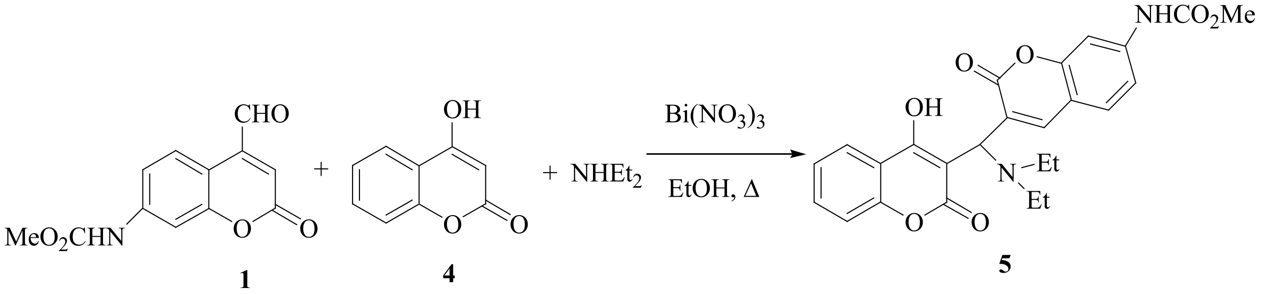
Natural and synthetic derivatives of 2-oxo-2*H*-chromene exhibit a variety of pharmacological activities such as anticoagulant, antimicrobial, anticancer, antioxidant, anti-inflammatory, and antiviral properties.

Previously, methyl *N*-(4-formyl-2-oxo-2*H*-chromen-7-yl)carbamate (**1**) was obtained in our laboratory in 81% yield by oxidation of methyl *N*-(4-methyl-2-oxo-2*H*-chromen- 7-yl)carbamate with selenium dioxide at the boiling in *o*-xylene [1]. This work presents the results of further functionalization of compound **1**. The corresponding hydrazones **2,3** were obtained in 84-87% yields by condensation of aldehyde **1** with 3-hydrazilidene-1,3-dihydro-2*H*-indol-2-one and 4-methylbenzenesulfonylhydrazide in ethanol in the presence of catalytic amounts of glacial AcOH. Methyl *N*-3-[(diethylamino)(4-hydroxy-2-oxo-2*H*-chromen-3-yl)methyl]-2-oxo-2H-chromen-7-ylcarbamate (**5**) was obtained in 78% yield by the reaction of methyl *N*-(4-formyl-2-oxo-2*H*-chromen-7-yl)carbamate (**1**), 4-hydroxy-2*H*-chromen-2-one (**4**) and diethylamine in ethanol in the presence of bismuth (III) nitrate pentahydrate.



R=NHCO$_2$Me, R'=1,3-dihydro-2H-indol-2-on-3-ylidene (2); R=NHCO$_2$Me, R''=Ts



The structures of new compounds **2-5** were confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy.

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THREE-DIMENSIONAL CRYSTALLINE ORGANIC SALTS AS A MEDIA STABILIZING METAL NANOPARTICLES AND PROVIDING EFFICIENT HETEROGENEOUS HYDROGENATION CATALYSIS

Kuznetsova S.A.,[1] **Yunusov S.M.**,[1] **Naumkin A.**,[1] **Zhereb V.P.**,[2] **Chusov D.**,[1] **Kalyuzhnaya E.S.**,[1] **Khrustalev V.N.** [1], **Belokon Yu.N.**

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A new, three-dimensional crystalline organic frameworks (**F-2** and **CF-2**) were obtained, linked by hydrogen bonds and additionally stabilized by the opposite charges of the components (Fig. 1). The materials were proved to be an efficient media for stabilizing metal nanoparticles. A new class of palladium nanoparticles encapsulated in the organic crystalline salt matrix **Pd@F2** and **Pd@CF2** was developed. The matrixes were readily prepared by mixing the dipalladium salt of tetraphenylmethane tetrasulfonic acid and the tetraamine hydrochloride under hydrogen in water. Matrixes **Pd@F2** and **Pd@CF2** contained 15-20% of palladium and were not pyrophoric. The average size of the palladium metal particles was 7 nm (**Pd@F2**) and 2 nm (**Pd@CF2**). The materials could be used as an efficient heterogeneous catalyst for the reduction of acetylene derivatives and had activity similar to that of Pd/C. **Pd@F2** reduced the aldehyde and epoxide groups very slowly and allowed the reduction of the acetylene groups to be hydrogenated selectively in the presence of the aldehyde groups. The behavior contrasts with that of Pd/C which reduces both aldehyde and acetylene groups simultaneously. A rational for the behaviour was put forward. **Pd@CF2** is being used for asymmetric reduction of double C-C bonds and the reduction of nitrobenzene to aniline

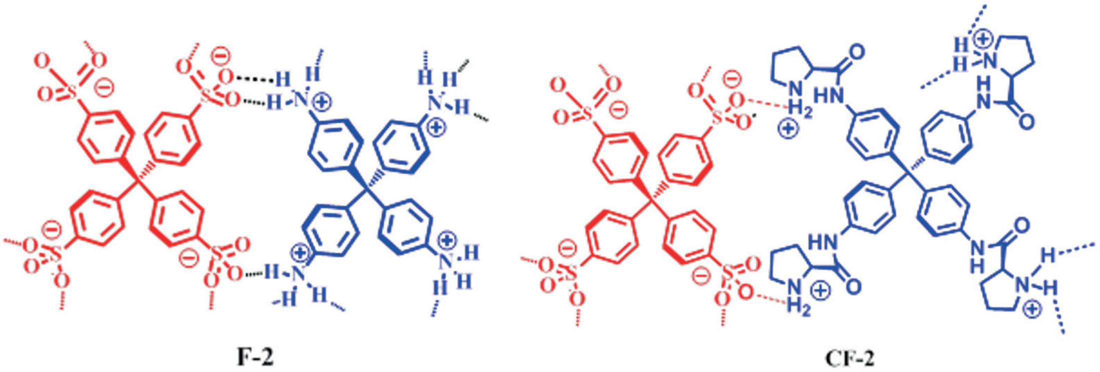

Figure 1. Three-dimensional crystalline organic frameworks (**F-2** and **CF-2**)

Acknowledgements. We gratefully acknowledge Russian Science Foundation for funding our studies on project number 22-23-00088.

CHIRAL NON-CLASSICAL METAL-TEMPLATED ORGANOCATALYSTS

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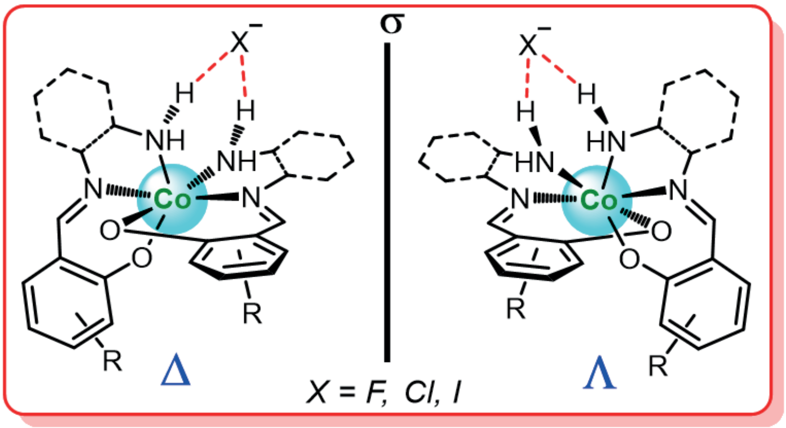
Chiral organocatalysts are environmentally friendly, easily available, and cheap catalytic systems which extensively applied in many asymmetric transformations. However, one of the main problems in their case is the need of high catalyst loadings (up to 50 mol%) to achieve high asymmetric induction. Recently, a new class of stereochemically inert transition metal complexes has been proposed as an alternative, named "organocatalysts in disguise".1 These metal-templated complexes have shown high catalytic activity and enantiocontrol even at 0.001 mol% loading (ppm level).[1]

In this work, we have developed a new class of octahedral Co(III) complexes of Λ and Δ-configurations based on commercially available (1*R*,2*R*)-cyclohexanediamine and (1*R*,2*R*)-diphenylethylenediamine and various salicylaldehydes (Figure). In these complexes, the amino groups become effective hydrogen bond donors (or Brønsted acids) due to the coordination with the metal ion. The resulting chiral complexes efficiently catalyzed various asymmetric reactions with enantioselectivity up to 96% ee.[2-6] The high efficiency can be traced back to the fact that these catalysts activate their substrates via (non-)covalent interactions (in particular, via multiple cooperative hydrogen-bonding interactions) within the chiral, rigid propeller-shaped ligand sphere of these catalysts.[1]



This work has been supported by the Russian Science Foundation (RSF grant 20-13-00155).

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AN EFFICIENT APPROACH FOR THE SYNTHESIS OF FLUOROPHORES BASED ON 2*H*-IMIDAZOLE OXIDES

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Recently, organic fluorophores have found their application in various fields of science and technology. Unlike aromatic ones, heteroaromatic luminophores are known to be more promising due to the variety of properties, as well as many ways of modifying them to obtain the target molecules. According to the literature data, imidazole and its derivatives are likely to be one of the most prospective motifs to develop advanced push-pull molecules.

In this work, we wish to discuss a convenient method for the synthesis of new 2*H*-imidazole derivatives containing an N-oxide group in their structure. The polyaromatic structures (pyrene) and heterocyclic substituents (triphenylamine, carbazole, thiophene) have been utilized as electron-releasing groups. Meanwhile, the imidazole act as elytron-withdrawing group.

The synthesis of target compounds includes three steps. At the first stage, *p*-bromoacetophenone **1** reacts with isopropyl nitrite **2** in the presence of sodium ethoxide to form oxime **3** in 75% yield. Further cyclization of the resulting substrate in the presence of ammonium acetate, acetic acid, and acetone lead to the formation of 2*H*-imidazole oxide **4** in 64% yield. The final step is the Suzuki-Miyaura reaction. Thus, two new compounds **5a-b** were obtained in 75-90% yields herein.

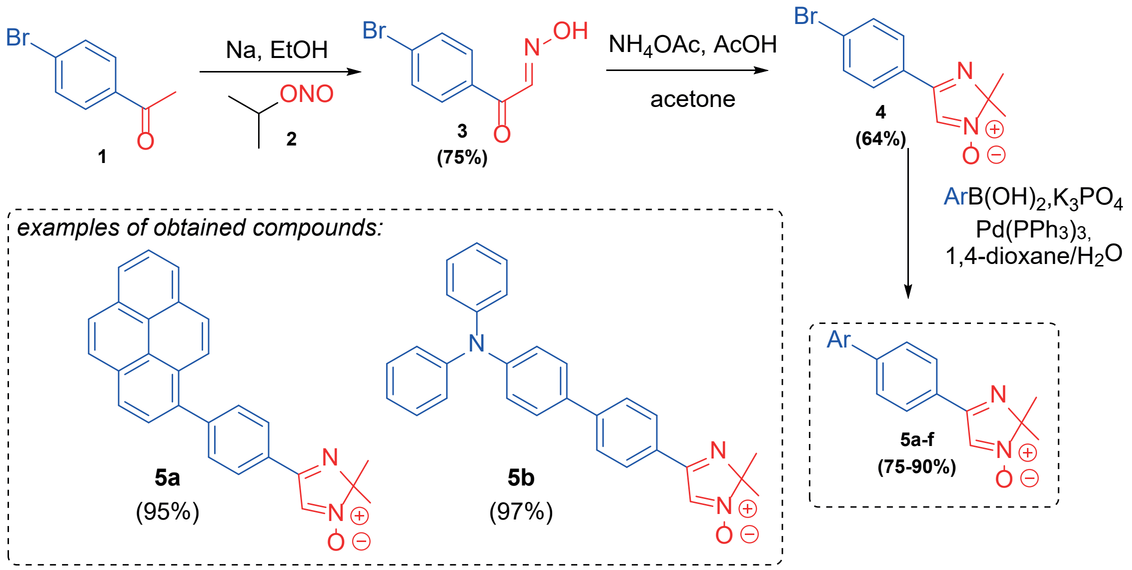

Figure 1. Synthesis of fluorophores based on 2*H*-imidazole oxide.

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University project within the Priority-2030 Program) is gratefully acknowledged.

HETEROFUNCTIONAL STILBENES AND AZOBENZENES FOR BRIDGING DIVERSE MOLECULAR BUILDING BLOCKS WITH PHOTOSENSITIVE LINKERS

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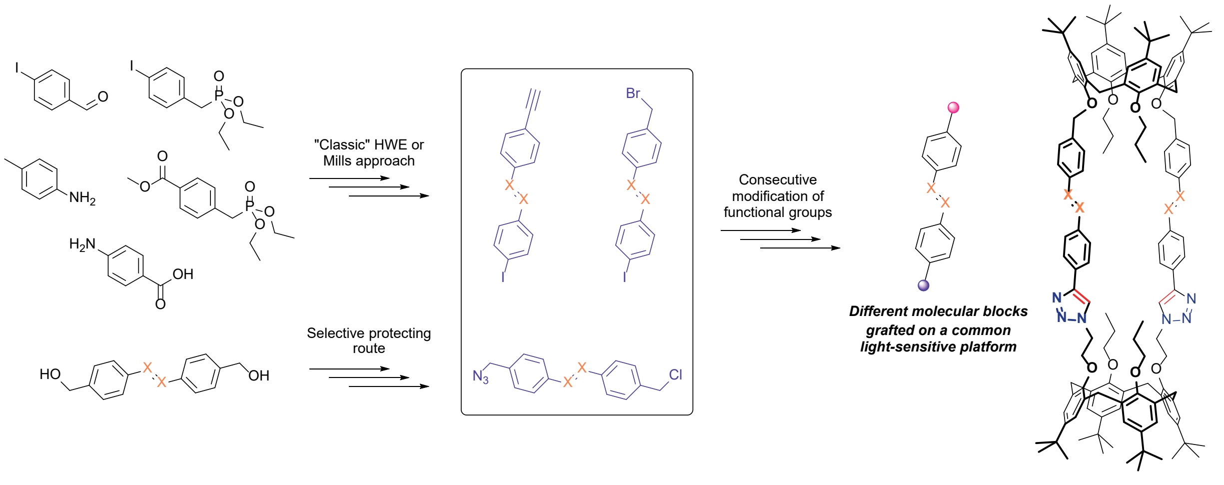
Stilbenes and azobenzenes as structural units are both widely used in modern organic and material chemistry to construct light-tunable (supra)molecular systems. Their well-studied photochemical properties enable the rational design of molecular switches, light-controlled ion channels and receptors, while certain stilbenes and the recently discovered red- and NIR-absorbing azobenzenes show a potential in biochemical and biomedical applications. Over the years various methods to construct these photosensitive cores have been developed, most notable being Wittig/Horner-Wadsworth-Emmons and Heck reactions in the case of stilbenes; while azo-coupling, Mills reaction, oxidation of anilines and reductive coupling of aromatic nitro derivatives are the most convenient routes toward azobenzenes. Despite the abundance of methods, many of them feature drastic reaction conditions in certain synthetic steps, so a unique synthetic strategy is commonly developed for each targeted compound, hindering the design of new stilbene- or azobenzene-containing structures.

In this work we synthesized a series of stilbenes and azobenzenes bearing two different functional groups in *p*-position to the double bond, which can be orthogonally modified in CuAAC, nucleophilic substitution or cross-coupling reactions. Haloalkyl, azido, ethynyl and iodo groups were chosen so that after the first functional group is used, the second one can be used directly or transformed to another reactive unit in one or two steps. This enables the facile bridging of various molecular blocks required for a specific task with a photosensitive linker, as the conditions of both coupling and a second group modification are tolerant to a wide range of functionalities.



To assess the synthetic capabilities of the approach a number of calix[4]arene semitubes comprising two calixarene and two photosensitive fragments of different structures were synthesized. Notably, most of these new macrocycles can hardly be obtained in a direct azobenzene or stilbene synthesis or require more complicated synthetic procedures to be applied and/or uncommon precursors, which need to be obtained beforehand. Lastly, developed procedures allow for the presence of other functionalities and different substitution patterns in stilbene/azobenzene cores so the list of linkers showed in this study can easily be extended given that required precursors are available.

Financial support from the Russian Science Foundation (Grant No. 22-23-00584, https://rscf.ru/en/project/22-23-00584/) is gratefully acknowledged.

MIXED-LIGAND COMPLEXES OF ESSENTIAL METALS WITH BIPYRIDINE/PHENANTHROLINE AND TETRAZOLE DERIVATIVES AS PROMISING AGENTS FOR ANTICANCER THERAPY

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The search for promising agents for antitumor therapy is an urgent task of modern medical chemistry. For many years, for the treatment of some aggressive types of cancer, and when other types of drugs have failed, platinum drugs have been used for therapy, which have a wide range of side effects associated with the low specificity of these drugs. The *Casiopeínas*® family of copper(II)-based coordination compounds exhibits antiproliferative activity against many tumor cell lines through oxidative cell damage and mitochondrial dysfunction, which lead to cell death by apoptosis. Moreover, many compounds of this series in some cases show a higher antiproliferative activity than cisplatin.

In this work, a series of mixed-ligand complexes of essential metals (manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II)) with tetrazole derivatives (5-benzyl-1H-tetrazole, 5-methyl-1H-tetrazole, 5-phenyl-1H-tetrazole, 5-(4-chloro-phenyl)tetrazole, and others) and pyridines (1,10-phenanthroline, 2,2'-bipyridine, 2,2'-bi-4-picoline, 4,7-dimethyl-1,10-phenanthroline, 1,10-phenanthroline-5,6-dione). The compounds have been characterized by elemental and powder X-ray diffraction analyzes IR and EPR spectroscopy, and thermogravimetry. The molecular and crystal structures of some compounds have been established using single-crystal X-ray diffraction analysis. The behavior of the complexes in solutions was studied using mass spectrometry and optical spectroscopy.

The cytotoxic properties of the complexes and ligands has been evaluated *in vitro* using IN Cell Analyzer 2200 (GE Healthcare, UK) by double staining of cells with fluorescent dyes with an assessment of the percentage of live, apoptotic, and dead cells. We used several human cancer cell lines: Hep-2 (larynx carcinoma), MCF-7 (breast adenocarcinoma), HepG2 (hepatocellular carcinoma), and non-cancerous cell lines HEK293-A (embryonic kidney cells) and MRC-5 (normal lung fibroblast) to assess the selectivity of the complexes. The toxicity of the complexes that showed the greatest effect in the in vitro study on a monolayer 2D model have been studied using 3D cell models, as well as using resistant cell cultures to assess the ability of compounds to overcome multidrug resistance.

The obtained data are in good agreement with the regularities of cytotoxic properties in a number of complexes of the *Casiopeínas*® series. Mixed-ligand copper(II) complexes based on 1,10-phenanthroline exhibit higher cytotoxic activity compared to complexes based on 2,2'-bipyridine. At the same time, the values of the calculated selectivity indexes indicate that compounds based on 2,2'-bipyridine, being generally less toxic to cancer cells, have higher selectivity, which makes them promising for further research.

This work has been supported by the Russian Science Foundation (project № 20-73-10207).

LIPOSOMAL DELIVERY SYSTEMS FOR SMALL MOLECULAR DRUGS: FROM STRUCTURAL AND FUNCTIONAL DESIGN TO BIOLOGICAL ACTIVITY

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The necessity for developing novel, safe, and effective drugs is urgent at the present time. In cases of serious chronic illnesses such as cancer, tuberculosis, pneumonia, etc., when long-term pharmaceutical therapy with an intensive strategy and the use of high dosages is required, this issue becomes especially significant.

By carefully balancing the physicochemical and biological characteristics of the carrier, one may modify the features of the drug formulation and create systems with different properties for the same drug molecule, according to an analysis of the literature data. This improves the effectiveness of therapy.To improve therapy effectiveness, shorten treatment times and dosages, and lessen the severity of side effects, it is evidently necessary to create innovative methods for the chemical design of nanoscale drug delivery systems.

Due to their great biocompatibility and low immunogenicity, liposomes are desirable delivery vehicles for both hydrophilic and hydrophobic pharmaceuticals. However, the reticuloendothelial system rapidly excretes liposomes in the bloodstream and liposomes thermodynamic instable. A promising solution to this issue involves the formation of complexes of liposomes with different polymeric ligands. As a result, a liposomal delivery system can be conceptualized as a three-component system made up of lipids, an active chemical, and a stabilizing polymer.

The aim of this work is the design of liposomal delivery systems for a number of important drugs in order to achieve optimal physicochemical and biological properties. Here we used antibiotics, which the task of increasing bioavailability and improving biopharmaceutical properties is relevant: broad-spectrum antibacterial drugs fluoroquinolones (levofloxacin, moxifloxacin, ciprofloxacin), first-line anti-tuberculosis drug rifampicin.

To examine the interaction between the active molecule and the delivery system matrix, a method based on spectral analysis techniques (ATR-FTIR spectroscopy, circular dichroism spectroscopy, and fluorescence spectroscopy) was devised. The method enables you to identify differences between carriers of various structures as well as the mechanism of interaction, primary drug binding sites, and way of interaction. This method eliminates the need for expensive and time-consuming tests and enables for the precise design of delivery systems and formulation optimization.

For the treatment of pulmonary forms of tuberculosis and post-COVID lung fibrosis, we have developed the platform for the targeted administration of fluoroquinolones via inhalation based on a lipid-polymer system. After drug loading liposomes of varying composition were functionalized with a polymer as a result of the creation of a multipoint non-covalent complex. We suggested to use chitosan modified with PEG and mannose residues as a polymer to target lung alveolar macrophages. The physicochemical characteristics of delivery systems have been thoroughly studied, and correlations between the system's composition and structure and its key characteristics have been found. Mice *in vivo* tests showed that the produced formulations had a strong affinity for lung tissues that was much higher than the control.

A lipid-polymer system for the simultaneous delivery of levofloxacin and rifampicin was created to combat resistant forms of tuberculosis. This system is based on a complex of a liposomal form of rifampicin with an optimized composition with a conjugate of low molecular weight chitosan with beta-cyclodextrin. Cyclodextrin tori act as binding sites for levofloxacin. The design of the system made it possible to achieve the mass ratio of drugs corresponding to clinical recommendations, high antibacterial activity and an optimal release profile in biological media.

This work is supported by the President of Russia grant for young PhDs 075-15-2022-397 and by the Developmental Program of Lomonosov Moscow State University (PNR 5.13).

G-QUADRUPLEX LIGANDS DERIVED FROM TRISUBSTITUTED NAPHTHO[2,3-*f*]INDOLES AND NAPHTHO[2,3-*G*]QUINOLINES

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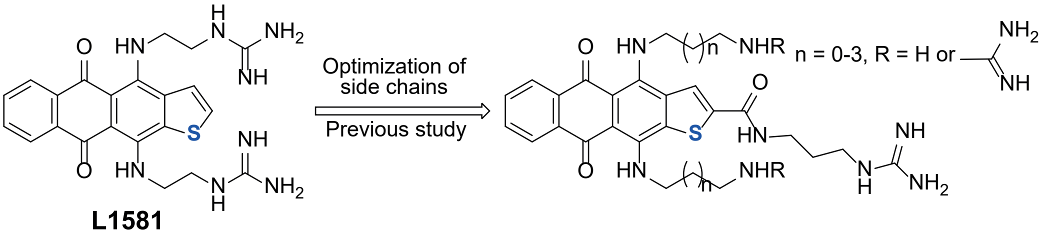
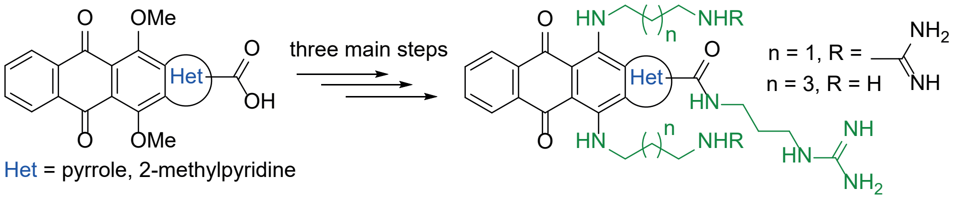
G-quadruplexes (G4) of nucleic acids are important targets for anticancer chemotherapy. Their stabilization can inhibit telomerase activity and transcription of specific oncogenes resulting in the suppression of tumor cell growth [1]. Anthra[2,3-*b*]thiophene derivative L1581 demonstrated strong binding of H-Ras G4 [2] but had modest selectivity towards duplex DNA. Structure optimization of L1581 gave a series of derivatives with three side chains: these ligands showed an improved preference for G-quadruplexes over dsDNA [3]. To investigate the influence of the heterocyclic core on ligand's affinity and specificity a series of new structural analogs based on naphthoindole and naphthoquinoline scaffolds have been synthesized and evaluated.



As starting compounds for the synthesis of potential G4 ligands 4,11-dimethoxynaphtho[2,3-*f*]indole-2- and naphtho[2,3-*g*]quinoline-3-carboxylic acids were taken. The principal scheme of transformations included three main stages. At first, above mentioned acids were coupled with *N*-Boc-diaminopropane resulting in corresponding Boc-protected amides. These intermediates were transformed into 4,11-diaminoalkyl derivatives by substituting the methoxy groups with diaminoalkanes. Lastly, the terminal amino groups of the side chains were guanidinated to enhance the binding properties of the final derivatives. The FRET melting assays revealed that the synthesized compounds exhibited high binding affinity to G-quadruplexes, with specificity towards telomeric 22CTA and c-Kit G4s. The selectivity of these derivatives over duplex DNA and its activity against cancer cells are currently being investigated.



The study was performed with partial financial support of the Russian Science Foundation grant No. 22-23-01073, https://rscf.ru/project/22-23-01073/

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SYNTHESIS OF NEW MONOTERPENE-CONTAINING AZOLES AND THEIR ANTIFUNGAL ACTIVITY

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Fungal diseases are a major public health concern as about 600 fungi species can cause human disease, and there are no licensed vaccines to prevent them. Fungal diseases have a significant impact on public health, with over one million humans dying every year from them [1]. World Health Organization published WHO Fungal Priority Pathogens List to Guide Research, Development and Public Health Action on 25th October 2022 to underline the need for action [2]. The number of cases of fungal infections is increasing, particularly in immunocompromised patients, and current treatments are expensive and toxic. Additionally, many mycoses require hospitalization, and the most effective drugs for combating them have low availability in regions where fungal infections are prevalent, which is exacerbated by the emergence of species resistant to current therapies. Compared to the development of new antibacterial drugs, the development of antifungal drugs is more challenging because fungi are eukaryotes and many potential treatment targets also occur in humans, increasing the risk of toxicity. There are four main families of antifungals: polyenes, azoles, echinocandins, and pyrimidine analogues. However, these antifungals are associated with therapeutic failures and antifungal resistance, making treatment difficult.

The present work aimed at creating new derivatives of azoles, for the first time including natural monoterpene fragments, which, as known, themselves have antifungal potential. The new synthesized hybrids show superior activity compared to the control drug fluconazole against both azole-susceptible and azole-resistant strains of *Candida* spp. Many of these molecules have excellent minimum inhibitory concentration (MIC) values, which are 100-fold lower than the values of MICs of fluconazole.

Acknowledgement: The research was financially supported by the Russian Science Foundation, RSF grant 22-73-00046.

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“TRUE CHIRAL” AND “RACEMIC COMPOUND-LIKE” MOTIFS AS TWO ALTERNATIVE WAYS OF CRYSTALLIZING PYRIDINOYLHYDRAZONE DERIVATIVES OF ISOSTEVIOL

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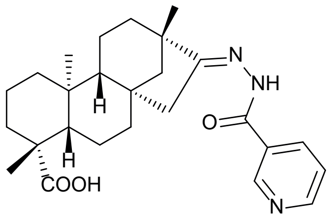
The structure of pyridinoylhydrazones with a diterpene backbone **1**-**3** is interesting due to the combination of a chiral natural fragment and an achiral substituent carrying functional groups capable of hydrogen bonding. The combination of these two fragments in the molecule makes it possible to realize in the crystals of compounds both true chiral supramolecular motifs – double helices and a translational chain, and a “racemic compound-like” motif.



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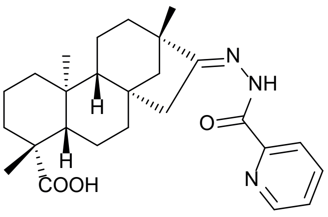

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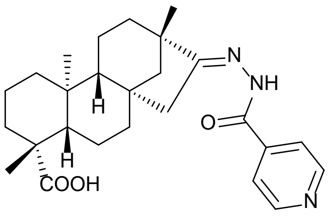

3

Polymorphic screening was performed for three isomers of this series, two different crystal forms were detected for each compound. It is established that the “double helix” type packing motif is realized in both crystals of the *meta*-isomer **1**. In one of the crystal forms of the *ortho*-isomer **2**, a motif of the “translational chain” type is realized, and in the second – a “racemic compound-like” motif (Figure 1*)*. Crystals of both forms of the *para*-isomer **3** are formed in a “racemic compound-like” manner. The latter motif is interesting because classical hydrogen bonds are supplemented by a secondary $\pi \ldots \pi$ interaction between the carbonyl group of one molecule and the aromatic fragment of a neighboring molecule, and stereochemically different, namely diastereotopic sides of the carbonyl group are involved in this secondary cross-linking. This case can be considered as an example of the formation of supramolecular diastereomers in a crystal, differing in the supramolecular configuration of the carbonyl oxygen atom.

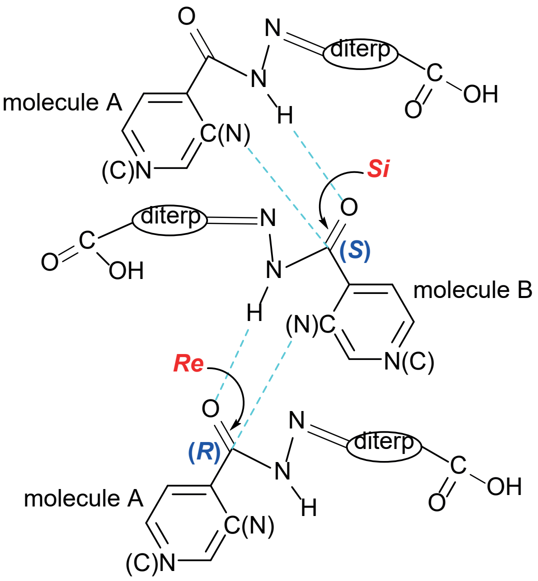

Figure 1. “Racemic compound-like” packing motif.

The work was supported by the Russian Science Foundation (grant No 22-13-00284).

QUANTUM MECHANICAL-CLUSTER APPROACH TO SOLVE THE BIOISOSTERIC REPLACEMENT PROBLEM IN DRUG DESIGN

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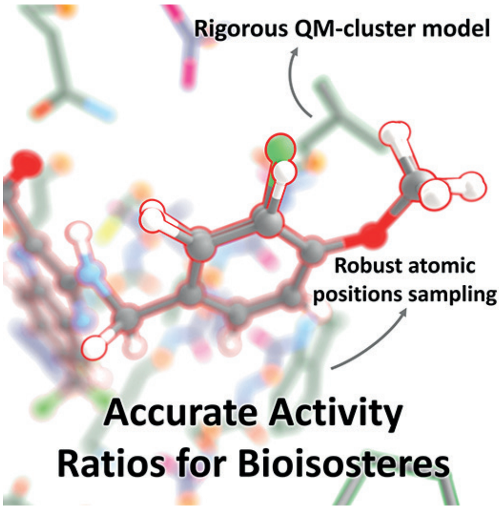
Bioisosteres are molecules which differ in substituents having very similar shapes. Bioisosteric replacements are ubiquitous in modern drug design, where they are used to alter metabolism, change bioavailability, or modify activity of the lead compound. Prediction of bioisosteres relative affinities with computational methods is a long-standing task; however, the very shape closeness makes bioisosteric substitutions almost intractable for computational methods which use standard empirical force fields.

Here [1], we design a QM-cluster approach based on GFN2-xTB [2] semi-empirical method and apply it to a set of H→F bioisosteric replacements. Our QM-cluster metodology based on few steps: extract ligand and the protein residues, which have at least one atom within 4 Å from the ligand, building convex hull and add residues penetrating it, move each atom (except for the fixed one) by 0.03(3) Å to create 101 different structures and find lowest energy during geometry optimization and finally calculate relative affinity. Finally, we estimate computational errors using bootstrap method.



The proposed methodology enables advanced prediction of biological activity change upon bioisosteric substitution of −H with −F, with the standard deviation of 0.60 kcal/mol, surpassing the ChemPLP scoring function (0.83 kcal/mol), and making QM-based ΔΔG estimation comparable to ~0.42 kcal/mol standard deviation of *in vitro* experimental measurement.

The speed of the method (~5 hours on a laptop) and lack of tunable parameters makes it affordable in current drug research.

This work was supported by the Russian Science Foundation (#22-73-10124)

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IONICALLY CROSS-LINKED MICRO-SIZED HYDROGELS WITH ENCAPSULATED DRUG: STRUCTURE, ENZYMATIC DEGRADATION KINETICS AND CYTOTOXICITY

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One of the tasks of modern pharmacology is the creation of systems for controlled delivery and release of drugs. The immobilization of a drug makes it possible to concentrate biologically active molecules in a small volume. With this technique, the maximum therapeutic effect of the drug is achieved with minimal side effects. This problem can be solved with the help of containers capable of breaking down under the action of enzymes. The polysaccharide sodium alginate is a promising candidate for such containers. Anionic polymers are of particular interest because of their ability to electrostatically bind various cationic biologically active substances. The polyvalent cations act as crosslinkers, causing the formation of nanoscale ionically crosslinked hydrogels. And after completion of drug delivery, the polysaccharide carrier can be cleaved by enzymes and excreted from the body. Therefore, the purpose of this work is to synthesize nanocomposites based on sodium alginate, to study their enzymatic stability under the action of specific (alginate lyase) and nonspecific (hyaluronidase) enzymes, as well as encapsulating the resulting containers with the antitumor antibiotic doxorubicin (Dox) and studying the cytotoxicity of Dox-loaded hydrogels.

Hydrogels were synthesized by electrostatic crosslinking of sodium alginate with Ca^{2+} cations in three different ratios of the alginate unit to the crosslinking agent: 15÷1, 10÷1 and 7÷1. The electrophoretic mobility of particles, hydrodynamic diameter and molecular weight of hydrogels obtained using dynamic light scattering and static light scattering, respectively, were studied. The effect of enzymes on the synthesized nanocomposites was studied at 37°C in physiological saline using the dynamic light scattering method. Dependences of the hydrodynamic diameter of the studied systems on time were obtained in the presence of both specific and nonspecific enzymes.

Dox was incorporated into three Ca^{2+}-Alg hydrogels with different Ca^{2+} contents by mixing aqueous solutions of hydrogels and aqueous solution of Dox at [Alg]/[Dox] = 10 for each case. The biological activity of Dox in triple hydrogels was tested against three cell lines: HCT116, human breast adenocarcinoma MCF-7, and hTERT-immortalized fibroblasts. The cytotoxicity of triple hydrogels and free Dox was assessed in in vitro experiments using a standard MTT assay that quantifies the percentage of surviving cells. The half-maximal inhibitory concentration of Dox (IC50) was taken as a measure of cytotoxicity.

Thus, the cross-linking of sodium alginate with Ca^{2+} cations in an aqueous solution leads to Ca^{2+}-Alg hydrogels, which decompose in a physiological environment under the action of enzymes. In addition, hydrogels may include the cationic antitumor antibiotic Dox. Dox-containing hydrogels retained or even reduced their toxicity to tumor and healthy cells. The results of the work can be used to design containers for the encapsulation and delivery of drugs and control their interaction with cells.

The work was supported by RSCF (project no. № 23-23-00156)

THE NEED TO RAISE AWARENESS OF PHARMACY STAFF TO RECOMMEND COMPLEX HOMEOPATHIC MEDICINES

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The global Homeopathic Medicines market size was valued at USD 942.84 million in 2022 and is expected to expand at a CAGR of 7.37% during the forecast period, reaching USD 1444.37 million by 2028. [1] The pharmaceutical market of the Republic of Armenia has complex homeopathic medicines registered as non-prescription drugs in the Drug Register of the Republic of Armenia [2] and List of non-prescription drugs registered in the Republic of Armenia [3] can be used for self-medication. Therefore, pharmacy employees have the authorization and obligation to assist pharmacy customers in choosing drugs and to provide necessary information when dispensing drugs. Doing this requires awareness, as advice on these drugs requires a differentiated approach with respect to dosage, method of use, and storage conditions.

Aim: Given the above, the goal of this study was to identify the need for additional information about homeopathic medicines among pharmacy staff.

Method. The studies were conducted according to observational research and questionnaire survey data.

Results: The results of the survey showed that almost half of the pharmacists expressed a desire to gain more knowledge in the field of homeopathy within the framework of advanced training (*figure 1*).

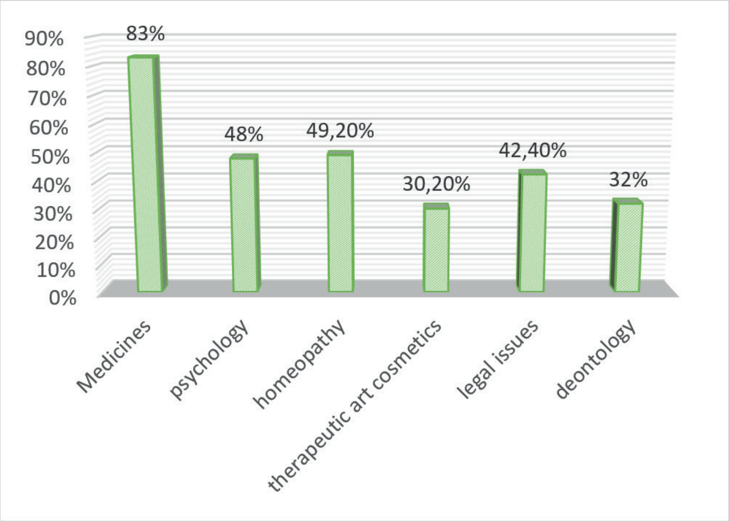

Figure 1: The desire of pharmacy employees to gain knowledge in the qualification courses in the specified fields.

Summary: It can be concluded that complex homeopathic medicines can be recommended by pharmacists as over-the-counter drugs. Therefore, as a first step, it is an imperative requirement to include information on homeopathic treatments and homeopathy in training programs.

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3. List of non-prescription drugs registered in the Republic of Armenia (as of 31.01.2022)

THE PHOTOCHEMICAL AQUATION OF *cis*-[Rh(dppz)(phen)Cl$_2$]Cl COMPLEX

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Light-activated complexes are very perspective substances for developing anti-cancer treatment methods such as a photodynamic therapy. The use of photoactivated drugs allows reducing thread and damage to healthy tissue by control over toxicity. Nevertheless, most approaches rely on a formation of reactive oxygen species what makes application of these complexes problematic due to tumor cell resistance related to hypoxia. Thus, the development of drugs having toxicity mechanism which doesn't involve oxygen is essential for successful cancer treatment. Recently, light-activated organometallic complexes have been of a great interest because of their nuclease activity after the irradiation with the UV and visible light. However, literature analysis shows a lack or even absence of descriptions of basic photochemical mechanisms. In this work we have focused on investigation of *cis*-[Rh(dppz)(phen)Cl$_2$]Cl (DPPZPHEN, Fig. 1)[1] water solutions and specifically on replacement of inner chloride ions by water molecules under UV light.

The DPPZPHEN absorbance spectrum in deionized water is shown in (Fig. 1 *left*). It is known that the substitution of chloride ligands by water attributes to octahedral bis(bipyridyl)rhodium(III) complexes, therefore it was decided to investigate photosubstitution in case of DPPZPHEN. Because aquo complexes had almost identical absorption spectral properties, the main method of kinetic observations of aquation was HPLC. Detection of concentrations of chloride ions, which are not covalently bonded to Rh(III), was conducted after irradiation of DPPZPHEN solution by means of 308 nm light from XeCl excilamp (Fig. 1 *right*). Having started from 4.8 mg/l of chloride ions that initially had been in outer coordination sphere, during first 70-80 minutes there was the linear correlation of chloride quantity from time of light exposition, after that anion concentration reached a plateau at approximately 8.0 mg/l. The quantum yield of photoaquation was estimated to be $\Phi_{308nm} = 0.01$.

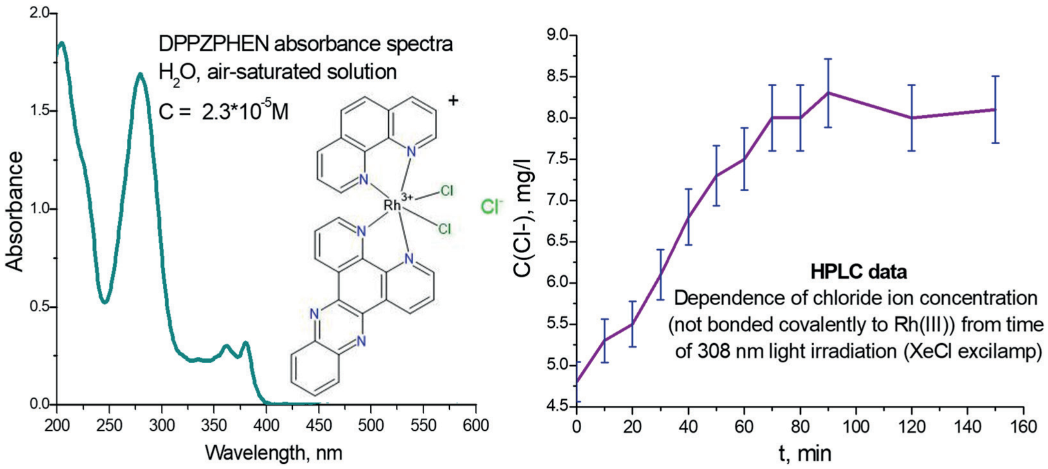

Figure 1. ***left***: absorbance spectra of DPPXPHEN complex solution in H$_2$O;
right: kinetics of complex aquation under UV light of 308 nm.

The work was supported by the Russian Science Foundation (Grant № 23-13-00226).

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EFFECT OF MODIFIER LA ON CARBON DIOXIDE CONVERSION OF METHANE ON NiO-BASED CATALYSTS

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The production of syngas from natural gas and other methane-rich feedstocks using supported catalysts is represented by large scale industrial processes of paramount importance. Catalytic carbon dioxide conversion of methane (CCM) has been of considerable scientific and practical interest in recent years, since it makes it possible to simultaneously utilize two greenhouse gases into useful chemical products. This is an urgent task when exploring new concepts and new opportunities for catalysis and the chemical industry. Carbon dioxide is produced in huge quantities when fossil fuels are burned, and hydrogen-rich methane is an inexpensive, readily available fossil fuel [1]. Fossil resources can be more useful when recycled CO_2 is used as a feedstock. In addition, additional advantages of using CO_2 are its low cost and non-toxicity, as well as the possibility of discovering completely new catalysts for the CCM process and ways of synthesizing existing chemicals and intermediates, possibly more valuable and with less environmental impact. In recent studies, bimetallic catalysts have shown promising results both in terms of high activity and durability. It should be noted that in addition to the active metal, the catalyst carrier also plays an important role in the overall functioning of the catalyst. The catalyst carrier not only provides a large surface area, but is also responsible for uniform dispersion and better anchoring of the active metal for improved stability [2].

In this work, the effect of a modifying additive (La_2O_3) on the activity of Ni-Fe oxides deposited on a support - Al_2O_3 in the process of carbon dioxide conversion of methane was studied. The catalysts were obtained by impregnation according to the moisture capacity of the carrier with aqueous solutions of metal nitrate salts. The heat treatment of the samples was carried out in air at 300-500°C and characterized by SEM and XRD. Testing the activity of the synthesized catalysts in the reaction under study was carried out on an automated flow-type laboratory setup. Process conditions: pressure P = 0.15 bar, reaction temperature Tp = 500–850 °C, gas flow rate $W = 1000\ h^{-1}$, CH_4/CO_2 ratio =1:1. The composition of the starting reagents and reaction products was analyzed by gas chromatography using a Khromos GH-1000 chromatograph.

It is shown that the introduction of 1.5 wt.% La_2O_3 into the Ni-Fe/Al_2O_3 composition leads to an increase in the activity of the catalyst, the highest efficiency is achieved at T = 850 °C, the conversion of methane is 98%, carbon dioxide is 94% and does not lose its activity during testing. up to 20 hours. The results of X-ray phase analysis showed that the modified Ni-Fe catalyst has an ultrafine (nanostructural) structure with crystallite sizes of all components smaller than the size of coherent X-ray scattering (<100Å), which positively affects its activity. According to the SEM analysis data, morphological features are observed, which are obviously associated with a strong interaction between the support, Al_2O_3, and nanoparticles of the active phase of the catalyst, leading to the formation of a nanostructured $NiAl_2O_4$ spinel phase at high temperatures.

The work was supported by the International Science and Technology Center within the framework of the GE2606 scientific project "Development of Sorbents-Carriers, Catalysts, and Technology for Utilization of Methane and Carbon Dioxide Greenhouse Gases".

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HYDRODEOXYGENATION OF SYRINGOL AS BIO-OIL MODEL COMPOUND OVER *in situ* OBTAINED NIMO SULFIDE CATALYSTS

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Introduction. The development of effective methods of lignin conversion into bio-oil and value-added chemicals is still an important and relevant task due to the gradual depletion of fossil fuels. Using thermochemical and catalytic depolymerization processes, lignin can be decomposed into lower molecular monomeric oxygen-containing compounds to obtain bio-oil [1]. However, the resulting compounds cannot be directly applicable as a potential biofuel or high grade chemicals due to the high oxygen content and low chemical stability [2]. Catalytic hydrodeoxygenation (HDO) is a fundamental technology to upgrade the lignin-derived phenolic compounds by removing the oxygen in the form of water. However, traditionally used in HDO process Ni(Co)-Mo(W)/γ-Al2O3 sulfide catalysts can deactivate in the presence of water [3]. This problem can be solved by the use of catalyst precursors, allowing to obtain unsupported nanosize catalysts.

Experimental/methodology. Syringol is one of the main lignin depolymerization products, therefore it was chosen as a model compound. Octane was used as a solvent and elemental sulfur in an amount of 1.25 wt.% (based on the feed) was used as a sulfiding agent. Catalytic tests were carried out at 300 and 350 °C, at initial hydrogen pressure 1-7 MPa and process duration from 15 minutes to 5 hours in a steel batch autoclave-type reactor. The obtained catalysts were characterizied by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (XRD).

Results and discussion. Phenol, cyclohexene, cyclohexane have been obtained as main reaction products. It should be noted that syringol conversion remained practically unchanged and reached > 95% independently of the experimental conditions. Based on the experimental results, the possible reaction pathway of syringol HDO over unsupported NiMoS catalysts have been proposed (Figure 1).

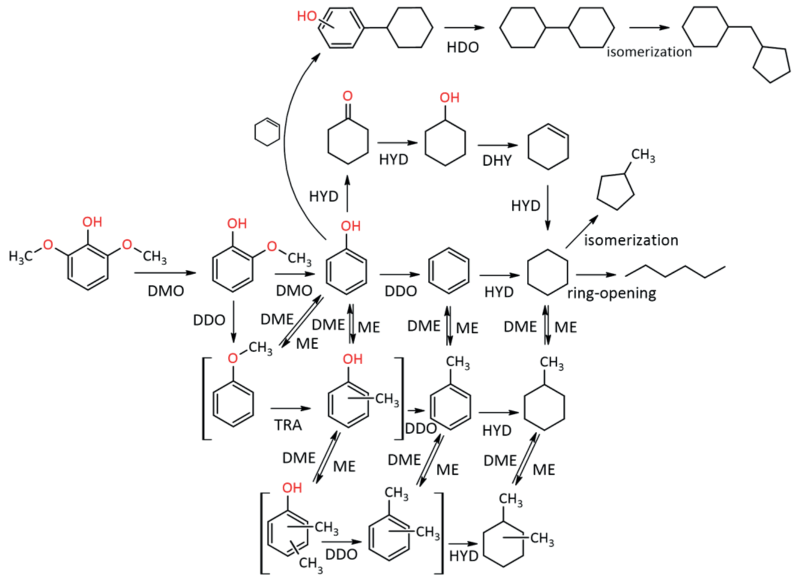

Figure 1. Proposed reaction pathways of syringol HDO over *in situ* obtained NiMoS catalysts (DMO–demethoxylation, DME–demethylation, ME–methylation, DDO–direct deoxygenation, HYD-hydeogenation, DHY–dehydration, TRA-transalkylation).

Acknowledgments. This study was performed within the framework of the State Assignment of the Institute of Petrochemical Synthesis of the Russian Academy of Sciences.

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SYNTHESIS AND PROPERTIES OF NANOCARRIERS FOR THE DELIVERY OF DRUGS AND ANTIDOTES

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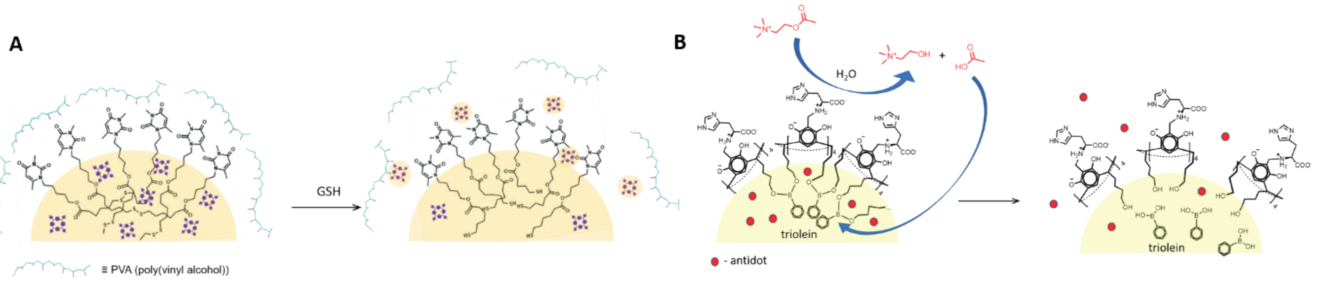
One of the topics of modern medicinal chemistry is the development of nanocarriers based on various biocompatible substrates. Multifunctional systems that formed spontaneously and are capable of selective detection of lesions, targeted medication delivery, and its regulated release are crucial for enhancing the efficacy of therapy [1]. Targeted medication delivery and biologically active receptor-sensitive fragments at the base of nanocarriers encourage an improvement in the therapeutic effect of pharmaceuticals.

In this work, we present two new nanocarriers for drug delivery. The first is intended for photodynamic anticancer therapy (PDT), and the second is developed to provide an antidote for organophosphoric chemical toxicity. The nanocarrier for PDT is a polymer particle containing a redox-sensitive core with an encapsulated photosensitizer and coated with a polymer shell (Scheme 1A). While the encapsulated photosensitizer encourages the development of cancer-cell-killing reactive oxygen species under the influence of light, the uracil groups on the surface of the nanocarrier increase the penetration into cancer cells [2]. The second nanocarrier consists of histidine resorcinarene molecules bonded together with boronate linkages (Scheme 1B). It has been demonstrated the ability of the nanocarrier to bind acetylcholine (Ach) and possibly function as an acetylcholinesterase (AChE) to hydrolyze Ach. The hydrolysis-produced acetic acid reacts with the boronate bonds in the nanocarrier and degrades it, which leads to antidote release.



Scheme 1.

We thank the Russian Science Foundation for financial support of this research (grant N 23-23-00381).

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ANTIRADICAL REACTION CENTERS OF FOLIC ACID. QUANTUM-CHEMICAL CALCULATION

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The study of the antiradical ability of the multifunctional water-soluble vitamin of the B group (vitamin B9) - folic acid (FA) (Figure) is an urgent task.

The main aim of the research is to identify the reaction centers of folic acid responsible for its antiradical/antioxidant activity at the molecular level. The obtained data gives necessary information to improve pharmaceutical forms of folic acid and to increase the efficiency of medical therapy.

In the present work, reaction centers of folic acid responsible for its antiradical/antioxidant activity were determined by quantum chemical calculations in vacuum.

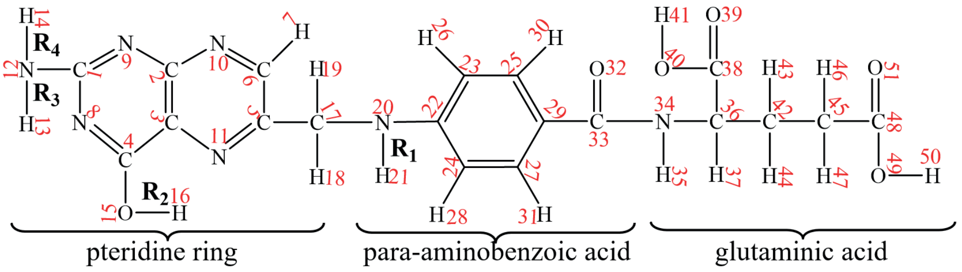

Figure. Chemical structure of folic acid.

Phenolic and aromatic amines antioxidants scavenge free radicals via phenolic O-H and N-H groups mainly through three distinct mechanisms yielding the same products: One-step transfer of a hydrogen atom: HAT (Hydrogen Atom Transfer); A sequential two-step process: SPLET (Sequential Proton-Loss Electron-Transfer); A single electron transfer followed by proton transfer: SET-PT (Single Electron Transfer-Proton Transfer). The thermodynamics of the mechanisms of free radical scavenging reactions by phenolic O-H and aromatic amine N-H bonds of folic acid are largely determined by the enthalpies (H) of the following processes:

(1) $\mathrm{BDE}=H(\mathrm{A}^{\bullet})+H(\mathrm{H}^{\bullet})-H(\mathrm{AH})$ BDE (bond dissociation enthalpy)
(2) $\mathrm{PA}=H(\mathrm{A}^{-})+H(\mathrm{H}^{+})-H(\mathrm{AH})$ PA (phenoxide and amide anions proton affinity)
(3) $\mathrm{ETE}=H(\mathrm{A}^{\bullet})+H(\mathrm{e}^{-})-H(\mathrm{A}^{-})$ ETE (electron transfer enthalpy)
(4) $\mathrm{IP}=H(\mathrm{AH}^{+\bullet})+H(\mathrm{e}^{-})-H(\mathrm{AH})$ IP (ionization potential)
(5) $\mathrm{PDE}=H(\mathrm{A}^{\bullet})+H(\mathrm{H}^{+})-H(\mathrm{AH}^{+\bullet})$ PDE (proton dissociation enthalpy)

The reactions enthalpies were calculated using the hybrid methods B3LYP and M06-2X of the density functional theory (DFT) (6-31G(d,p) basis set). The obtained parameters for three mechanisms are given in the table, where R1, R2, R3 and R4 are the antiradical reaction centers of folic acid.

Table. Thermochemical parameters for three antioxidant mechanisms for the free radical scavenging reaction by phenolic O-H and aromatic amine N-H bonds of the folic acid molecule.

Reaction Center	HAT		SPLET				SET-PT			
	BDE (kcal/mol)		PA (kcal/mol)		ETE (kcal/mol)		IP (kcal/mol)		PDE (kcal/mol)	
	B3LYP	M06-2X	B3LYP	M06-2X	B3LYP	M06-2X	B3LYP	M06-2X	B3LYP	M06-2X
FA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
R1	86.38	91.09	352.95	350.25	47.35	52.50	153.47	165.50	246.84	237.25
R2	95.62	102.44	327.17	330.99	82.37	83.11			256.08	248.61
R3	101.84	106.39	348.19	351.45	67.58	66.60			262.30	252.55
R4	102.87	107.49	349.90	353.46	66.90	65.69			263.33	253.65

The obtained data confirm the antiradical properties of folic acid. Meanwhile, high ionization potentials prove that a free radical scavenging reaction by the SET-PT mechanism is unlikely.

An analysis of the data in the table shows that the energy efficiency of free radical scavenging reaction by phenolic and aromatic amine bonds increases in the series:

R4 < R3 < R2 < R1.

SYNTHESIS OF OPTICALLY PURE (*S,E*)-2-AMINO-3-(4-(2-(DIPHENYLPHOSPHORYL) VINYL)PHENYL)PROPANOIC ACID BY USING HECK REACTION

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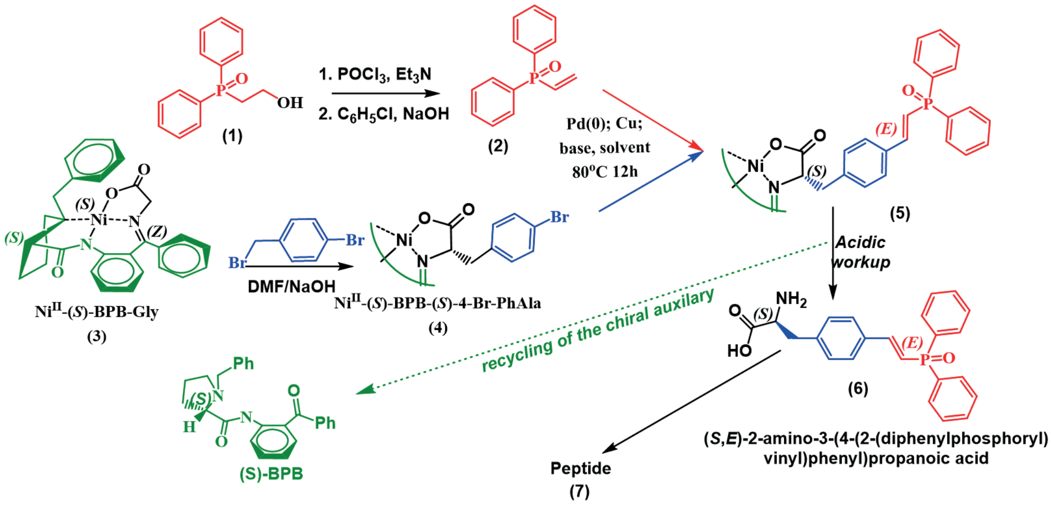
It is known from the literature that amino acids are widely used in various fields of the economy, especially in the pharmaceutical industry. The combination of amino acids and phosphorus containing compounds will provide new opportunities in the study of both material science and biochemical reactions.To select the optimal reaction conditions, temperature, catalizator, bases as well as the ratios of starting substances were investigated.

Scheme



As a result effective way for synthesis novel enantiomerically enriched derivative of (S)-α amino acide (ee>99%) was developed.

This work was supported in part by the RA MES State Committee of Science

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IGNITION OF MIXTURES OF ALIPHATIC ALDEHYDES WITH OXYGEN, INITIATED BY AN ADSORBED PEROXIDE COMPOUND

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Previously, the influence of the nature of the surface (KCl and H_3BO_3) on the ignition temperature (TB) of CH_3CHO and C_2H_5CHO-O_2 mixtures [1, 2] upon heating was established. It manifested itself in a decrease in T_B, and in the case of H_3BO_3 up to the room temperature. To the evidence of the possibility of heterogeneous interaction of CH_3O_2 and $C_2H_5O_2$ radicals with RCOH [3, 4], as well as to the discovery of a correlation between the rate of interaction of RO_2 with RCOH and T_B RCOH-O_2 mixtures on surfaces (KCl and H_3BO_3), indicating the heterogeneous nature of the ignition initiation.

In this case, to clarify some features of the ignition of aldehyde-oxygen mixtures [1-2], initiated by an adsorbed peroxide compound that generates radicals upon heating.

It is known that RO_2 radicals are formed on the surface and partially pass into the gas phase [5]. This made it possible to explain some features of the ignition of the above mixtures.

Based on the joint review of data on the ignition of RCOH-O_2 mixtures initiated by an adsorbed peroxide compound upon heating, and the heterogeneous interaction of peroxide radicals RO_2 with RCOH, it was concluded that the constancy of T_B in a certain range of changes in the amount of peroxide compound is due to the limited number of active sites on the surface, which leads to its saturation with heterogeneous radical reactions.

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ROYAL JELLY AS A MEANS OF REGULATING PROCESSES DISTURBED BY EXPOSED MILLIMETER WAVES

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The influence of different types of electromagnetic radiation on living organisms is increasing day by day, and currently, the focus of scientists' attention is the discovery of molecular mechanisms of such effects. It is more important to clarify the possibilities of preserving living organisms from the negative effects of radiation and eliminating radiation damage.

Royal Jelly, which is known for its anti-inflammatory, antibacterial, and immune system-activating effects, can become a natural remedy for repairing radiation damage in living cells.

This study aims to discover Royal Jelly's role in the repair processes of some metabolic disorders in *C. guilliermondii* NP-4 yeast cells exposed to millimeter waves of 51.8 GHz frequency.

It has been shown that metabolic changes occur in yeast cells under the influence of millimeter waves. The lipid peroxidation processes are stimulated, and the activity of antioxidant enzymes SOD and catalase increases. At the same time, changes also occur in the process of deamination of purine nucleotides. The intensity of ATP deamination in exposed yeasts increases by 53%, which is partially reduced during yeasts' post-exposure repair. The intensity of ADP deamination in exposed yeasts increases by 13%, and during the repair period, it decreases by 30.9%.

Under the influence of Royal Jelly, noticeable shifts are observed in the studied metabolic changes of exposed yeasts. It was shown that lipid peroxidation processes in exposed yeasts grown in the presence of Royal Jelly and exposed to millimeter waves are suppressed by 16.4% in comparison with yeasts grown without Royal Jelly. In the case of repaired yeasts, the lipid peroxidation process is suppressed by 27.7%. At the same time, the antioxidant enzymes SOD and catalase are also stimulated in yeasts, however, their activity in the presence of Royal Jelly was stimulated less than in yeasts grown without Royal Jelly. We suppose, that due to their antioxidant properties, the Royalisin peptide and short-chain fatty acids contained in the Royal Jelly [1, 2] bind the reactive forms of oxygen (ROS) generated in the yeasts under the influence of electromagnetic waves, reducing the oxidative stress, as a result of which the processes studied by us do not undergo sharp changes in the cells.

In yeasts grown in the presence of Royal Jelly, the intensity of ADP deamination under the influence of millimeter waves increases 2 times more than in yeasts grown without Royal Jelly, and the intensity of ATP deamination, on the contrary, falls by 55%. After the yeast repair period, the deamination intensity of both ATP and ADP decreases in the presence of Royal Jelly. It can be assumed that in yeast exposed to millimeter waves, Royal Jelly inhibits the deamination of ATP, i.e. its catabolism decreases, and ATP undergoes more hydrolysis, releasing energy that the stressed yeast needs to survive. During yeast repair, the rate of deamination of both ADP and ATP decreases as energy-intensive repair processes begin and ADP begins to be used as an alternative energy source along with ATP.

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PREPARATION OF NEW FLUORINATED DERIVATIVES OF PEROVSKITE-LIKE LAYERED OXIDES $M_2Ln_2Ti_3O_{10}$ (M = alkali metal, Ln = La, Nd)

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Layered perovskite-like oxides are compounds in the structure of which there is a sequential alternation of blocks having a perovskite structure with layers having a different type of structure. (Figure 1). Some of the reactions of layered perovskite-like oxides (which is most typical for the protonated forms obtained by ion exchange - Figure 1 a-b) involve topochemical condensation, during which lattice oxygen is removed and as the result, the formation of defective perovskite-like compounds containing anionic and/or cationic vacancies occurs (Figure 1 b-c). When heating protonated compounds belonging to the Raddlesden-Popper phases, for example $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) between 350 and 500 °C, water elimination occurs along the interlayer space to form oxygen defect layered oxides. The possibility of filling the formed voids and vacancies with new ions interested us as a way to obtain new fluorine-containing compounds by introducing fluorine-containing anionic structures into the interlayer space. In practice it can be made, when fusing with salts of the corresponding metals (Figure 1 in-d). In particular, alkali metal fluorides may be suitable for these purposes. The present work describes the results of sintering two perovskite-like oxides, namely $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) with such fluorides as NaF and CsF, which as a result made it possible to obtain a new fluorine-containing phases.

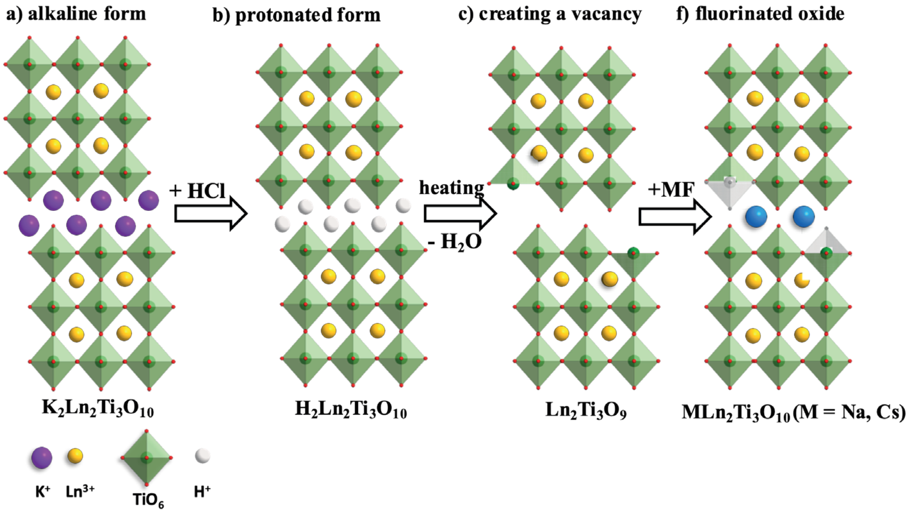

Figure 1. Proposed scheme for the production of fluorinated titanates

Acknowledgements The work was supported by Russian Science Foundation (grant №22-73-10110). Authors are also grateful to Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Materials Research, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics.

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SYNTHESIS, STRUCTURE AND PHOTOPHYSICAL PROPERTIES OF COORDINATION POLYMERS BASED ON DI(1H-IMIDAZOL-1-YL)BENZO[C][1,2,5]OXADIAZOLES

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The excessive emission of pollutants has become a pressing global issue as these pollutants, with high dissolution and fluidity, can easily diffuse into the air, soil, and water, threatening the environment and biological health. Heavy metal ion accumulation can cause cancer, malformation, neuron degradation, and organ damage, while excess intake of pesticides and antibiotics can result in drug-resistant superbugs. Although various laboratory methods, such as atomic absorption spectrometry, atomic emission spectrometry, and inductively coupled plasma mass spectrometry, have been developed to quantitatively measure various pollutants, these methods require expensive measurement instruments, tedious sample preparation, and preconcentration procedures, and cannot be used as portable devices for in situ detection. Therefore, it remains a significant challenge to explore novel pollutant sensors with high efficiency and universality.

Metal-organic frameworks (MOFs) are a fascinating class of porous crystalline materials with broad applications in luminescence, gas storage and separation, catalysis, biomedicine, and proton conductivity. MOFs offer an optimal platform to generate multidimensional luminescence, due to the judicious choice of ligands and metal nodes, and tunable pore size and shape. Luminescent coordination polymers are of particular interest because they can be used as sensors with a luminescent response to various analytes. By selecting ligands with desired luminescent characteristics, efficient and selective sensors can be obtained for detecting a wide range of analytes, including heavy metal cations, nitroaromatic compounds, antibiotics, etc. In this regard, benzo-2,1,3-oxadiazole derivatives, which exhibit bright luminescence and high quantum yields, can be used as fluorophore ligands to synthesize luminescent coordination polymers. The change in the photophysical properties of MOFs in the presence of an analyte serves as an analytical signal.

Herein we report synthesis of novel luminescent organic ligands - 4,6-di(1H-imidazol-1-yl)benzo[c][1,2,5] oxadiazole (**4,6-ImBOD**) and 4,7-di(1Himidazol-1 yl)benzo[c][1,2,5] oxadiazole (**4,7-ImBOD**), and series of 1D and 2D d^{10} metal coordination polymers based on them. Photophysical properties, including sensing, have been studied in detail for both coordination polymers and ligands.

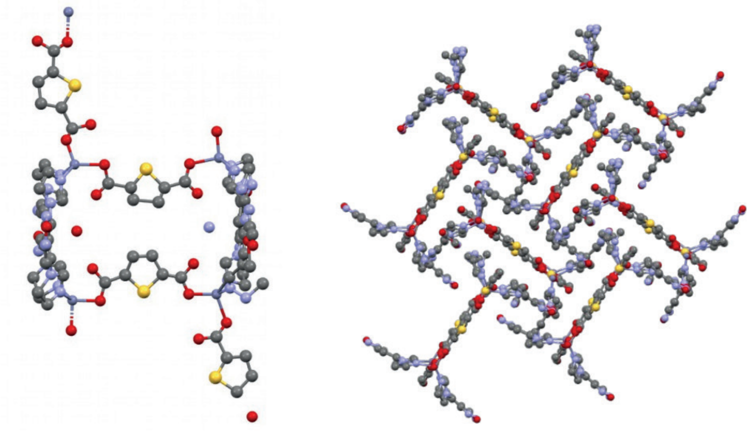

Figure 1 – Crystal structure of Zn(II) coordination polymer based on **4,6-ImBOD**

This work was supported by the Russian Science Foundation, grant No. 23-43-00017 “Novel metal-organic frameworks with high luminescence for the detection of biologically active substances and environmental pollutants”, https://rscf.ru/project/23-43-00017/.

FEATURES OF THE TBA CLUSTERING IN CCl_4 SOLUTION. MOLECULAR DYNAMICS SIMULATION

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The tert-butyl alcohol (TBA) molecule has a large compact hydrophobic group, which determines many properties of its solutions. Aqueous solutions of TBA are widely studied, where, at low concentrations, pronounced extrema are observed on the curves of the partial molar volume, heat capacity, light scattering, etc. This is due to the peculiarities of water, which has a three-dimensional network of hydrogen bonds, the presence of which leads to a hydrophobic effect. However, interesting properties were also noted for non-aqueous solutions of TBA.

We calculated the MD models of TBA solutions in CCl4 over the entire concentration range and carried out a detailed structural analysis of the resulting models. For the analysis, both standard approaches (calculation of radial distribution functions, determination of hydrogen-bonded associates of alcohol), and new ones proposed in a recent work [1], were used, where it was proposed to use the Voronoi tesselation, known in the studies of liquids and glasses, to define neighboring alcohol molecules in solution , Fig. 1. Within the framework of this approach, the “geometric” connectivity of molecules in solution is determined, which makes it possible to obtain a graph representing the arrangement of molecules in solution.

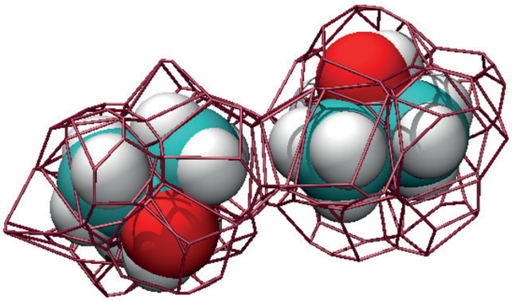

Fig.1. Neighboring TBA molecules. The Voronoi regions of such molecules have at least one common face. Voronoi regions are calculated taking into account all solution molecules. CCl_4 molecules are not shown.

The analysis of such graphs at different concentrations makes it possible to quantitatively characterize the clustering process of solute molecules. As the structural characteristics of the solution, the fractions of TBA molecules $p_i(x)$ with i=0, 1, 2, 3 and more TBA neighbors were calculated. The behavior of these characteristics depending on the concentration x demonstrates the features of clustering in solution. It is shown that at low concentrations of TBA, intensive clustering of TBA molecules begins, which is caused by the formation of hydrogen bonds between them. With increasing concentration, the number of molecules with few neighbors decreases rapidly, the molecules are surrounded by a large number of their neighbors, which can be considered the emergence of a “microphase” of this component in which a percolation cluster occurs at a concentration of $x \sim 0.168$. A fundamental difference in the clustering of TBA in CCl_4 and CCl_4 in TBA at low concentrations is shown.

This work was supported by the RSF grant no. 22-23-00620.

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1,2-ARYL SHIFT IN NAPHTO[2,1-B]FURANS: A CONVENIENT PATH TO THE SYNTHESIS OF NEW ISOMERIC FLUOROPHORES

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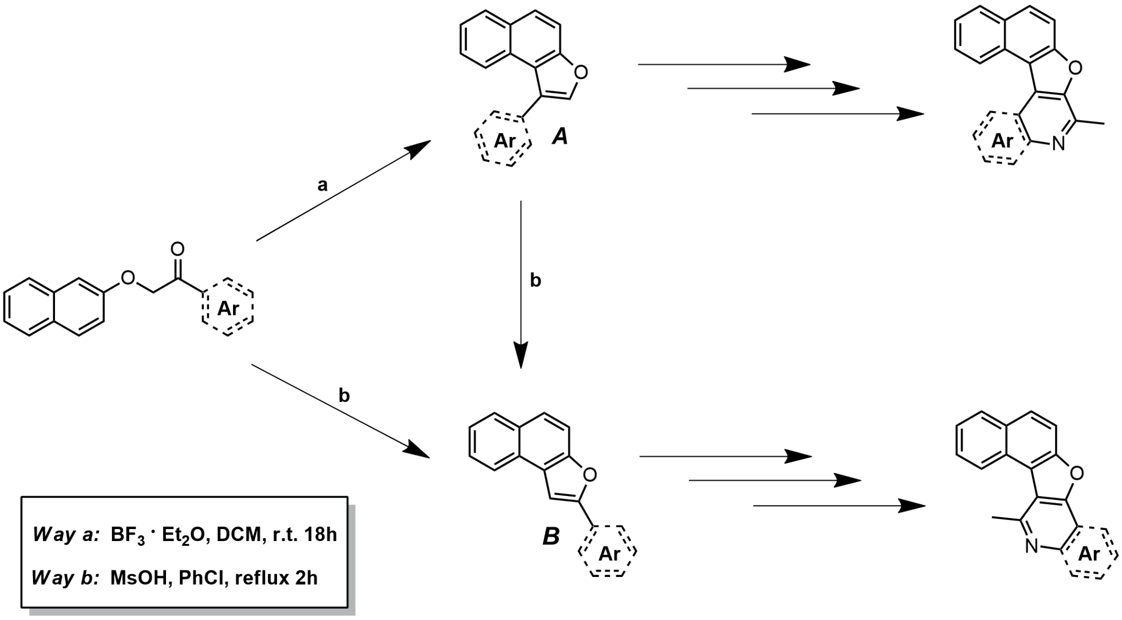

Way a: $BF_3 \cdot Et_2O$, DCM, r.t. 18h
Way b: MsOH, PhCl, reflux 2h

Naphtho[2,1-b]furan derivatives are important polyaromatic scaffolds widely used in pharmaceuticals and material chemistry. In particular, these compounds are in great demand for the development of poly(hetero) aromatic systems with promising fluorescent properties. One of the main methods for the synthesis of naphtho[2,1-b]furans is the cyclization of the corresponding ketoesters in an acidic medium, but the generally accepted reaction conditions (PPA, heating) have a limited substrate scope. This is due to rather harsh reaction conditions that promote to the 1,2-aryl shift, this is especially true for aryl moieties with electron donor substituents. Such a sigmatropic rearrangement often leads to a mixture of difficult-to-separate isomers ***A*** and ***B*** and this reaction is typical not only for naphtho[2,1-b]furans, but also for other arylheteroles [1].

Herein we have developed new preparative methods for the synthesis of each isomer A and B in pure form with high yields from the same starting substance, applicable to a wide substrate scope. The variation of the reaction conditions makes it possible to obtain kinetic and thermodynamic control products. These synthetic protocols open a convenient way to the development of new polyconjugated heterocyclic compounds of interest for potential use as a base for various fluorescent materials [2].

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SYNTHESIS OF FUNCTIONAL SILICONE CONTAINING MONOMERS AND POLYMERS WITH 1,2,3-TRIAZOLE FRAGMENT

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Silicone containing monomers and polymers based on them are the most important class of organosilicon compounds of great practical importance: in medicine, mechanical engineering, aerospace, in the production of defoamers, softeners, lubricants, and many other areas of household and industrial chemicals.

The introduction of organic substituents and functional groups of various nature into the structure of such compounds is, in turn, a defining synthetic step on the way to the creation of materials based on them.

In our work, we have developed an integrated approach to the preparation of a wide range of organosilicon monomers and polymers using azide-alkyne cycloaddition reactions (CuAAC) [1–3].

We believe that our proposed strategy for obtaining organosilicon monomers and polymers with virtually any organic and functional framework, can significantly affect the development of polymeric organosilicon chemistry in science and its practical application, and can also be extended to the synthesis of other classes of polymers.

The work was supported by the Russian Science Foundation № 21-73-10082.

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ONE-POT MULTI-COMPONENT SYNTHESIS OF 9-ARYL/ ALKYL-OCTAHYDROXANTHENE-1,8-DIONES IN IONIC LIQUIDS

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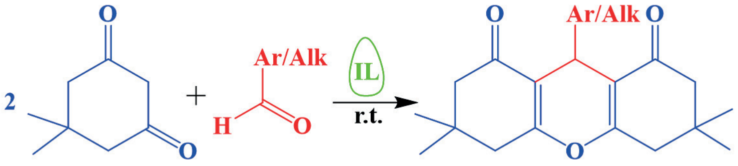
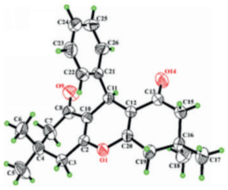
The modern trend in organic chemistry is actually the synthesis of combined organic molecules, especially heterocycles, as potentially useful structural motifs for drugs and the pharmaceutical industry [1]. The use of green chemistry to elaborate bioorganic-nanomaterial hybrids has recently evidenced impactful biomedical applications [2].

We introduce an efficient and reusable method for the synthesis of biologically active xanthene derivatives [3-4] through a one-pot condensation of aldehydes and dimedone using different ionic liquids.





The noteworthy advantages of the present method were short reaction times, high product yields (90-99%), performed at room temperature, straightforward procedure, and easy work-up procedure. In addition, the IL can be easily separated from the reaction mixture by filtration and reused in five consecutive cycles without significant loss. If the reaction mixture was left alone formed single crystals. Various spectroscopic techniques like IR, ^{1}H NMR, and ^{13}C NMR were used to study and confirm their structure, and the monocrystals were further confirmed by X-ray examination.

The work was supported by the Science Committee of RA, in the frames of the research project № 20TTSG-1D011

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SYNTHESIS OF 8*(E)*,10*(E)*-DODECADIEN-1-OL AS A APPLE MOTH PHEROMONE

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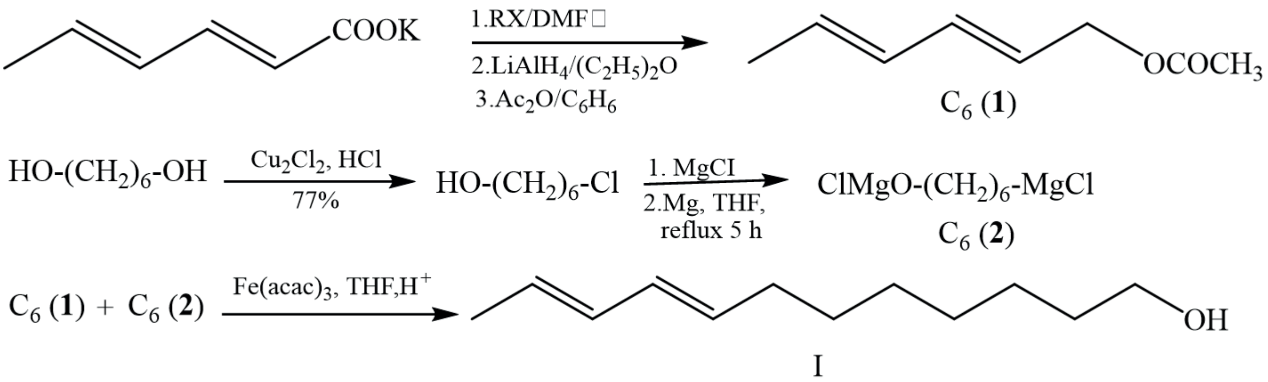
8(*E*),10(*E*)-Dodecadien-1-ol (Codlemon) **(I)** is known as the main component of the pheromone of the codling moth *Cydia pomonella L.* and is widely used to control this pest. It is also a malicious pest of peach, walnut, prunes, pears, elderberries, etc. [1,2].

A number of methods in the literature for the synthesis of codlemone based on not only various methods for constructing an intermediate conjugated diene [1,3-5], but also an enine group has been described [6].

We have selected C6(1) + C6(2) scheme for the synthesis of 8(E),10(E)-dodecadien-1-ol **(I),** as well as for improvement of some stages.



8(*E*),10(*E*)-dodecadien-1-ol **(I)**

The choice of this scheme is contingent on the availability and low cost of starting materials, the stereoselectivity of individual stages, manufacturability and high yields.

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ARYLATION OF [1,2,4]TRIAZOLO[5,1-C][1,2,4]TRIAZIN-4(1*H*)-ONE USING PD-CATALYZED SUZUKI-MIYAURA REACTION

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Azoloazine compounds have garnered significant scientific interest due to their structural similarity to natural purine compounds. There is a considerable topic of research devoted to diverse aspects of synthesis and biological activities of azoloazine-derived molecules. Modifying compounds within this scaffold leads to the formation of compounds that demonstrate a wide range of useful properties.

Among azoloazines, numerous biologically active compounds associated with various biological targets have been reported. Different derivatives have been found to possess anticancer, antiviral, and antibacterial activities. Many of the described azoloazines demonstrate antidiabetic effects, with sugar-lowering derivatives of azoloazines, such as linagliptin and anagliptin, the dipeptidyl peptidase-4 inhibitors, are being utilized in clinical practice. Thus, the development of new methodology for obtaining molecules that contain the azoloazine scaffold is an actual task for modern organic chemistry.

This work deals with the arylation of [1,2,4]triazolo[5,1-c][1,2,4]triazin-4(1*H*)-one using by the Pd-catalyzed Suzuki-Miyaura reaction. The synthesis of target compounds contains two steps. At the first stage, azoloazine reacts with NBS in chloroform at 40 °C to give regioselectivity the 3-bromo product in 75% yield. On the last step, the Suzuki-Miyaura reaction was applied using (3-(diphenylamino)phenyl)boronic acid. Thereby, the desired compounds were obtained in two steps with good yields.

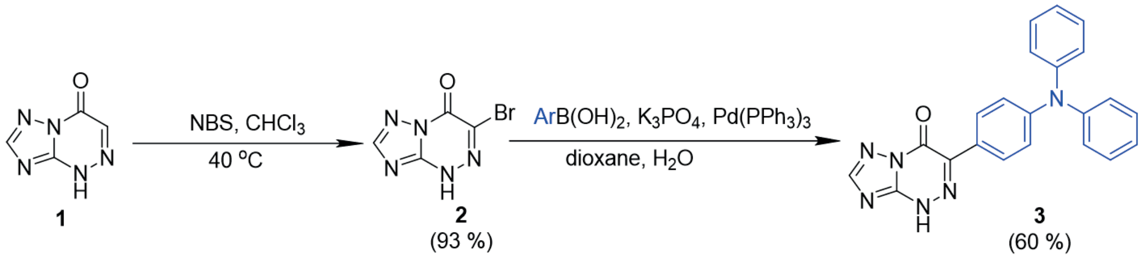

Figure 1. Arylation of [1,2,4]triazolo[5,1-c][1,2,4]triazin-4(1*H*)-one using Pd-catalyzed Suzuki-Miyaura reaction

This research was funded by the Ministry of Science and Higher Education of Russia (Agreement No. 075-15-2020-777)

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5-ARYL(THIENYL)TRIAZOLOQUINAZOLINES: DESIGN, SYNTHESIS AND PRACTICAL PROSPECTS

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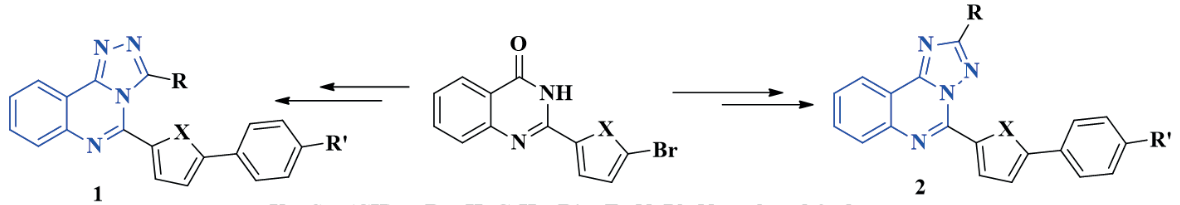
Quinazolines are an attractive class of heterocycles and serve as building blocks in making advanced fluorescent molecules. For the last decades the different quinazoline-based structures with ESIPT, AIE properties, TADF fluorescence, sensing and detecting abilities have been synthesized.[1-3] Our research group are working on 2,4-disubstituted quinazolines and studing their structure – photophysical properties relationship[4-6]. Recently, the 3-aryl-5-aminobiphenyl substituted [1,2,4]triazolo[4,3-*c*]quinazolines have been designed and synthesized. The compounds emit in broad range of wavelengths and display fluorescent quantum yields up to 94% in toluene solutions; moreover, they are sensitive to presence of TFA and water.[7]

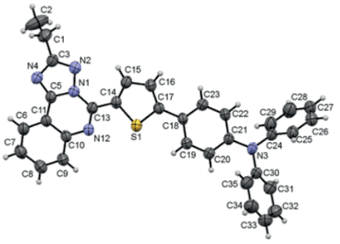
The [1,2,4]triazolo[4,3-*c*]quinazolines **1** and their isomers [1,2,4]triazolo[1,5-*c*]quinazolines 2 have been obtained in four steps starting from described previously 2-aryl(tienyl)quinazol-4(3*H*)-one. It was found that Dimroth rearrangement upon triazole cycle formation can be occur when water or acid are present in reaction media. The structure of target compounds are confirmed by X-ray diffraction and 2D-NMR spectroscopy (^{1}H-^{13}C, HMBC)

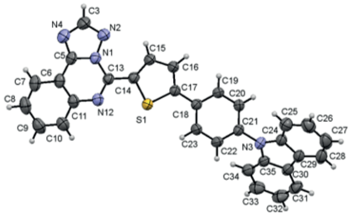


1

2

X = S, -(CH)$_2$-; R = H, C$_2$H$_5$; R' = Et$_2$N, Ph$_2$N, carbazol-9-yl





The synthesized compounds demonstrate strong emission both in solution and solid state. The detailed photophisical properties are under investigation.

This work was supported by the Russian Scientific Foundation (project № 23-73-01147).

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HYDROPROCESSING OF DIPHENYL ETHER OVER *in situ* GENERATED MOLYBDENUM AND TUNGSTEN OXIDES

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Keywords: lignocellulosic biomass, diphenyl ether, hydrodeoxygenation, transition metal oxides, benzene.

The conversion of lignocellulosic biomass is the most available step for the transition from fossil fuels to renewable and carbon-neutral resources. Lignin is an aromatic biopolymer that accounts about 40 % of all lignocellulosic biomass renewable energy [1]. The major challenge associated with development of catalyst for selective hydroprocessing of lignin-derived products into valuable chemicals or fuel components [2]. Most of the works are devoted to the study of monomeric substrate hydroprocessing using catalysts based on noble metals, which have a high cost, and a high rate of coke formation during the hydrodeoxygenation process [3]. Transition metal oxides can be considered as an alternative inexpensive and high-active catalysts for the hydroprocessing of lignin and its model compounds. Moreover, the understanding of the aryl dimers transformation reactions makes it possible to proceed to the direct hydroprocessing of lignin. In this work, the hydroprocessing of diphenyl ether over *in situ* generated molybdenum and tungsten oxides were studied.

Molybdenum and tungsten oxide catalysts were obtained during hydrodeoxygenation of diphenyl ether from molybdenum and tungsten carbonyls. The experiments were carried out in a stainless-steel autoclave at 340–400 °C, under initial H_2 pressure of 5 MPa, and for 6 h. The full conversion of diphenyl ether was reached at 380 °C and 400 °C using MoO_x and WO_x, respectively. Benzene was the main product over both catalysts. Cyclohexane was also formed over MoO_x, and phenol – over WO_x. The effect of substrate/metal molar ratio on product selectivity and conversion of substrate was studied at 340 °C, 5 MPa, and 6 h. The product distribution changed insignificantly over MoO_x at different substrate/metal molar ratios. In the case of WO_x, the increase of substrate/metal molar ratio led to increasing the phenol selectivity.

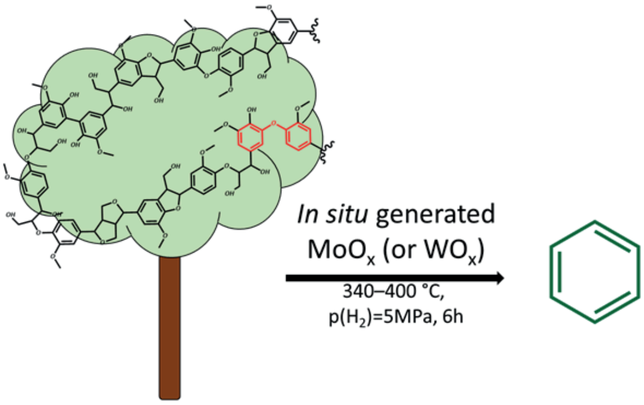

Figure 1. Diphenyl ether (structural unit of lignin) conversion into benzene over *in situ* generated molybdenum and tungsten oxides.

Acknowledgments. This work was carried out within the State Program of TIPS RAS.

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REGIOSELECTIVE SYNTHESIS OF BIOLOGICALLY ACTIVE 1,1′-DISUBSTITUTED AZINYLFERROCENES

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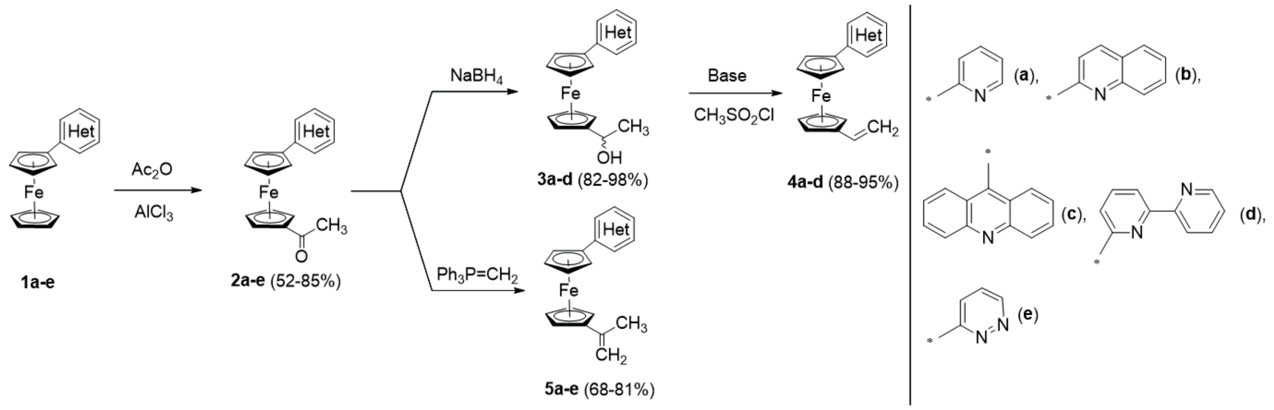
Ferrocene and its derivatives are attractive molecular systems due to their magnetic, electrical, electrochemical properties and low toxicity. After the discovery of it, the ferrocenes moiety have been incorporated into different substrates to obtain electrochemical sensors, biosensors, thin film transistors, light emitting diodes, molecular magnets, as well as semiconductors, conductors and charge storage materials. The introduction of a ferrocene fragment into the structure of azines makes it possible to modulate both the molecular characteristics of the resulting derivatives (solubility, hydrophobicity/lipophilicity) and to effect on the biological properties, often enhancing them.[1]

Previously, it was shown that Friedel-Crafts acetylation of monosubstituted azinylferrocenes occured regioselectively at the 1'-position of the ferrocene ring with an $Ac_2O/AlCl_3$ mixture (Scheme 1). Acetylated derivatives **2a-e** entered to the Wittig reaction with $Ph_3P{=}CH_2$ to form 1-azinyl-1'-isopropenyl-ferrocenes **5a-e** under mild conditions.[2] Moreover compounds **2a-e** are reduction under action of $NaBH_4$ followed by dehydration of alcohols **3a-e** to form 1-vinyl-1'- azinylferrocenes **4a-d** with high yields.



Scheme 1. Synthesis of vinylferrocenes.

It was found that the obtained vinylferrocenes exhibit high inhibitory activity against butyrylcholinesterase (BChE), high radical-scavenging activity, comparable or exceeding the activity of the standard antioxidant Trolox, as well as a high inhibitory activity against spontaneous of $A\beta_{42}$ self-aggregation. Therefore, these substances are perspective as potential multitarget drugs for the treatment of Alzheimer's disease.

This work was supported by the Russian Science Foundation (grant № 22-13-00298).

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REDETERMINATION OF SUPPOSEDLY KNOWN HYDRAZINE AND HYDROXYLAMINE CRYSTAL STRUCTURES

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The structure of hydrazine was published back in 1951, the structure of hydroxylamine – a little later, in 1955 [1, 2]. Both structures were determined doubtful; positions of H atoms were not found and crystal packing was poorly analyzed. Surprisingly, even though both hydrazine and hydroxylamine have found widespread use, including as rocket fuel and industrial chemicals, the qualitative determination of these structures – hydrazine and hydroxylamine – have somehow been neglected. So, after almost 70 years, it became possible to obtain and structurally characterize the crystals of hydrazine and hydroxylamine.

The previous crystal structure of hydrazine was found to be monoclinic $P2_1/m$ with two N_2H_4 molecules in a cell of dimensions a = 3.56(1), b = 5.78(1), c = 4.53(1) Å, β = 109.5(1)°, V = 87.9 Å^3 (from [1]) and monoclinic $P2_1/n$ with four N_2H_4 molecules in a cell of dimensions a = 4.6803(4), b = 5.7350(4), c = 6.5732(5) Å, β = 104.626(3)°, V = 170.72(2) Å^3 (this work).

Four molecules of hydroxylamine are in an orthorhombic unit cell of symmetry $P2_12_12_1$ and dimensions a = 7.29, b = 4.39, c = 4.88 Å, V = 156.6 Å^3 (from [2]) and a = 4.4388(4), b = 4.8175(4), c = 4.1720(6) Å, V = 153.37(2) Å^3 (this work).

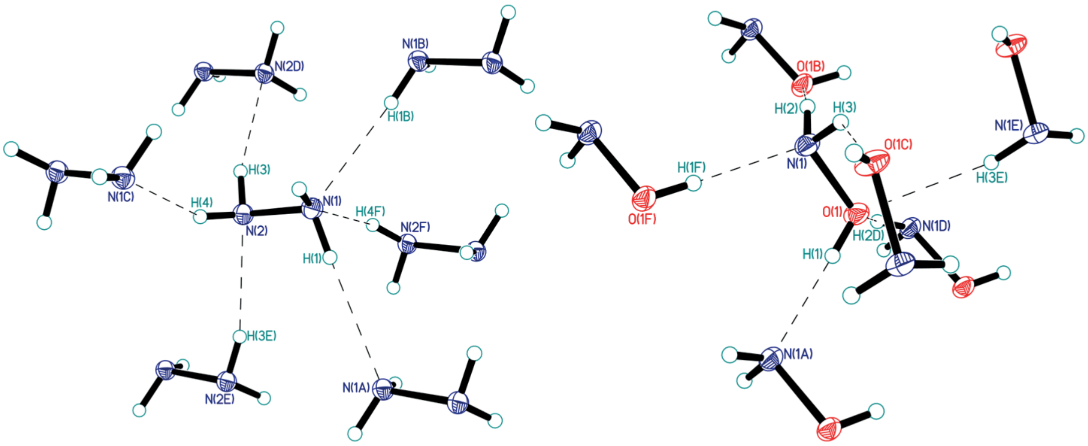

Figure 1. The 3D-system of H-bonds, formed by hydrazine (left) and hydroxylamine (right). Displacement ellipsoids are shown at 50% probability level. Hydrogen bonds are drawn by dashed lines.

Hydrazine molecule forms six H-bonds: three as H-donor N_H…N and three as H-acceptor N…N_H, for hydroxylamine molecule N-atom forms three H-bonds (two N_H…O and one O_H…N), and O-atom two O…N_H and one O_H…N. The N…N contacts ranging in 3.162-3.286 Å (for hydrazine) and N…O contacts vary within 2.735-3.143 Å (for hydroxylamine). The all N-H…N and N-H…O angles lie between 135.7 and 178.1°.

Acknowledgements. This work was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the State Assignment of the Kurnakov IGIC RAS.

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THE PREPARATION OF HIGH-ENTROPY ALLOYS BY COMBUSTION SYNTHESIS

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Materials containing of at least five metals with concentration between 5 and 35 at.% lead to new to a class of materials called high-entropy alloys (HEAs) [1]. The mechanical properties of HEA can vary significantly depending on the properties of each composing phase in the alloy; their volume ratio and distribution. HEAs containing Al, Fe, Co, Ni, Cr, Mn and Cu have been widely studied due to their excellent mechanical and magnetic properties from room to elevated temperatures, and even better properties at cryogenic temperatures. Among various HEAs, the manganese containing alloys are prone to exhibit new functional properties, such as superparamagneticity, superconductivity and superplasticity, while aluminum containg alloys exhibit corrosion and oxidation resistance [2]. In this work the preparation and characterization of the high-entropy alloys (MnFeCoNiCu, MnFeCoNiCr, $Al_2FeCoNiCr$, $AlFe_7Co_3Ni_2Cu_{0.4}$) by self-propagating high-temperature synthesis (SHS) using aluminothermic reduction from metal oxides is reported. Due to the high exothermicity of the aluminothermic process the combustion product is formed as a high-temperature multicomponent melt. Owing to the difference in densities of the combustion products (alumina slag and alloy) under the influence of normal gravity the phase separation occurs. Optimum conditions for the complete phase separation are as follows: combustion temperature should be higher than the melting point of alumina (2050°C). In this case, Al_2O_3 remains at the top of the melt, and the alloy of higher density is going down. The schematic representation of the HEA alloy formation process is as follows:

$$\varphi_1 Me'_xO_y + \varphi_2 Me''_xO_y + \varphi_3 Me'''_xO_y + Me'''' + Me^V + Al \rightarrow HEA + Al_2O_3$$

Combustion temperature and velocity for the studied mixtures were about 2100°C and 2 cm/s, respectively. Fast heating and slow cooling are characteristic to these processes (the heating and cooling rates were 15700 °/s and 7.6 °/s, respectively). As the combustion temperature is higher than the melting temperature of all components, complete phase separation was observed leading to the formation of single-phase products in the form of ingots. The composition of the synthesized HEAs was confirmed by XRD analysis. According to the latter, MnFeCoNiCu, MnFeCoNiCr HEA with FCC and $Al_2FeCoNiCr$, $AlFe_7Co_3Ni_2Cu_{0.4}$ HEA with BCC crystal structures were produced.

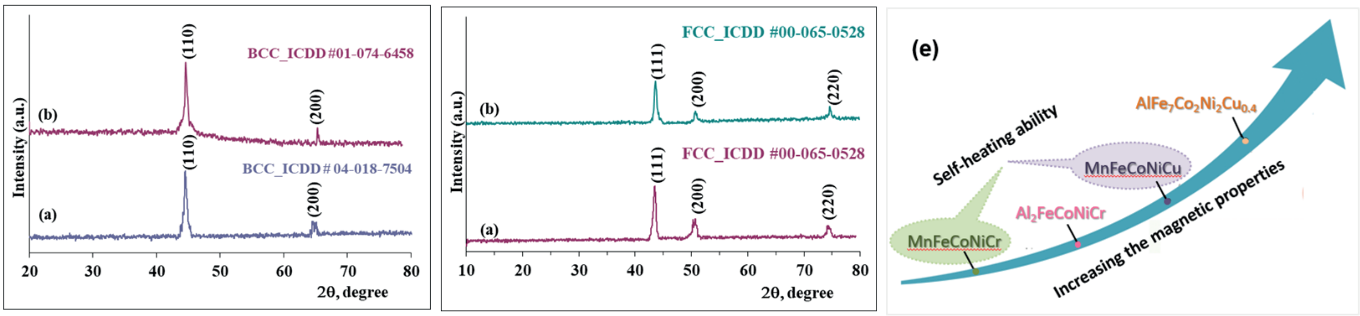

Fig. 1. XRD patterns of synthesized HEAs (a) MnFeCoNiCu, (b) MnFeCoNiCr, (c) $Al_2FeCoNiCr$, (d) $AlFe_7Co_3Ni_2Cu_{0.4}$ and (e) the ordering of HEAs according to properties

All investigated alloys are characterized by magnetic properties and are arranged in ascending order of magnetic properties evaluated against permanent magnet (Fig. 1d). Hence, Al-containing high entropy alloys are characterized by BCC structure, and Mn-containing ones by FCC structure. Furthermore, Mn containing alloys are prone to self-heating under the mechanical impact.

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ANTITUMOR Ru AND Pt COMPLEXES WITH TARGETING LIGANDS

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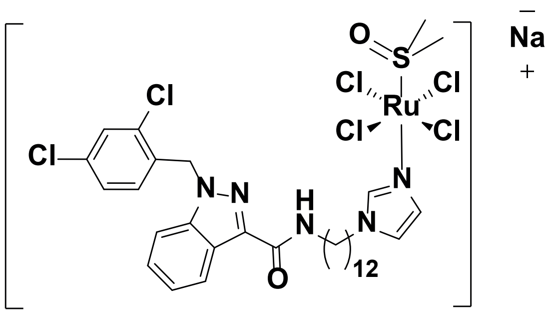
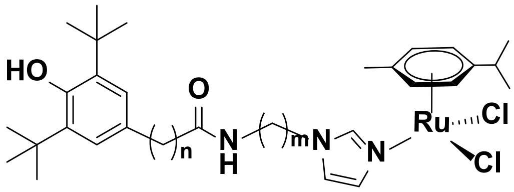
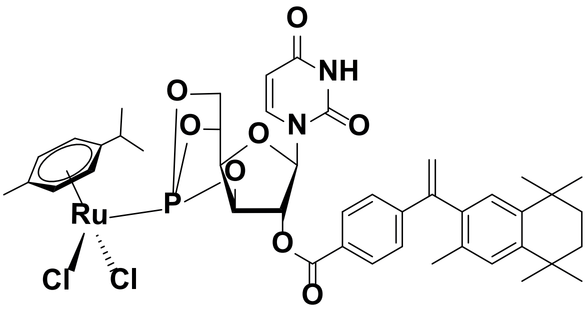
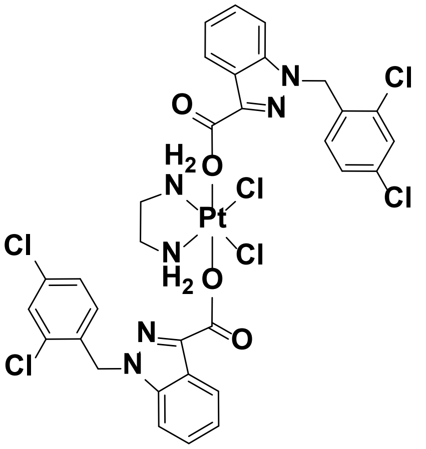
The search for the new metal-based anticancer compounds mostly focused on platinum(II) compounds; however, in the recent years much of interest is shifting towards development of Pt (IV) [1] and non-platinum anticancer drugs [2] and it was shown that the ruthenium-based compounds could be an excellent alternative of platinum drugs for the number of tumours. The antitumor activity of Pt and Ru compounds can be influenced oxidation state of the metal and by ligand sphere around a metal center. Linking Pt and Ru moiety to the targeting biologically active organic molecules can improve the anticancer properties.









This presentation will focus on the hybrid complexes of Pt(IV), Ru(II) and Ru(III) bearing biologically active moiety. Several compounds found to be highly cytotoxic against several of the human cancer cell lines with excellent selectivity towards cancer cells.

Acknowledgements: This work was supported by RSF project № 22-63-00016

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IODINE-CATALYZED C-H AMINATION OF CYCLIC NITRONES: A MECHANISTIC STUDY

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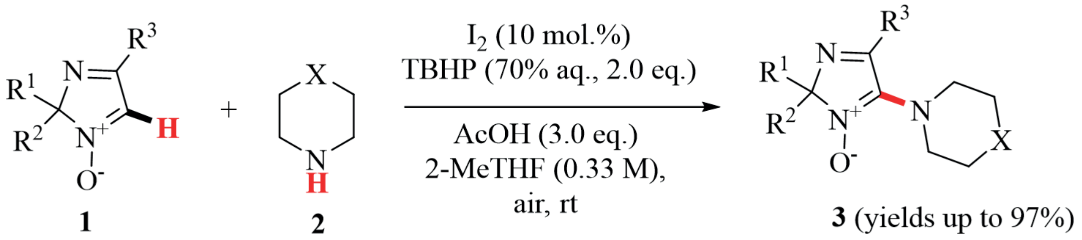
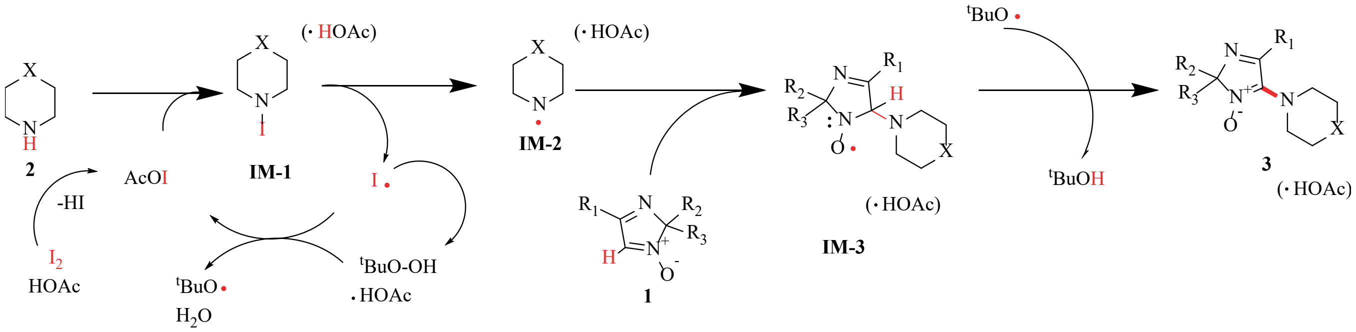
Cyclic nitrones represent a class of compounds of great interest not only because of the pronounced antiradical activities but also due to their synthetic versatility. For few previous years, our research group has been studying the reactivity of these compounds within the C(sp^2)-H functionalization methodology to develop original cross-dehydrogenative coupling approaches to be regarded as promising ones in terms of their "green" potential.

The current work deals with cross-dehydrogenative amination of model cyclic aldonitrones, non-aromatic imidazole oxides **1**, with alicyclic amines **2** (Scheme 1). The reaction is carried out in the presence of the oxidative system I_2 (cat.) / *tert*-butyl hydroperoxide (TBHP) to afford a series of 19 novel aminated cyclic nitrones in yields of up to 97%.



Scheme 1. C–H amination of nitrones **1**.

The mechanism for the discussed reaction initially was studied using conventional radical-scavenging experiments in the presence of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT), resulting in significant decrease in yields of **3**. The following in-depth investigation by EPR spectroscopy underpinned our suggestions for the radical nature of the process. Based on the collected experimental data, a plausible reaction mechanism has been proposed (Scheme 2).



Scheme 2. Proposed mechanism of the reaction.

The next step of our study is to expand the reaction scope and to assess the biological activity of the synthesized compounds **3**.

This research was funded by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-1118)

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MICHAEL ADDUCTS OF NEW METHYL 4(2-METHOXY-2-OXOETHYL)-1,2,3-THIADIAZOLE-5-CARBOXYLATE AND THEIR FUNGICIDAL ACTIVITY

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Substances containing a thiadiazole nucleus exhibit various biological activities, such as antifungal, antidepressant, antibacterial and antitumor activity, etc.[1]. Cyclic imides, that due to their structure easily pass through the cell membrane, also have a significant spectrum of biological activity, such as antifungal, antibacterial and insecticidal [2].

In this work, a new 1,2,3-thiadiazole **1** being CH-acid was reacted with a number of *N*-aryl-substituted maleimides in the presence of base. During the study of the influence of solvent, the nature of the catalyst and the conditions of the reaction, the best results were achieved with using triethylamine (25 mol.%) in a methanol solution under r.t.. The antifungal activity of the obtained substances against *Candida Albicans* was studied. Adducts **3 a-c** showed excellent fungicidal activity (6.25 - 390.6 μg/ml) together with good water solubility. The structures of the all obtained compounds were determined using ^{1}H, ^{13}C, ^{1}H-^{1}H COZY, ^{1}H-^{13}C HSQC NMR-spectroscopy and mass-spectrometry.

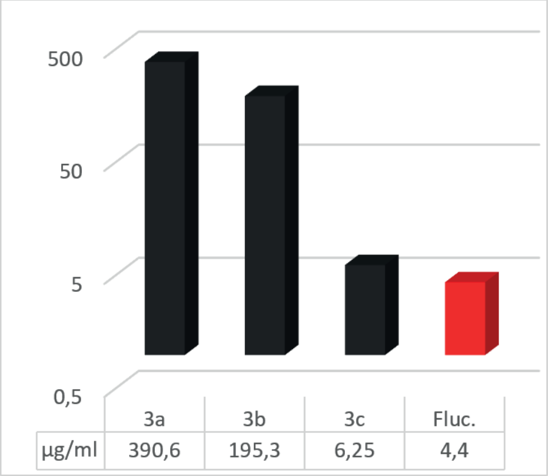
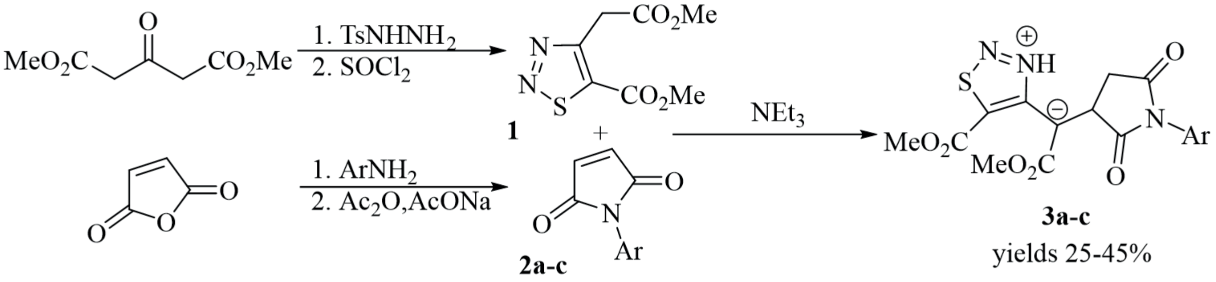


Figure 1. Fungicidal activity of compounds in comparison with Fluconazole.



Scheme 1. Synthesis of precursors and Michael adducts. Ar=Ph(a); Ar=4-CH$_3$Ph(b); Ar=4-ClPh(c).

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C(sp^2)-H FUCTIONALIZAION IN THE SYNTHESIS OF (THIO) PHENOLIC DERIVATIVES OF 2*H*-IMIDAZOLES

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Currently metal-free C(sp^2)-H functionalization reactions are of particular interest in the synthesis of various azaheterocyclic ensembles. Meanwhile, nucleophilic substitution of hydrogen (S_N^H) has become a convenient synthetic tool which is used for modification of heteroaromatic substrates. However, there are not many examples of its application for non-aromatic azaheterocyclic substrates. It's well known that imidazolic derivatives have a wide range of biological activities. Moreover, molecules with (thio)phenol and thiophenol moieties are exploited as pharmaceutical agents in treatment of different types of pathogenesis.

Thus, this study deals with systematic study of C-H functionalization of 2*H*-imidazole N-oxides by coupling with phenols and thiophenols in synthesis of promising molecules for medical chemistry.

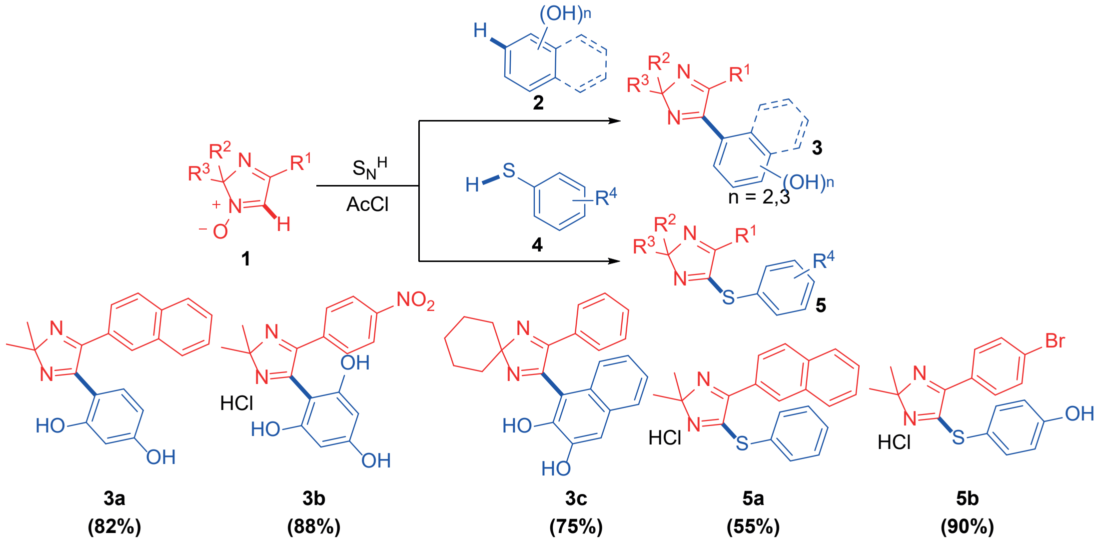

Figure 1 – C-H functionalization of 2*H*-imidazole N-oxides by (thio)phenoles

The study was funded by the Russian Science Foundation (RSF) according to the research project № 23-63-10011, https://www.rscf.ru/en/project/23-63-10011/

BODIPY CONJUGATES WITH TERPENE MOIETY AS FUNCTIONAL COMPOUNDS FOR MEDICAL DIAGNOSTICS AND TREATMENT

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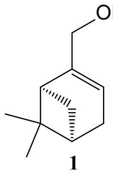
Fluorescent dyes absorbing and emitting in the visible and near-IR regions are promising for the development of fluorescent probes for labeling and bio-visualization of body cells. Compared to other fluorescent dyes, boron(III) dipyrromethenates (BODIPYs) are attractive due to their excellent photophysical properties. As part of conjugates with biomolecules, BODIPY could act as biomarker, but as therapeutic agent, which allows solving several problems at once - labeling or bioimaging and treatment based on the suppression of pathogenic microflora and cancer cells, which provides a huge potential for practical application of BODIPY conjugates in medicine [1].

The present investigation aims to synthesize new BODIPY conjugates with terpene fragment offered as tools for biological objects visualization. We demonstrated the effect of various *meso*-substituents in BODIPY molecules on their properties. For example, the fusion of the solely terpenic alcohol – (+)-myrtenol ***1*** to BODIPY fluorophore ***2*** in the *meso*-substituent (conjugate ***3***) facilitated the penetration into filamentous fungi *F. solani*, while impaired the binding of the latter with *S. aureus, K. pneumonia* and *P. aeruginosa* [2]. The additional quaternary ammonium group between myrtenol and fluorophore moieties (conjugate ***4***) restored the bacterial cells staining did not affect staining of fungi.



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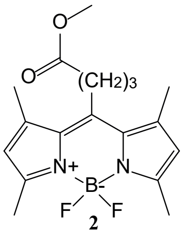

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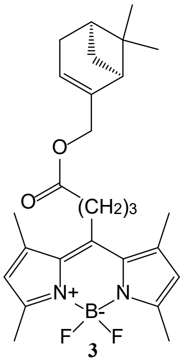

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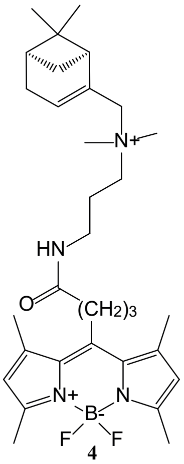

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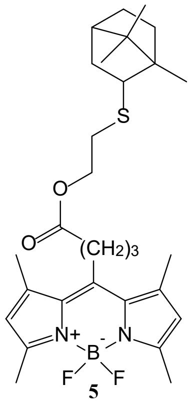

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The BODIPY fused to myrtenol via quaternary ammonium group exhibited high fluorescence efficiency in media of various nature and stability over a wide pH range, assuming the practical potential of the synthesized BODIPY conjugates as fluorescent markers for biomedical applications. In addition, our results demonstrated that covalent binding of the sulfur-containing terpenoids to the carboxylic acid residue of meso-substituted BODIPY (conjugate **5**) is an excellent way to increase affinity dyes to biostructures, including blood components [3].

This work was supported by the Russian Science Foundation (grants N 20-64-47014(biology) and 20-63-47026 (spectral investigations)) and by Kazan State Medical University (Project N 58-012-2022 (synthesis)).

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3. G.B. Guseva, E.V. Antina, M.B. Berezin, et al. Bioengineering (2022) 210.

SYNTHESIS OF *bis*-THIOALKYLDERIVATIVES OF THENO[3,2-*d*]PYRIMIDINES

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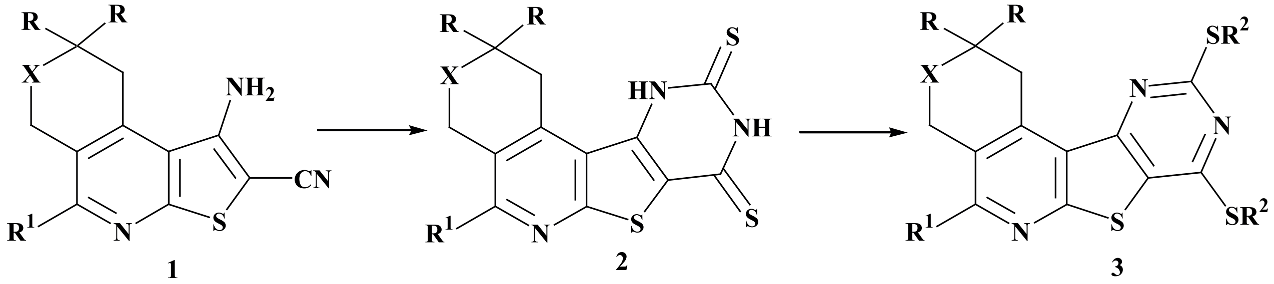
Heterocyclic compounds and their fused analogs which containing pharmacophore fragments such as pyridine, thiophene and pyrimidine ring are of great interest due to their broad spectrum of biological activity. Chemical compounds containing two or more pharmacophore groups due to additional interactions with active receptor centers usually enhance biological activity and even lead to a new type of biological activity [1, 2]. Moreover, tri-; tetra- and pentacyclic systems containing pyridine and pyrimidine rings were endowed biological properties and the addition of a cycle does not reduce biological activity [3]. In continuation of the work on the synthesis of condensed tetracyclic thieno[3,2-*d*]pyrimidines, we have developed method for obtaining new *bis*-thioalkylderivatives of thieno[3,2-*d*]pyrimidines. Thus, a method for obtaining condensed thieno[3,2-*d*]pyrimidine-dithiones **2** based on 1-amino substituted condensed thieno[2,3-*b*] pyridine-2-carbonitrile **1** was developed. Based on tetracyclic thieno[3,2-*d*]pyrimidine-dithiones **2** and alkylating agents bis-thioalkylderivatives of thieno[3,2-*d*]pyrimidine **3** were synthesized. The structures and purity of new synthesized fused pharmacophore heterocycles by physicochemical methods were confirmed.



$X = CH_2$, O; R = H, Me; R^1 = cycloamino; R^2 = Alkyl.

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CONSTRAINED DFT-BASED MAGNETIC MACHINE-LEARNING POTENTIALS FOR MAGNETIC ALLOYS

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In this talk, we propose a machine-learning interatomic potential for multi-component magnetic materials. In this potential we consider magnetic moments as degrees of freedom (features) along with atomic positions, atomic types, and lattice vectors. Our multi-component magnetic MLIP is based on the previously developed non-magnetic MLIP for multi-component systems [1] and magnetic MLIP for single-component systems [2].

We create a training set with constrained DFT (cDFT) [3] that allows us to calculate energies of configurations with non-equilibrium (excited) magnetic moments and, thus, it is possible to construct the training set in a wide configuration space with great variety of non-equilibrium atomic positions, magnetic moments, and lattice vectors. Such a training set makes possible to fit reliable potentials that will allow us to predict properties of configurations in the excited states (including the ones with non-equilibrium magnetic moments). We use ABINIT [4] for DFT (cDFT) calculations.

We verify the trained potentials on the system of bcc Fe-Al with different concentrations of Al and Fe and different ways Al and Fe atoms occupy the supercell sites. Here, we show that the formation energies, the equilibrium lattice parameters, and the total magnetic moments of the unit cell for different Fe-Al structures calculated with machine-learning potentials are in good correspondence with the ones obtained with DFT. We also demonstrate that both the machine-learning interatomic potentials and DFT qualitatively reproduce the experimentally-observed anomalous volume-composition dependence in the Fe-Al system.

This work was supported by Russian Science Foundation (grant number 22-524 73-10206, https://rscf.ru/project/22-73-10206/).

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NOVEL AMBIVALENT HYBRID PHOTOCATALYSTS BASED ON PORPHYRIN SURMOFS AND GRAPHENE OXIDE

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In this work, we report a new method for the synthesis of hybrid photocatalysts comprising graphene oxide (GO) and zinc porphyrin complexes ordered into surface-attached metal organic frameworks (SURMOFs). To obtain the SURMOF/GO hybrids in a powdered form, we developed a one-pot synthesis in the GO-stabilized oil-in-water Pickering emulsions. The oxidized groups on the GO sheets promote the adsorption of metal clusters followed by anchoring of porphyrins to the surface of 2D carbon.

The results of experimental studies involving X-ray diffraction, UV-vis spectroscopy, BET nitrogen absorption, gas chromatography and MALDI-TOF mass-spectrometry. The data suggest that these mesoporous SURMOF/GO hybrids can exploit two different mechanisms yielding different products of photocatalytic degradation of model organic compounds such as rhodamine 6G (Rh6G) and 1,5-dihydroxynaphtalene (DHN). The oxidation through photoinduced generation of singlet oxygen on porphyrin centers occurs in the presence of oxygen. In anaerobic conditions, the catalysts can promote reduction by a direct electron transfer to the substrates in the SURMOF pores. The SURMOF/GO with the pore size of 1.6 nm can transform both Rh6G and DHN (fig. 1), whereas the material with 1.1-nm pores is active only with respect to the small DHN molecules. The results provide a rational basis for the substrate-selective GO-based hybrid photocatalytic materials integrated with SURMOF components with tunable porosity [1].

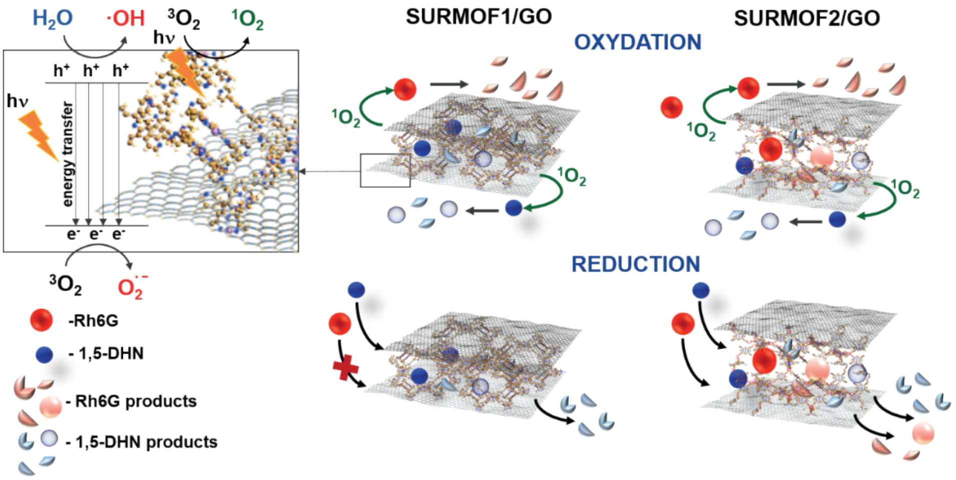

Figure 1. Schematic illustration of the proposed size-selective mechanism of photodestruction of Rh6G and DHN in the presence of the SURMOF1/GO and SURMOF2/GO under aerobic and anaerobic conditions.

Acknowledgements: The Russian Science Foundation supported this work (project No 23-73-00095).

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TRANSFORMATIONS OF 1-R-1-CARBMETHOXYETHYNYL-2-CARBMETHOXYVINYL-1,2,3,4-TETRAHYDROISOQUINOLINES IN HEXAFLUORO-2-PROPANOL AND ACETIC ACID

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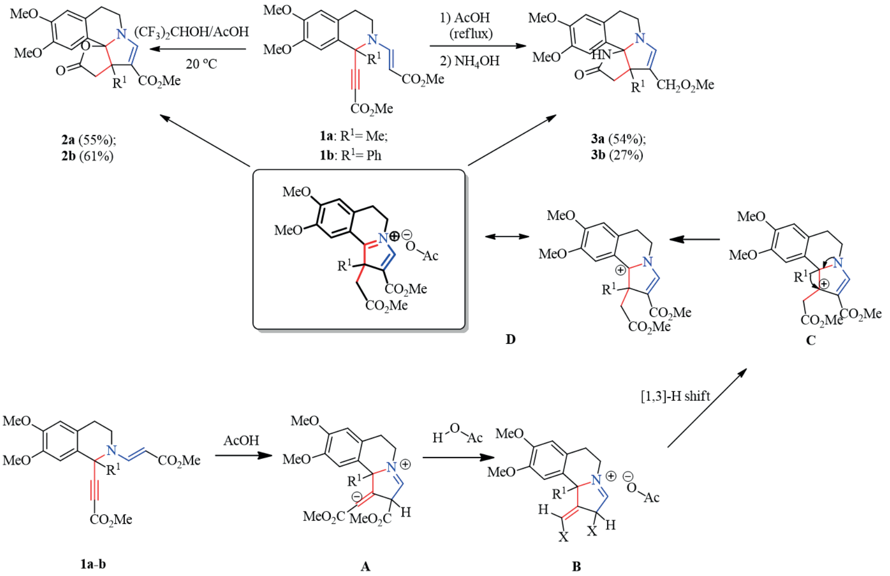
[3,3]-Sigmatropic and *N*-propargyl aza-Claisen rearrangements are widely used in organic synthesis to construct pyrrole and pyridine rings or to annelate their fragments to various cyclic compounds[1]. In this work, we report a new approach to the synthesis of furo[2’,3’:2,3]pyrrolo[2,1-*a*]isoquinolines and pyrrolo[2’,3’:2,3]pyrrolo[2,1-*a*]isoquinolines from isoquinolines **1a,b** in hexafluoroisopropanol and acetic acid. Starting compounds **1a,b** were obtained by the reaction of 1-R^1-6,7-dimethoxy-3,4-dihydroisoquinolines with an excess of methyl propiolate in CH_2Cl_2 at 20 °C.



On the one hand, lactones **2a**,**b** were formed in 55-61% yield from starting isoquinolines under the influence of hexafluoroisopropanol with the addition of acetic acid. On the other hand, refluxing compounds **1a**,**b** in acetic acid followed by extraction with aqueous ammonia led to lactams **3a**,**b** in 27-54% yield. In our opinion, the formation of salt **D** is the key stage of the reactions.

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QUATERNIZED SEMISYNTHETIC DERIVATIVES OF POLYENE ANTIFUNGAL ANTIBIOTICS

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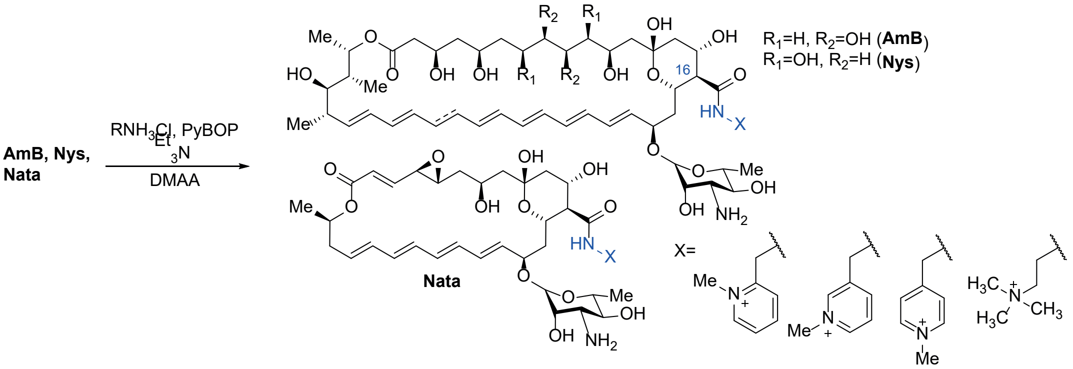
Systemic mycoses pose a serious danger, especially for patients with reduced immunity. Despite over sixty years of clinical use, amphotericin B (AmB) remains the gold standard in the treatment of severe fungal infections due to its wide spectrum of antifungal activity and low rate of clinically significant drug resistance [1]. Violation of the zwitterionic nature can significantly improve the pharmacological profile of polyene antibiotics [2]. However, to date, no derivatives of amphotericin or other polyenes containing a constant positive charge in their structure have been described, although this modification seems quite interesting in relation to the structure-property relationship data. Here, we present an investigation of a series of quaternized amides of polyene antibiotics (amphotericin B, nystatin, and natamycin).



Amphotericin B, nystatin, and natamycin were condensed with the hydrochlorides of 2-, 3-, and 4-*N*-methylpicoline and *N*,*N*,*N*-trimethylethylenediamine. The activity of *N*-(2-(trimethylamino)ethyl)amide of AmB was close to that of the parent antibiotic and the corresponding amides of nystatin and natamycin showed slightly reduced activity. Among the various picolylamide isomers, 4-*N*-methylpicolylamides showed the best activity for all tested polyene types (AmB, Nys, Nata). Additionally, the 4-*N*-methylpicolylamide of natamycin showed the ability to induce calcein leakage from POPC/Erg-liposomes at a concentration of 5 μM and to produce pronounced aggregation of the POPC/Erg (67/33 mol%) vesicles, in contrast to the parent antibiotic and other tested semisynthetic derivatives. The most active 4-*N*-methylpicolylamide of AmB was tested for antibiofilm activity against *Candida* spp. The ability of this derivative to cause cell death in the biofilm was equal to that of AmB, but its action led to the eradication of both the biofilm at the early stages of development (24 hours) and the formed dense 48-hour biofilm of *C. parapsilosis* 58L at a concentration of 2 μg/ml, unlike amphotericin B, which did not show such an effect. Quaternized amides of AmB and nystatin did not show a difference in their ability to disrupt Erg-containing membranes compared to Chol-containing ones when compared to native antibiotics. However, derivatives of nystatin and natamycin were less toxic to mammalian cells than natural polyenes. Quaternized amides of AmB produced pores of smaller amplitude than AmB did under the same conditions. Modification of the negatively charged carboxyl group with a positive radical led to a decrease in the lifetime of the transmembrane pores and their probability of being open due to electrostatic repulsion between positively charged derivative molecules, destabilizing the channel. However, these observations were also noted in the case of other AmB derivatives with neutral radicals, bearing additional basic groups in the amide moiety [3].

This research was funded by the Russian Science Foundation, grant number 21-74-20102

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β-NITRO-SUBSTITUTED 4*H*-CHROMENES AND BENZOFURANS AS A PLATFORM FOR THE SYNTHESIS OF HYBRID HETEROCYCLES

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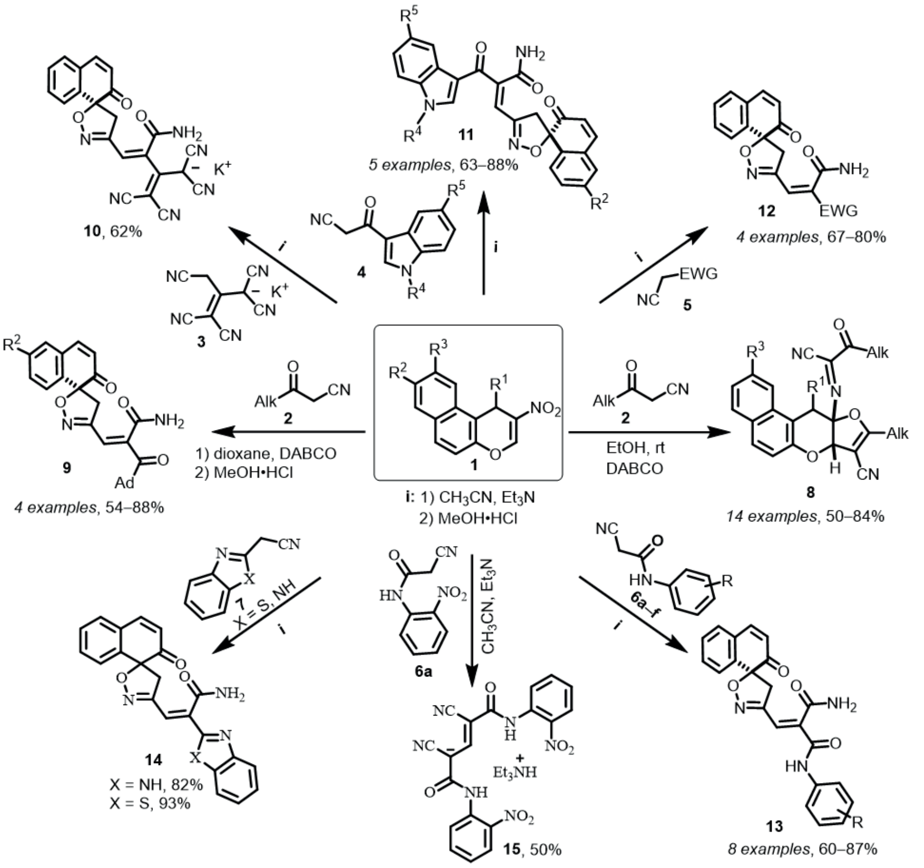
3-Nitro-4*H*-chromenes and closely related 3-nitrobenzofurans are grouped together by a common structural unit [–OCH=C(NO_2)–], which determines their high reactivity both in the processes of conjugated addition and cycloaddition and makes them useful in the synthesis of various hybrid heterocycles, including fused and spirocyclic ones.

We have shown that the reaction of 2-nitro-1*H*-benzo[*f*]chromenes **1** with methylene active nitriles **2-7** in the presence of a base leads to the opening of the pyran ring and the formation of the salts, which rearrange in an acid medium to form spiroisoxazolines **9-14**. It was found that the reaction of benzo[*f*]chromene **1a** with an excess of *N*-(2-nitrophenyl)-2-cyanoacetamide **6a** in the presence of a base leads to the formation of triethylammonium 1,3-dicyanoprop-2-en-1-ide **15**. At the same time, carrying out the reaction of benzo[*f*]chromenes **1** with aliphatic β-ketonitriles **2** in an alcoholic medium in the presence of catalytic amounts of base provides access to 11*H*-benzo[*f*]furo[3,2-*b*]chromenes **8**. In addition, the report will discuss new transformations of 3-nitrobenzofurans under the conditions of the Michael reaction and dipolar cycloaddition.



This work was supported by the Russian Science Foundation (grant no. 22-73-10104).

ASSESSMENT OF ANTIOXIDANT PROPERTIES OF PHENOLIC DERIVATIVES OF PROLINE

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The antioxidant properties of chiral thioacetyl derivatives of proline – (L)-, (D)-methyl (2-((2-hydroxyphenyl)thio)acetyl)prolinate (**1**), (**2**) and (L)-, (D)-(2-((1-hydroxynaphthalen-2-yl)thio)acetyl)prolinate (**3**), (**4**) – were studied in this work. The ability of compounds to reduce Cu(II) to Cu(I) in the neocuproine complex (CUPRAC assay) and the Fe(III) reduction to Fe(II) (FRAP assay) was determined by spectrophotometry using known procedures. The results have been presented in Trolox Equivalent Antioxidant Capacity (TEAC), a water-soluble vitamin E analog. The studies demonstrated no significant difference among the stereoisomers in activity to reduction of iron and copper ions (tabl.). Wherein, the activity of compounds **1-4** in relation to the reduction of copper was at the level of Trolox, with respect iron, the activity of enantiomers **3** and **4** exceeded Trolox of 1.5 times.

compounds	$TEAC_{CUPRAC}$	$TEAC_{FRAP}$
1	1.02 ± 0.10	0.45 ± 0.05
2	0.85 ± 0.07	0.34 ± 0.05
3	1.00 ± 0.09	1.57 ± 0.11
4	0.86 ± 0.07	1.53 ± 0.13

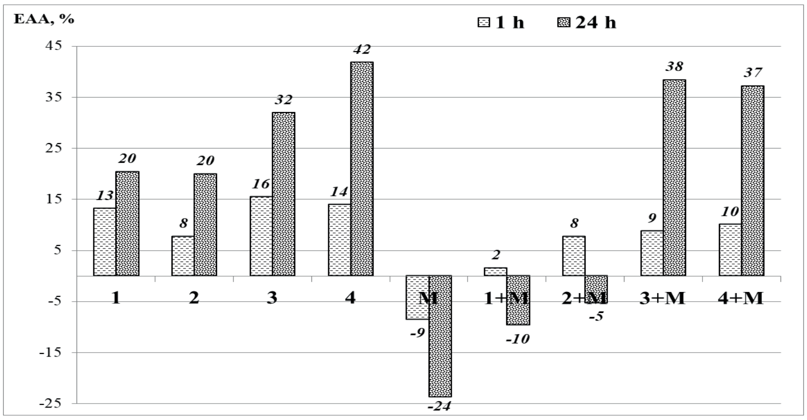

*Fig. Efficiency of the antioxidant action (EAA, %) of proline derivatives **1-4** in the conditions of autoxidation of beluga sperm lipids and at promotion of the $FeCl_2$ (**M**) process of lipid peroxidation.*

Excess transition metal ions, such as Fe(II), can generate $OH^{\bullet}$ in biological systems through Fenton-like reactions. Potential antioxidants are able to chelate Fe(II), inhibiting the formation of $OH^{\bullet}$ and oxidative damage. The Ferrous Ion Chelating (FIC) activity was determined as the percent of total ferrozine/Fe(II) binding. It was found that proline derivatives **1-4** were significantly inferior in FIC activity to the positive control EDTA. The effect of 2 pairs of enantiomers on the level of lipid peroxidation (LPO) of beluga sperm was also studied in the work. The effect of the compounds on the LPO was determined through 1 h and 24 h in the conditions of autoxidation of beluga sperm lipids and at promotion of the $FeCl_2$ (**M**) process of lipid peroxidation. To assess the anti-/pro-oxidant action of the compounds, the effectiveness of the antioxidant action (EAA, %) was calculated, where a positive value indicates an antioxidant effect, a negative value indicates a pro-oxidant one. After 1 h of incubation of beluga sperm with the compounds **1-4**, an antioxidant effect was established under autoxidation conditions (8-16%) and in the presence of the promoting agent $FeCl_2$, but much less (2-10%). $FeCl_2$ has a promoting effect, increasing over time from 9% (1 h) to 24% after 24 hours. The EAA of the compounds after 24 hours increases to 20-42%, enantiomers **3** and **4** have demonstrated the highest activity. In the presence of $FeCl_2$, the antioxidant properties of derivatives **1** and **2** were inverted (5-10% promoting), in contrast to derivatives **3** and **4**, the effectiveness of which remains at the level of 37-38%, which indicates their ability to reduce the promoting effect of transition metal ions. Thus, a high antioxidant activity of (L)- and (D)-(2-((1-hydroxynaphthalen-2-yl)thio)acetyl)prolinates has been established, which allows us to consider the possibility of their use as effective inhibitors of oxidative processes.

This work was supported by the Russian Science Foundation (grant № 22-16-00095).

THEORETICAL INVESTIGATION OF Cs AND Sr RADIONUCLIDES EXTRACTION FROM HIGH-LEVEL WASTE

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Development of new separation techniques of radionuclides from high-level waste (HLW) is one of the most important parts of nuclear industry, due to high potential adverse influence of radioactive isotopes on human health and environment. Although a lot of various separation technologies were proposed in recent years, selective removing of radiocesium ^{137}Cs and radiostrontium ^{90}Sr from wastewater still remains a challenge task.

In this work we performed a quantum chemical modelling in order to study the extraction of cesium and strontium ions from nitric acid media to organic phase. As extragents for Cs and Sr we considered 4,4’(5’)-di-tert-butyldicyclohexyl-18-crown-6 ethers and as both diluents and organic media we considered bis-(2,2,3,3-tetrafluoropropyl)carbonate (BK-1) and bis(2,2,3,3-tetrafluoropropoxy)methane (FN-1). All calculations were carried out on density functional theory (DFT) level, which is a reliable and efficient electronic structure method for the supramolecular systems.

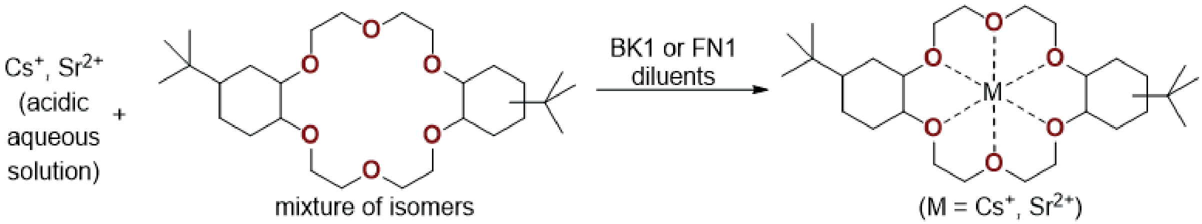

Fig.1 Scheme of cesium and strontium ions extraction by crown ethers into organic phase

Our first goal was to obtain the most possible structures of cesium and strontium complexes with different isomers of 4,4’(5’)-di-tert-butyldicyclohexyl-18-crown-6 ethers in water and organic solutions and evaluate their geometrical parameters. The second goal was to study the thermodynamics of extraction process by determining stability constants of metal-crown complexes as well as overall extraction constant.

NEW ASPECTS OF THE REACTIVITY OF HIGHLY POLARIZED 4*H*-CHROMENES AND THEIR BENZO ANALOGS

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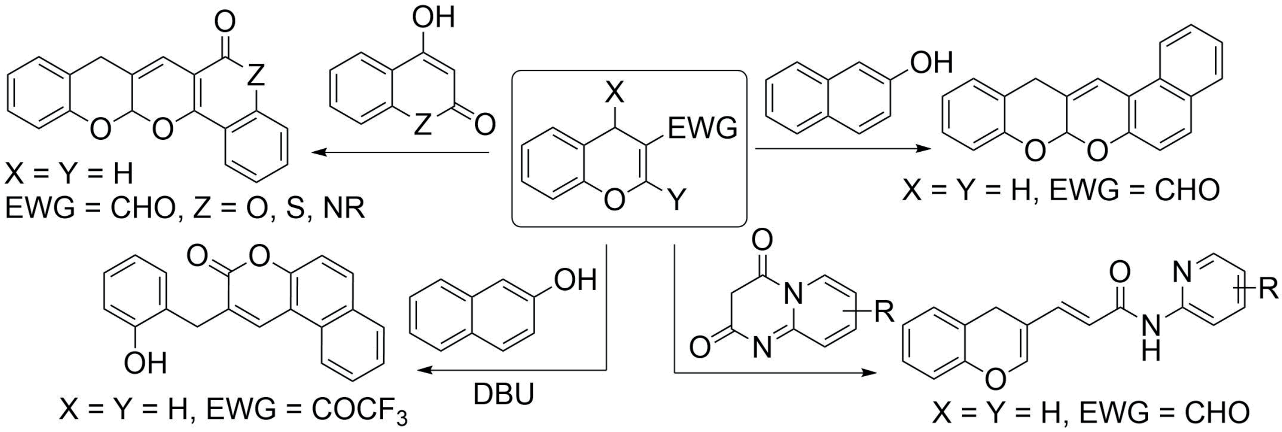
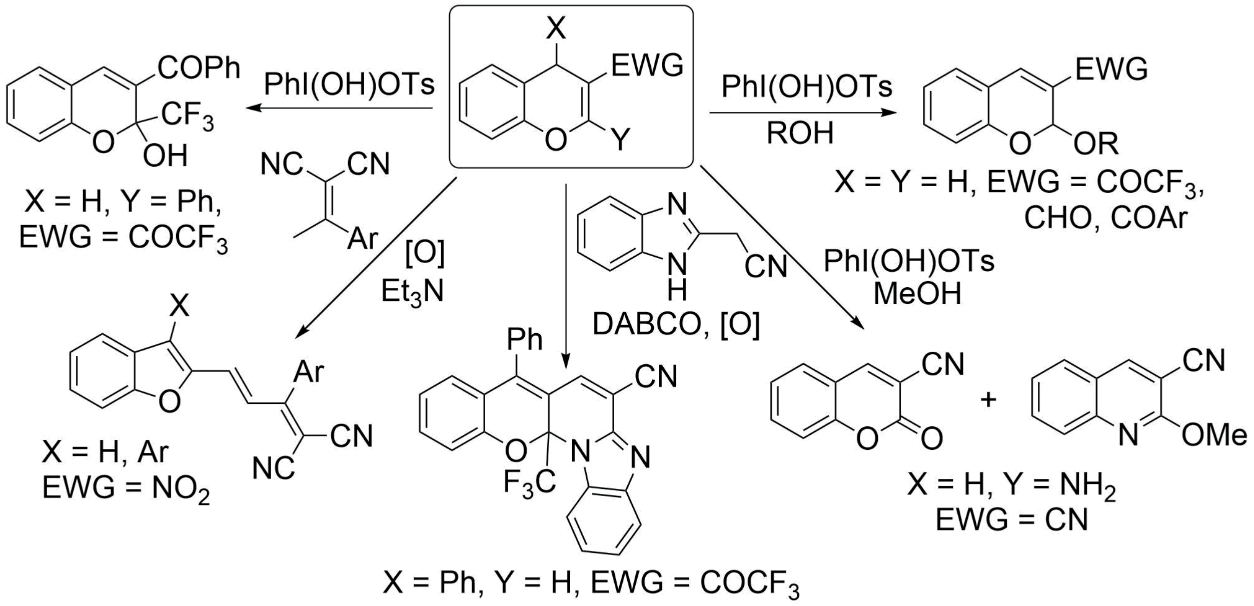
The presence of an electron-withdrawing group at the β-position of 4*H*-chromenes sharply increases the susceptibility of the pyran ring to the action of various nucleophiles, which makes these compounds valuable building blocks in the synthesis of a wide variety of heterocyclic compounds.

The report will consider the transformations of push-pull 4*H*-chromenes and their benzo analogs with various mono- and binucleophiles, in which both opening and preservation of the pyran ring occurs, as well as cascade transformations, including pericyclic processes, for example:



In addition, domino processes involving oxidants (primarily polyvalent iodine compounds) and nucleophiles will be discussed.



This work was supported by the Russian Science Foundation (grant no. 22-13-00253).

SPIROPYRAN-BASED PHOTOACIDS BEARING A FRAGMENT OF β-ESTRADIOL WITH PHOTOMODULATED BIOACTIVITY

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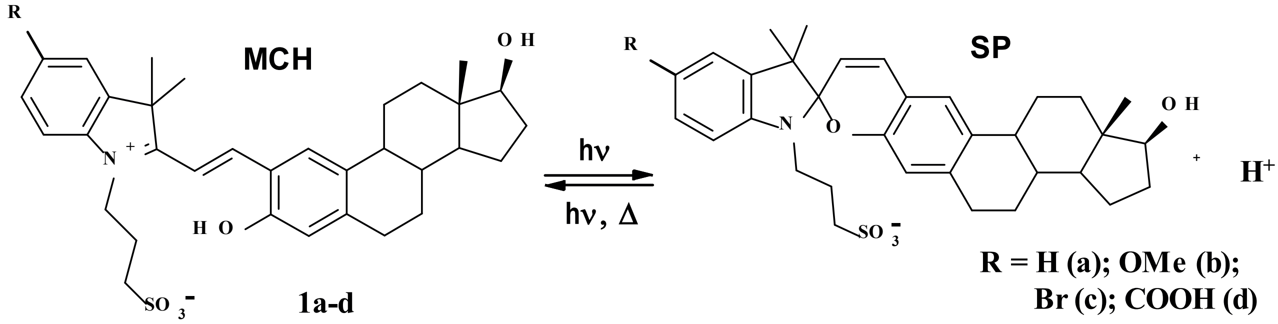
Spiropyrans are one of the most interesting and promising classes of organic photochromic compounds capable of switching between different forms under the action of activating radiation and other external stimuli [1]. Several past years special attention has been paid to self-protonated merocyanine forms of spiropyrans (MCH), which recommended themselves as effective reversible photoacids (PA) – molecules capable of generating protons upon visible-light irradiation [2]. Due to these properties PAs are of great interest for controlling catalytic reactions, ion exchange and other processes, especially in biological systems.

In this work we synthesized novel PAs of indoline series **1a-d** containing a fragment of *β*-estradiol – one of the most important female sex hormones possessing a wide range of biological activities including anti-atherosclerotic, anti-inflammatory and antioxidant properties. Particular attention is drawn to some estrogenic metabolites and their synthetic analogues possessing anticancer activity against various types of cancer cells. The presence of a photoswitchable function in a bioactive compound can give it the ability to control biological activity using light in a unique and natural way.



1a-d

R = H (a); OMe (b); Br (c); COOH (d)

Photochemical studies revealed different photochromic activity for synthesized compounds. Thus, **1a-c** demonstrated negative photochromism under both visible and UV irradiation, while **1d** exhibited the unusual for PAs photochromic "balance" properties.

A series of biological studies were performed to assess the potential activity of compound **1a** with photoactivation and without it on the model of HeLa cells, such as cytotoxicity, the effects on signaling activity of the *NFE2L2/AP-1* cascade, the delayed effects on cell viability, proliferation, and xenoresistance, as well as a signaling pattern in the supersystem of the epithelial-mesenchymal transition (EMT) of cells. It was found that PA **1a** possesses low toxicity, which can be lowered by irradiation with visible light, demonstrates signaling activity associated with AP-1 deregulation and moderate prooxidant activity. Moreover, it reduced the representation of the cell population enriched with cancer stem cells, regardless of photoactivation and at both concentrations studied. These facts make PA **1a** a potential anti-cancer stem cell agent without pronounced signaling side effects.

The study was financially supported by the Russian Science Foundation grant No. 21-73-10300, https://rscf.ru/project/21-73-10300/, and carried out at Southern Federal University.

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SYNTHESIS OF NEW DERIVATIVES OF CONDENSED THIENO[2,3-*b*]PYRIDINES AND THIENO[3,2-*d*]PYRIMIDINES

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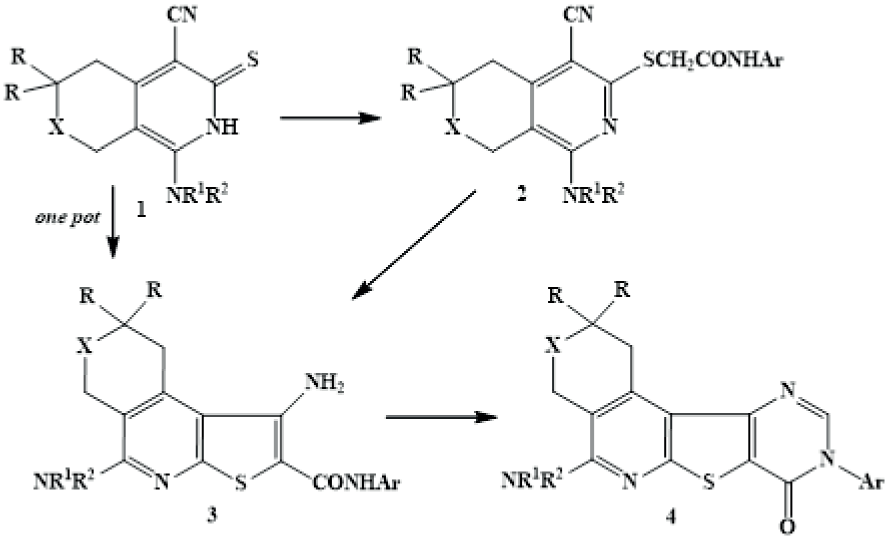
In the aspect of the synthesis of difficult heterocyclic compounds thieno[2,3-*b*]pyridines and thieno[3,2-*d*] pyrimidines are of great importance. In addition, derivatives of these heterosystems have wide spectrum of biological activity [1, 2]. In continuation of the work on the synthesis of biologically active compounds in the series of fused pyridines, we have developed methods for obtaining new derivatives of thieno[2,3-*b*]pyridines and pyrido[3′,2′:4,5]thieno[3,2-*d*]pyrimidines condensed with tetrahydropyran and cyclohexane rings. The synthesis of new heterocyclic compounds based on pyridinethiones **1** was carried out [3]. Thieno[2,3-*b*]pyridines **3** were synthesized via a one-pot reaction involving the interaction of pyridinethiones with chloroacetic acid amides. On the other hand, the synthesis method of thioalkyl derivatives **2** has been developed. Thieno[2,3-*b*] pyridines **3** also have been synthesized through the intramolecular cyclization of thioalkyl derivatives **2**. The presence of convenient functional groups in the thiophene ring of condensed thienopyridines made it possible to develop method for synthesis of *N*-aryl-substituted thieno[3,2-*d*]pyrimidines **4**.



$X = CH_2, O; R = H, Me; R^1R^2 = (CH_2)_4, (CH_2)_5, (CH_2)_2O(CH_2)_2; (CH_2)_2CH(Me)(CH_2)_2$

This work was supported by the Science Committee of RA (Research project № 21T-1D231).

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NEUROTROPIC ACTIVITY OF NEW S-ALKYL DERIVATIVES OF 8- PYRAZOL-1-YL PYRANO[3,4-*c*]PYRIDINES

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Synthesis of pharmaceuticals for the treatment of neuropsychiatric disorders, in particular epilepsy, is a serious challenge for synthetic organic chemistry. The most antiepileptic agents which used in medicine often cause toxic side responses from different organs and systems, emotional disturbances, impaired memory, etc. [1]. In this regard, in the new row of compounds the search and study of anticonvulsants possessing the combined psychotropic properties is of unquestionable interest.

The derivatives of condensed pyridines are of interest as biologically active substances. Thus, a large number of substituted pyrazolopyridine derivatives have been found to possess various biological properties such as A(1) adenosine receptor antagonists, antimicrobial, non-anionic antiplatelet agents, psychotropic effects.

Neurotropic activity of new derivatives of pyrazol-1-yl substituted pyrano[3,4-c]pyridine was studied. Anticonvulsant activity was investigated by maximal electroshock (MES) and pentylenetetrazole (PTZ) convulsions tests [2]. The PTZ subcutaneous test is a petit mal (generalized clonic seizures) model of epilepsy, while MES is grand mal (generalized tonic seizures). Comparison with the prominent antiepileptic drugs ethosuximide and the tranquilizer diazepam was performed [3].The neurotoxicity of the compounds was studied on the ‘’rotating rod’’ model. The psychotropic properties of the compounds were studied using the tests: “open field”, “elevated plus maze “, “forced swimming”.

Researched compounds were found to antagonized corazole. The ED_{50} (with intraperitoneal injection) of these compounds ranged from 24 mg/kg to 34 mg/kg. It should be noted that tested compounds are superior to ethosuximide, according to the anticorazole activity, but inferior to diazepam. TD_{50} of the studied compounds ranged from 505 mg/kg to 590 mg/kg. Ethosuximide has the same neurotoxic effect, unlike to diazepam, which causes muscle relaxation already at doses of 2-3 mg/kg. Maximal tolerated dose (MTD) of the studied compounds and ethosuximide are ranged in range of from 1000-1350 mg/kg and for diazepam – 200 mg/kg. It should be mentioned that replacement of the hydrazine fragment by the pyrazole ring in the pyranopyridine system increased the anticonvulsant activity. And replacement of the sulfur atom by the oxygen in the pyranopyridine system decreased the anticonvulsant activity. Substitution on the sulfur atom of the 6th position of the pyranopyridine ring with larger alkyl and prop-2-yn-1-yl group increased the anticonvulsant activity. The selected compounds exhibited pronounced anti-anxiety and some antidepressant activities similar to diazepam. Selected compounds as well indicates sedative activity. The investigated compounds can be used in pharmacology as anticonvulsants with anxiolytic properties.

This work was supported by the RA MES State Committee of Science,
in the frames of the research project № 20TTWS-1D032.

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SYNTHESIS AND NEUROTROPIC ACTIVITY OF NEW DERIVATIVES OF AMINO ACID HYDANTOINS AND THEIR LITHIUM SALTS

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Recently, in therapy with antiepileptic drugs, mainly of the second generation, there has been a tendency to optimize treatment, aimed at the use of anticonvulsants with extended combined properties [1]. Basically, anticonvulsant (antiepileptic) drugs include derivatives of barbituric acid, hydantoin, benzodiazepine, etc. One of the popular anticonvulsants are hydantoin derivatives, namely Dilantin or Difenin [2]. Numerous derivatives of Difenin are known in the literature. It should be noted that amino acid hydantoin derivatives are important products in the pharmaceutical industry, cosmetology, etc., their scope is very extensive - from antiseptic additives in cosmetics to the relief of manic syndrome in manic-depressive psychosis.

The well-known antiepileptic drug dilantin and hydantoins of DL-β-phenyl-α-alanine, DL-tryptophan and their lithium salts were synthesized. The anticonvulsant and psychotropic properties of these substances have been studied. The anticonvulsant spectrum of action of the compounds was studied using the tests: corazole (pentylenetetrazole) convulsions, maximal electric shock, and thiosemocarbazide convulsions [3] in mice of both sexes weighing 18–24 g. The psychotropic properties of the compounds were studied using the tests: “open field”, “elevated plus maze - PCL”, “forced swimming”, as well as the effect on the activity of monoamine oxidase (MAO). The side neurotoxic (muscle relaxant) effect of substances was also studied, which was investigated by the “rotating rod” test in mice. A morphological and pathohistological study of the synthesized hydantoins and lithium salts was carried out.

Five studied compounds, derivatives of amino acid hydantoins and their lithium salts have neurotropic properties, both anticonvulsant and psychotropic. Compounds that prevent clonic corazole, maximal electroshock generalized tonic convulsions, antithiocarbazide action in animals, have an pronounced anxiolytic and behavior activating effect in various models. At the same time, the compounds exhibit antidepressant and antiMAO effects. In the studied doses, the compounds do not have a muscle relaxant effect. In some of their neurotropic properties, the compounds surpass the drugs currently used in the clinic, such as dilantin, ethosuximide, the antimanic drug lithium chloride, etc.

The investigated compounds can be used in pharmacology as anticonvulsants with anxiolytic and antidepressant properties.

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в рамках научного проекта № 21T-3C101.

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NEW TYPE OF IMIDAZOLIUM NHC-PROLIGANDS WITH SPECIFIC ELECTRONIC PROPERTIES

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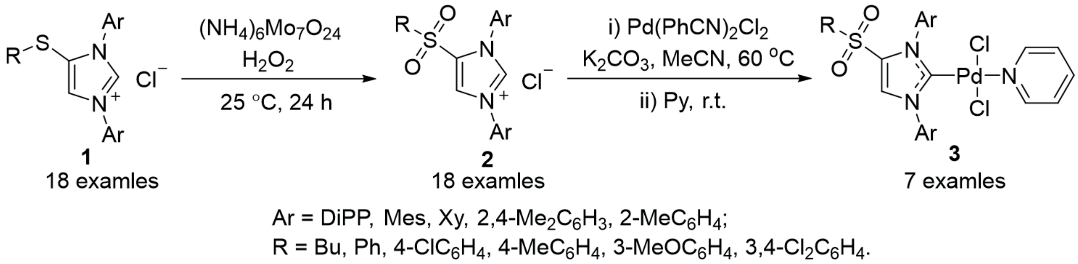
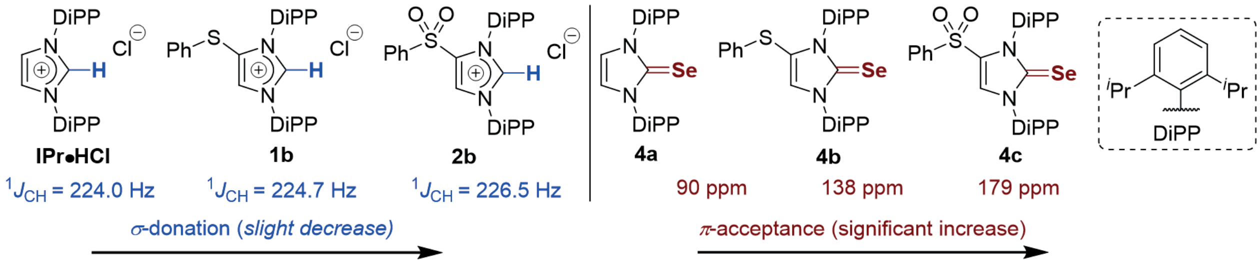
Imidazolium salts have been widely used as precursors of N-heterocyclic carbenes and stabilizers of metal nanoparticles in catalysis [1]. Previously, a single-stage method for the synthesis of 4(5)-substituted *N,N'*-diarylimidazolium salts, including 4-sulfanilimidazolium salts **1** [2], was reported. Herein we report a new approach for obtaining new imidazolium salts **2** containing a strongly electron withdrawing sulfonyl group (RSO_2-NHC) and their use as NHC-proligands for the synthesis of Pd/NHC complexes **3** (Scheme 1).



Scheme 1: Formation of NHC-proligands **2** and Pd/NHC complexes **3**

Experimental studies and DFT calculations revealed that the introduction of the RSO_2 group in the imidazole ring only slightly decreased sigma-donation whereas significantly increased π-acceptance of the RSO_2-functionalized NHC ligands (Scheme 2).



Scheme 2: Electronic properties of ligands **IPr•HCl**, **1b**, **2b**.

Complexes **3** containing bulky N-aryl substituents in the RSO_2-functionalized NHC ligands demonstrated enhanced performance in the catalysis of Suzuki-Miyaura, Buchwald-Hartwig and ketone alpha-arylation reactions compared to complexes with similar but unfunctionalized ligands.

The work has been supported by the Ministry of Science and Higher Education of the Russian Federation (project No 075-03-2021-016/4) at the Laboratory "Novel composite and functional materials with specific properties" within the framework of National Project "Science and Universities"

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2,1,3-BENZOCHALCOGENADIAZOLE DECORATED MOFS: SYNTHESIS, STRUCTURE AND LUMINESCENT PROPERTIES

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Metal-organic frameworks (MOFs) are an emerging class of functional materials. They are crystalline, often porous polymeric compound with finely tunable structures and properties, built from the metal ions or ion clusters and polytopic organic ligands. For two decades, they have been attracting significant research interest. This is due to the extremely broad scope of their potential applications: separation, purification and storage of gases and gaseous mixtures, catalysis (including stereoselective catalysis), wastewater treatment, water harvesting in arid regions, electrochemical applications, quantification and detection of pollutants in natural media.

Luminescent MOFs (LMOFs) are a particularly interesting class of MOFs due to their ability to exhibit a photophysical response towards the presence of various metal ions or organic molecules. Such response can be a change in luminescence intensity (enhancement or quenching), a change in quantum yield, lifetime or luminescence colour. Practical application of LMOFs for the detection of pollutants is highly desirable, because it allows the development of cheap, robust, quick and simple analytical methods that sometimes can be performed on-site or in a household environment. These advantages over classic analytical methods that LMOFs possess have led to the significant surge in LMOFs research in recent years.

We have been focusing or research on derivatives of 2,1,3-benzochalcogenadiazoles for a couple of reasons: first of all, they are known luminophores that found application in bioimaging and second, introduction of the polar 2,1,3-chalcogenadiazole fragment can facilitate MOF interactions with electron-rich analytes. For example, interaction of 4,7-dibromobenzo-2,1,3-thiadiazole with 1,2,4-triazole in DMSO in the presence of potassium phosphate yields (4,7-di(1,2,4-triazol-1-yl)benzo-2,1,3-thiadiazole) – **4,7-btbtd**. Interaction of **4,7-btbtd** with cadmium salt and di(4-carboxyphenyl)sulphone leads to the formation of three-dimensional coordination polymer **1** (figure 1)**.** Luminescent properties of this compound were studied in detail. It exhibited solid-state quantum yield of 70%, which is extremely high for cadmium-based MOFs. Furthermore, it was found that it is multiresponsive – additional of gossypol (toxic natural polyphenol) leads to the luminescence quenching, while addition of Ga(III) and Al(III) ions results in a significant luminescence enhancement. Calculated limits of detection for gossypol and Ga(III) are close to the lowest values recorded for LMOFs. To demonstrate possibility for practical application, test-strips and LEDs were prepared. Additionally, the compound was activated and texturally characterized.

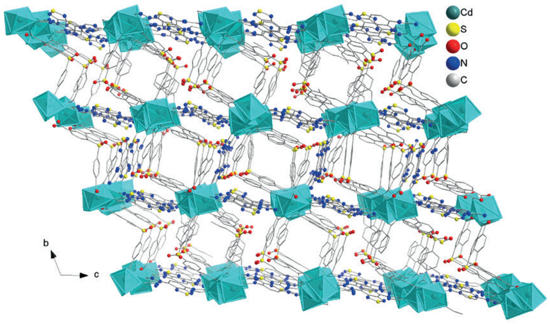

Figure 1 – crystal structure of coordination polymer **1.**

This work was supported by the Russian Science Foundation, grant No. 23-43-00017 "Novel metal-organic frameworks with high luminescence for the detection of biologically active substances and environmental pollutants", https://rscf.ru/project/23-43-00017/.

SELF-ASSEMBLY OF GOLD NANOPARTICLES AT THE LIQUID-LIQUID INTERFACE AS A PLATFORM FOR SURFACE-ENHANCED RAMAN SCATTERING

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Films and coatings of nanoparticles are key components of many emerging technologies because of their electrical and optical properties. To prepare ordered films of nanoparticles, soft interfaces, such as liquid-liquid interfaces, can be used. Since the discovery of the metal liquid-like films (MELLFs) by Yogev and Efrima in their pioneering work in 1988 [1], many attempts have been made to improve the synthetic procedure and investigate the properties of such films [2-4].

Here, we present a simple approach to the self-assembly of gold nanoparticles (AuNPs) without functionalization of AuNPs or the use of covalent linkers as a platform to develop Raman enhancing substrates. Self-assembly occurs due to tetrathiafulvalene (TTF) molecules in the organic phase (dichloroethane) upon contact with citrate AuNPs synthesized by the Frens method [6] with strong stirring in the emulsion, which leads to the formation of a continuous shiny gold film [5]. The resulting assemblies of AuNPs can self-repair after the redispersion process.

Nanoparticle colloids were characterized using UV spectroscopy and dynamic light scattering. Both methods showed that nanoparticles have an average diameter of 14 to 58 nm and were stable, since the zeta potential did not exceed −25–30 mV.

Further, such films of ordered nanoparticles were used in Raman spectroscopy to enhance a weak scattering signal. Close-packed films were transferred using the drain-to-deposit [7] and aquaprint methods onto solid substrates (silicon, plastic, ITO, etc.). The morphology of the obtained substrates was studied by scanning electron microscopy and atomic force microscopy showing ordering of nanoparticles in the film.

The enhancing properties of the substrates were studied using the dye rhodamine 6G, the addition of which leads to the appearance of characteristic peaks. The calculated enhanced factor (EF) for the lines 1508 cm^{-1} and 1360 cm^{-1} ranged from $\sim 10^3$ for nanoparticles with a diameter of 17 nm and $\sim 10^4$ for larger nanoparticles (44 nm). At the same time, prepared substrates can be washed up to ten times without lowering the enhancing properties. Further work will be devoted to improving the technique, increasing the EF, and testing substrates with natural phenolic compounds.

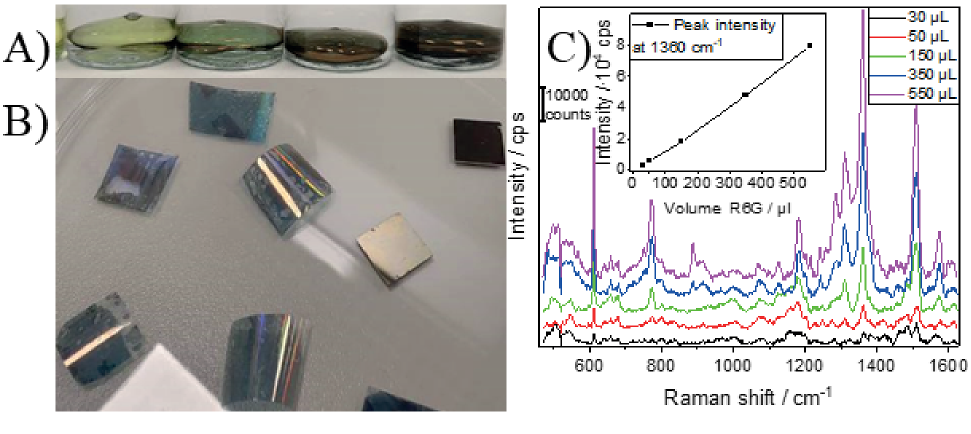

Figure 1. A) Stepwise increasing of AuNPs coverage of the LLI, B) Solid substrates coated with AuNPs, C) Raman spectra at increasing of R6G loading from 30 μL to 550 μL of 10^{-6} M R6G. Insert: Calibration curve demonstrating linear dependence of Raman scattering of R6G at 1360 cm^{-1}.

The work was carried out under a grant from the Russian Science Foundation (No. 22-73-00206).

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ALKYL 3-BROMO-3-NITROACRYLATES ARE PROMISING SUBSTRATES IN THE SYNTHESIS OF ACYCLIC, CARBO-, AND HETEROCYCLIC STRUCTURES

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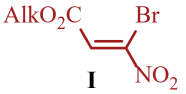
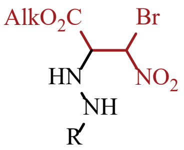
Alkyl 3-bromo-3-nitroacrylates – the original representatives of *gem*-halonitroalkenes containing several electrophilic reaction centers and being promising substrates for constructing various types of structures when interacting with nucleophilic reagents.

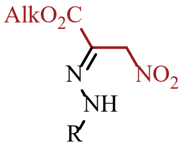
The chemical behavior of alkyl 3-bromo-3-nitroacrylates **I** studied by us in reactions with representatives of acyclic and cyclic CH-acids (diketones, ketoesters, diesters, cyclic amides), aliphatic and aromatic 1,4-binucleophilic reagents (ethane-1,2-diamine, 2-aminoethan-1-ol, 2-mercaptoethan-1-ol, pyrocatechol, benzene-1,2-diamine, 2-aminophenol, 2-aminobenzenethiol), as well as with substituted hydrazines, demonstrated the wide possibilities of synthesis various open-chain, carbo- and heterocyclic compounds on their basis.

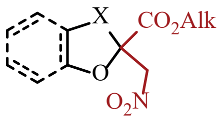


I

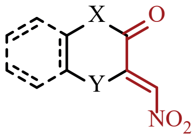
Alk = Me, Et



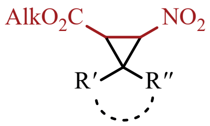


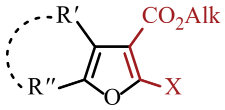


X = O, S



X = Y = NH;
X = O, Y = NH;
X = O, Y = S





X = H, NO$_2$

It has been shown that *gem*-bromonitroacrylates in reactions with nucleophilic reagents initially form Michael adducts, which undergo various transformation pathways:

– elimination of HBr and subsequent isomerization of the resulting C=C bond;

– elimination of HBr and intramolecular heterocyclization due to the second act of nucleophilic addition;

– intramolecular *N*- or *O*-acylation with the participation of an ester group and subsequent elimination of HBr;

– intramolecular *C*-alkylation with the participation of a bromonitromethyl group;

– intramolecular *O*-alkylation with the participation of a bromonitromethyl group.

The resulting polyfunctional acyclic, carbo- and heterocyclic structures are of interest as potential biologically active compounds.

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DNA-BASED ASSEMBLIES WITH BISCHROMOPHORIC STYRYL DYE-CHROMENE CONJUGATES AND CUCURBIT[7]URIL

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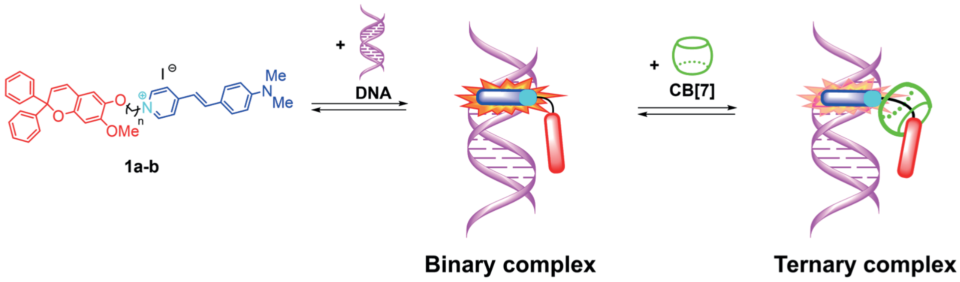
Recently there has been a wide interest in studying the interaction of small organic molecules with the DNA for medical and biological applications. Such studies help to understand the mechanism of action of drugs, as well as contribute to the development of various labels for intracellular imaging and bioanalysis. Molecular containers, in particular cucurbit[7]uril (CB[7]), are of considerable interest for the development of targeted drug-delivery carriers. In addition, ligand encapsulation makes it possible to increase their bioavailability by improving solubility and thermal stability in the aqueous media and reducing toxicity as well as to limit the off-site accumulation of drugs. Creation of multicomponent supramolecular systems based on DNA, cucurbit[7]uril and organic compounds allows not only to control the interaction between them, but can also lead to significant changes in the properties and functions of the original components [1].

In this work, bischromophoric conjugates **1a-b** consist of a 4-styrylpyridinium dye and a 2,2-diphenyl-2*H*-chromene moiety were synthesized, and their affinity to double stranded DNA and cucurbit[7]uril was investigated. With a combination of absorption, fluorescence and circular dichroism spectroscopies as well as MALDI-TOF mass spectrometry, we demonstrate that these compounds can interact with macromolecules to form of the supramolecular assemblies due to two suitable binding sites. The ternary complex is formed as a result of the intercalation of a positively charged styryl part between DNA base pairs, while cucurbit[7]uril is located on the alkyl chain between two moieties of conjugate (Scheme 1) [2].



Scheme 1. Schematic representation of equilibrium processes occurring in solutions of binary and ternary complexes.

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SELECTFLUOR-MEDIATED C-H AZOLATION OF PHENANTHRIDINE: INVESTIGATION OF THE REACTION MECHANISM

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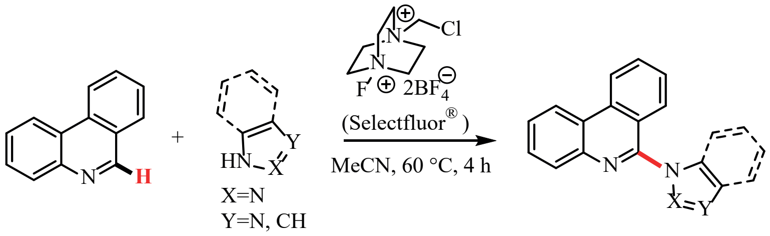
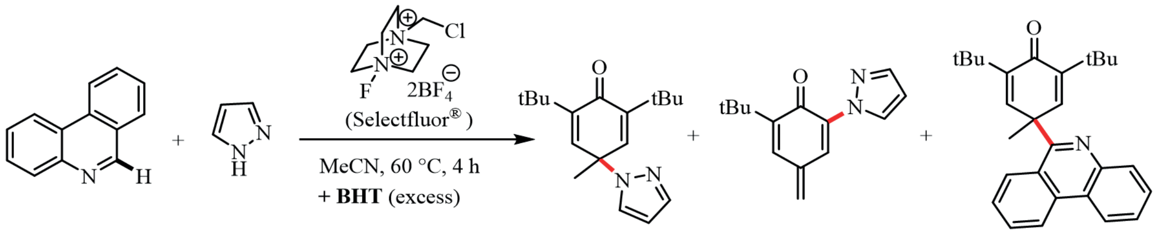
Phenanthridine derivatives are known to be promising compounds, being applied in the synthesis of biologically active substances, as well as fluorescent labels.1 Synthesis of novel derivatives of this class often appears to be quite challenging, dealing with multistep reaction pathways. One of the poorly explored but definitely promising approaches to these compounds is the strategy of direct C(sp^2)-H functionalization of the phenanthridine core. Our studies on the C-H reactivity of phenanthridines has indicated that these substrates are able to interact with different azoles **2** in the presence of the Selectfluor® reagent with the formation of new C(sp^2)-N bond to result in compounds **3** in 35-70% yields (Scheme 1).



1 **2** **3**

Scheme 1. Selectfluor-mediated C–H-azolation of phenanthridine **1**.

To get insight into the reaction mechanism, conventional radical-trapping experiments have been carried out using TEMPO, BHT, and galvynoxyl as radical scavengers. It has been found out that in the presence of any of these radical traps, the formation of the target product **3** is almost fully inhibited, whereas a series of probable radical adducts are detected by means of LC-HRMS analysis of the reaction mixtures (examples of such adducts in the reaction involving BHT are shown in Scheme 2).



1 **2** **4** (calc.: *m/z* 286.2045; found: 287.2118) **5** (calc.: 228.1263; found: 229.1335) **6** (calc.: 397.2406; found: 398.2488)

Scheme 2. Radical-trapping experiments.

Our ongoing research is aimed at the reaction scope expansion and evaluation of the practical applicability of the synthesized compounds.

The study was funded by the Russian Science Foundation (RSF) according to the research project № 20-73-10077, https://www.rscf.ru/en/project/20-73-10077/

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DFT AND EXPERIMENTAL UV/Vis SPECTRA OF SELECTED AZO DYES

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The development a low-cost dye-sensitized solar cell (DSSC) based on naturally abundant materials with satisfactory operational characteristics is of great practical interest. Usually the DSSCs are made of the following five major components: a transparent electrically conductive glass electrode, a porous wide band-gap semiconductor material film, a photosensitizer dye directly adsorbed onto semiconductor film, a redox couple liquid/solid electrolyte and a counter electrode. The main focus in this area of research is the modification of any of these components, which can increase efficiency as well as reduce costs of DSSC. In the present work, both theoretical density functional theory (DFT) quantum chemical calculations and experimental UV/Vis method have been used to screening the selected azo dyes, and to evaluate their further possible use as a dye compound in DSSC cells. The UV/Vis absorption spectra were collected at room temperature on a Specord 50 UV/Vis spectrophotometer within the wavelength range of 190-1100 nm in 1.0 cm quartz cells using water as reference. The analysis of UV/Vis absorption spectra of selected azo dyes in water shows an absorption band in the visible region with a peak at wavelength 508 nm for Ponceau 4R, 515 nm for carmoisine and 427 nm for tartrazine solutions. These spectra were used to further calculate the values of the optical bandgap of these dyes compounds. For this purpose, the practical method defined by Tauc was applied. The experimentally measured UV/Vis absorption spectra (absorbance vs. wavelength) of selected dyes were converted to obtain $(\alpha \cdot h\nu)^{1/r}$ vs. energy of photon ($h\nu$), where α is the absorption coefficient, and r depends on the type of electron transition, it can be equal to 1/2 for direct or 2 for indirect transition, respectively. The optical bandgaps were determined by extrapolating the linear part of the obtained plot to the X-axes. Thus, for compounds under study the following optical gaps were found: $E_g = 2.14$ eV for carmoisine, $E_g = 2.58$ eV for tartrazine, and $E_g = 2.2$ eV for Ponceau 4R. DFT calculations of HOMO and LUMO energies, as well as the theoretical UV/Vis spectra of some model dye compounds have been performed using Gaussian 03 program package. Preliminary results show good agreement with the experimental ones.

TRANSFER HYDROGENATION OVER HETEROGENEOUS NICKEL-BASED CATALYSTS

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Transfer hydrogenation (TH) is a type of chemical reduction, which is well known due to classical Meerwein-Ponndorf-Verley-Oppenauer process. Instead of conventional reductive agents, such as H_2 or metal hydrides, lower aliphatic alcohols, formic acid and some other simple organic molecules can be used as H-donors in TH [1]. Thus, this approach gives some important advantages compared to conventional hydrogenation, in particular, compliance with the principles of green chemistry and improving the safety of experiments. Also, it is important to notice that lower alcohols as well as formic acid can be comparatively easily obtained from plant biomass [2], in contrast to H_2 mostly producing from fossil sources.

As a rule, TH is catalyzed transformation and there are many studies describing activity of different homogeneous catalysts in enantioselective TH [3]. At the same time, heterogeneous catalysts cannot be effectively used in synthesis of enantiomeric products, however, they give another advantage – easy separation from reaction mixture that is critically important for bulk industrial processes. Usually, catalysts used in conventional hydrogenation demonstrate activity in TH, therefore, noble metals [4] and Ni-based systems [5]"ISBN":"2155-5435\\r2155-5435","ISSN":"2155-5435","abstract":"Reducing oxygen content in biomass-derived feedstocks via hydrodeoxygenation (HDO are widely used. In contrast to Pt, Pd or any other noble metals, Ni demonstrates comparatively low activity in TH, however, it is compensated by its low price.

Our report will consider in detail TH of the heterogeneous Ni-based catalysts and lower aliphatic alcohols. For instance, catalytic performance of Raney nickel was demonstrated on examples of many H-acceptors including low temperature transformations [6,7]. It has been shown that the Raney catalyst is effective in saturation of C=O, aromatic and aliphatic C=C bonds under TH conditions, whereas, the use of N- and S-containing molecules results in catalyst poisoning [8]. Raney nickel is quite useful for organic synthesis due to its simple preparation procedure and activity in TH under mild conditions, at the same time, this catalyst demonstrate low thermal stability. In contrast, supported nickel catalysts can be used in TH proceeding at higher temperature and pressure. For example, high-loaded Ni nanoparticles supported on different oxides showed promising results in TH of biomass-like phenolic anisole [9] under supercritical conditions. Also, effect of C_1-C_4 primary and secondary alcohols on catalytic activity of Ni-based catalysts was discussed.

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TERNARY COMPLEX POLYCATION/POLYANION/Ag_2O AS A PROMISING MATERIAL FOR CREATING COATINGS WITH DUAL BIOCIDAL ACTION

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The use of low molecular weight biocides for the treatment of premises with high sanitary standards has significant disadvantages associated with the durability of such coatings, as well as the increasing resistance of bacteria. Biocidal compositions based on interpolyelectrolyte complexes (IPEC) are of potential interest for practical use, since they contain regions with free charged cationic groups that can provide both a biocidal effect and adhesion to hydrophilic surfaces. Also, the hydrophobic regions of IPEC can improve adhesion to hydrophobic surfaces, as well as modify such systems with low molecular weight bioactive compounds, for example, silver oxide Ag_2O, which has widely proven itself as a biocide. Such a system will have increased durability along with a dual biocidal action. The decisive advantages of such ternary systems are increased wear resistance along with a dual biocidal action. In this work, we studied the formation and properties of water-soluble IPECs based on pH-independent polydiallyldimethylammonium chloride (PDADMAC), whose biocidal properties are widely known, and sodium polystyrenesulfonate (PSS). IPEC was also modified by incorporating Ag_2O nanoparticles to obtain a ternary composite PDADMAC/PSS/Ag_2O.

The interaction of PDADMAC with PSS was studied by turbidimetric titration of a PDAMAC solution. It has been established that water-soluble IPECs can be obtained at ratios of anionic and cationic groups in the composition of polymers χ = [PSS]/[PDADMAC] up to a critical value of 0.16. The phase separation in solutions of water-soluble IPECs with was studied in presence of simple salts with mono- and bi-valent ions. It has been established that all studied complexes are resistant to phase separation in a wide range of ionic strengths of solutions.

The inclusion of silver oxide nanoparticles into the complex was carried out by ultrasonic dispersion (UD) of a coarse-grained powder in an IPEC solution. The means size of the resulting particles was estimated using the method of transmission electron microscopy and was found to be 5-6 nm. The particles were demonstrated to retain their size during long time period after preparation by UD.

The aggregative stability of PDADMAC/PSS/Ag_2O in solution was evaluated using spectrophotometry and dynamic light scattering. The system was demonstrated to have sufficient colloidal stability.

The biocidal properties of PDADMAC, its complex with PSS, and the PDADMAC/PSS/Ag_2O system was studied by microbiology methods. The complexation with PSS did not affect the antibacterial effectiveness of the PDADMAC, while the formation of ternary complexes with Ag_2O resulted in increase of antimicrobial activity.

Thus, taking into account the high antibacterial activity and aggregative stability, ternary systems based on IPEC and silver oxide nanoparticles are a promising material for use as antibacterial coatings.

This work was supported in part by Russian Science Foundation (project 22-23- 00723)

APPLICATION OF THE METHODOLOGY OF OXIDATIVE NUCLEOPHILIC SUBSTITUTION IN THE ARYLAMINATION REACTION OF NITROQUINOLINES

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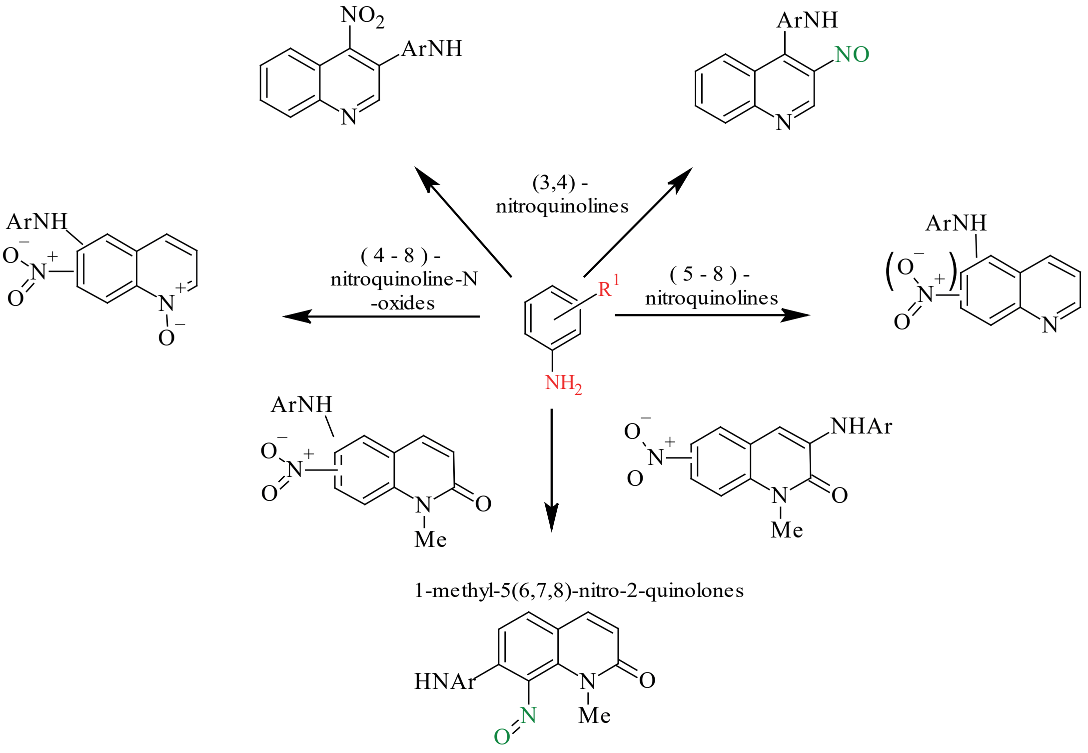
Against the background of well-known achievements in the field of direct C–H functionalization of π-deficient aromatic and heteroaromatic compounds by the action of nucleophilic reagents, criteria for the economy of all transformation parameters, as well as their compliance with the principles of "green" chemistry, come to the fore. To the greatest extent, these principles are satisfied by the reactions of oxidative nucleophilic hydrogen substitution (S_N^H), which do not require the preliminary introduction of a leaving group into the substrate or reagent molecule, as well as the use of expensive catalysts. They include the stage of addition with the formation of the σH-adduct and its subsequent aromatization due to an external oxidizing agent. The S_N^H methodology is sometimes a worthy alternative to cross-coupling reactions catalyzed by transition metals.



S_N^H-arylamination of (3-8)-nitro derivatives in anhydrous DMSO leads to the formation of arylamino derivatives not only of the corresponding nitro and nitroso derivatives, but also of previously unknown tetracyclic heterocycles.

The authors express their gratitude to the North Caucasian Federal University for financial support in the framework of the project to support projects of scientific groups and individual scientists.

SODIUM HYPOPHOSPHITE AS AN EFFICIENT AND ENVIRONMENTALLY BENIGN REDUCING AGENT IN REDUCTIVE AMINATION

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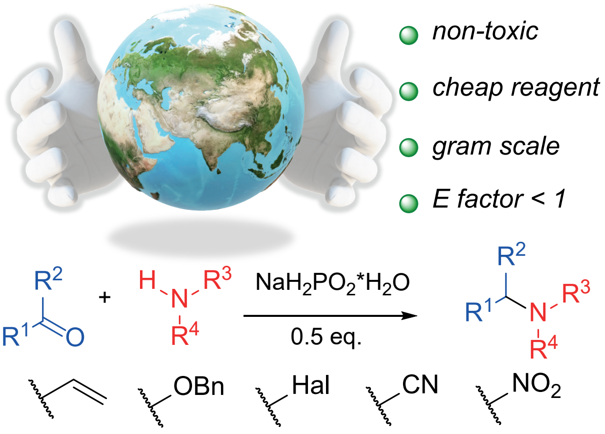
Reductive amination is a significant common approach to synthesis of amines which are of great importance in pharmaceutical and medicinal chemistry. Widely applied reductants such as molecular hydrogen or hydride reagents with B-H bond have multiple drawbacks such as low selectivity with simple hydrogenation catalysts, instability on air and high amount of wastes, in particular, toxic like HCN. In addition, NMe_2 fragment contains in many bioactive compounds, but such starting materials as dimethylamine are inconvenient to handle because it is a toxic gas. Therefore, we elaborated transition-metal-free approach to reductive amination using sodium hypophosphite as a selective, available in bulk amounts and environmentally friendly reductant. NaH_2PO_2 also allowed us to use dimethylformamide instead of gaseous Me_2NH in the target process.

Sodium hypophosphite demonstrated high versatility in reductive amination1. All types of carbony[1] compounds reacted with primary and secondary aromatic and aliphatic amines. Such functional groups as NO_2, CN, C=C, OBn and Br remained intact under developed conditions. Antianxiety agent, Ladasten, was obtained in 68% yield. Reaction conditions were scaled up to 200-fold.

Dimethylformamide was successfully used as a source of NMe_2 moiety instead of dimethylamine in reductive amination with NaH_2PO_2. Wide substrate scope of various dimethylamines was synthesized without chromatographic purification[2]. Elaborated conditions were compatible with BnO, CN, I, C≡CH, C=C and heteroaromatic fragments. Other formamides of cyclic and acyclic amines reacted with carbonyl compounds furnishing products in modest to high yields.



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MOLECULAR STRUCTURE AND ENERGETICS OF SEVERAL DYES: EXPERIMENTAL AND THEORETICAL STUDIES

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A study of the electronic and geometric structure of compounds is necessary to explain the chemical, biological, and physical properties of a particular class of compounds. Structural studies for the gas phase are advantageous in that the resulting structural parameters refer to individual molecules that do not depend on the environment. Among the existing experimental methods, gas electron diffraction (GED) is the most informative in terms of establishing the geometric structure of molecules, and the data obtained by this method will make it possible to test the performance of theoretical approaches to structure prediction.

Structural features of 4-(4-hydroxyphenylazo)phthalonitrile, 4-[(4-hydroxy-1-naphthyl)diazenyl]phthalonitrile, 4-[(2-hydroxy-1-naphthyl)diazenyl]phthalonitrile, 4-((4-hydroxy-[1,1'-biphenyl]-3-yl)diazenyl phthalonitrile were studied by DFT and DLPNO-CCSD(T) calculations. QTAIM, NPA, NBO, NCI, SAPT0 analyzes carried out. The conformational diversity, keto-enol tautomerism and cis-trans isomerism were studied for these compounds.

The sublimation of substances was studied using the Knudsen effusion method with mass spectrometric vapor monitoring. The assignment of the obtained peaks in the mass spectra and the study of the fragmentation pathways of the molecules were carried out using the results of QCxMS calculations.

The sensitivity of the GED method to structural changes typical for the molecules was analyzed. Different tautomers of the molecules can be distinguished based on the experimental GED data due to significant differences in corresponded internuclear distances between chemically bonded and non-bonded atoms.

The molecular structure of 4-(4-hydroxyphenylazo)phthalonitrile was studied by GED. The object is thermally stable at least up to 191˚C. The quasi-planar structure of the molecule was determined by experiment. There is a good agreement in the values of internuclear distances obtained by quantum chemical calculations and experimental treatment.

The study was supported by the Russian Science Foundation (grant № 22-73-00314).

METAL-ORGANIC FRAMEWORKS STUDIED VIA ENCAPSULATED SPIN PROBES

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Metal–organic frameworks (MOFs) are greatly attended nowadays in view of their numerous potential applications. These porous compounds, made of metal clusters connected by organic linkers, have noticeably large surface area and many other useful properties, which allow such applications as separation and storage of gases, liquids, as catalytic media], drug delivery agents, etc. In many cases MOFs can be tailor-made and structurally adjusted to serve particular tasks. Most of MOFs are diamagnetic, and, therefore, cannot be studied using Electron Paramagnetic Resonance (EPR) in their natural form. However, a number of MOFs contain paramagnetic sites and have been intensively studied by EPR. As an alternative, recently we have proposed using nitroxide spin probes to investigate various properties of MOFs.

Encapsulated nitroxides are spin probes of significant spectroscopic and practical interest. Encapsulation can take place when the size of nitroxide is small enough to be accommodated in the cavity of MOF, but at the same time large enough to prevent passing through the windows of the cavity. This situation is realized for the "caged" MOFs, where ZIF-8 is one of their broadly attended representatives. This MOF is based on Zn(II) and 2-methylimidazolate ions (in composition 1:2), with cavities (~11.6 Å) separated by smaller windows (formal aperture size ~3.6 Å) and is naturally diamagnetic. When nitroxide is embedded into ZIF-8 during self-assembling of MOF in solution, it becomes entrapped in the cavity and cannot leave it without destruction of MOF. At the same time, it is not chemically bound to the MOF and exhibits fast rotation at room temperature, yielding EPR spectrum similar to the typical one for nitroxide dissolved in low-viscosity liquids. We demonstrated that EPR spectrum of TEMPO@ZIF-8 is very sensitive to the presence of air (oxygen) or organic solvents in the cavity: oxygen leads to a drastic broadening of the spectrum due to the dipole–dipole interactions, whereas guest solvents can displace air/oxygen and lead to a narrowing of the spectrum to its normal shape in liquids. This simple effect was already employed for several applications such as separation of xylene isomers [1,2], separation of benzene/cyclohexene mixtures [3], stabilization of MOF under pressure [4], and formation of MOF-based pellets [5].

This work was supported by the Russian Science Foundation (No. 22-73-10239).

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SYNTHESIS, LUMINESCENT AND SENSING PROPERTIES OF METAL-ORGANIC FRAMEWORKS DECORATED WITH 2,1,3-BENZOCHALCOGENADIAZOLES

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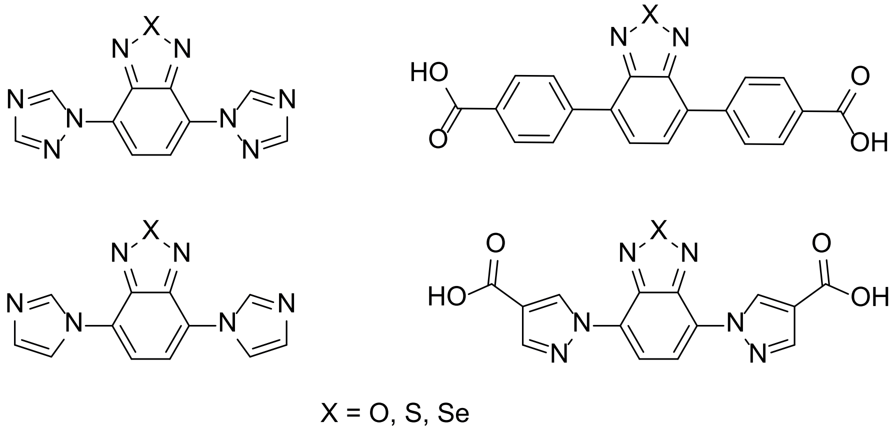
Metal-organic frameworks (MOFs) are assembled from metal cations and organic linkers into stable three-dimensional structures. Luminescent MOFs find applications as sensors for detection and determination of organic and inorganic pollutants, biomarkers, etc. Luminescence of MOFs may arise from metal- or ligand-centered emission, metal-to-ligand or ligand-to-metal charge transfer, encapsulated guest emission. The focus of our research is the use of highly emissive ligands based on the derivatives of 2,1,3-benzoxadiazole or 2,1,3-benzthiadiazole for the synthesis of luminescent MOFs.

In order to incorporate the luminophoric 2,1,3-benzochalcogenadiazole units into the structure of MOF, functional groups capable of forming the coordination bonds with the metal cations should be introduced into their aromatic rings. In our work, the following types of such groups are explored – azole rings (pyrazole, imidazole, 1,2,4-triazole), carboxylic groups or a combination of both (Scheme 1).



Scheme 1

Zinc(II) and cadmium(II) cations are commonly used as metal nodes of luminescent MOFs, since they have closed electronic shells, which do not quench the ligand emission. In addition to Zn^{2+} and Cd^{2+}, lanthanide(III) cations were used in our work to create MOFs with multicentered emission and zirconium(IV) oxo-clusters $[Zr_6O_4(OH)_4]^{12-}$ to obtain MOFs with enhanced thermal and hydrolytic stability.

The structure of all synthesized MOFs was established by single-crystal X-Ray diffraction analysis and their luminescent properties were studied in the solid state and in stable suspensions in water or organic solvents. Zinc and cadmium-based MOFs with 4,7-bis(azol-1-yl)-2,1,3-benzothiadiazole linkers demonstrated a strong luminescence “turn-on” response towards Al^{3+} and Ga^{3+} cations, while for zirconium-based MOF with 4,7-bis(4-carboxypyrazol-1-yl)-2,1,3-benzoxadiazole linkers a “turnon” response to aliphatic amines was observed making them promising for fabrication of sensing materials for toxic metal cations and organic pollutants.

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CORRELATION BETWEEN QUANTUM YIELDS OF PHOTOLYSIS AND GENERATION OF HYDROXYL RADICALS UPON EXCITATION OF NATURAL IRON CARBOXYLATE COMPLEXES

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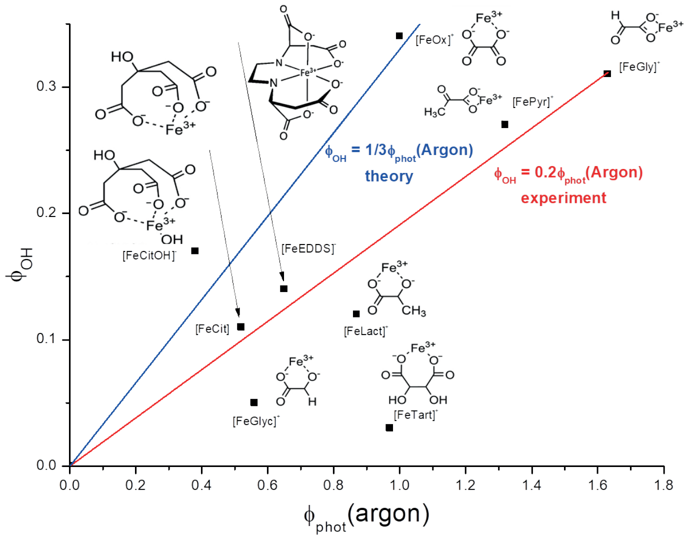
Fe(III) carboxylate complexes with natural ligands are intensively studied and considered as one of the promising photosystems for the degradation of pollutants in the so-called advanced oxidation processes (AOPs) [1]. However, there is very little information on the absolute values of the quantum yields of •OH radicals (φOH) upon excitation of such systems. Another unresolved question is the relationship between the values of φOH and the efficiency of complex photolysis, as well as the dependence of the latter on the excitation wavelength. At the same time, the values of φOH and the reactivity of •OH with respect to target compounds are the most important parameters for the application of any photosystem in AOPs. This paper presents an approach to determining the values of φOH upon UV excitation of natural Fe(III) carboxylate complexes and determining the dependence of this value on the efficiency of their photolysis.



The approach is based on the use of the FeOH2+ hydroxocomplex as a reference system with a well-known φOH value and benzene as a selective trap for •OH radicals [2]. φOH were determined for the first time for a number of Fe(III) complexes with natural ligands – oxalic, citric, lactic, tartaric, pyruvic, glycolic and glyoxalic acids. The good linear correlation between the efficiency of generation of the hydroxyl radical and the structure of the initial ligand and the quantum yield of photolysis of the initial complex (φphot) has been established (Figure). The data obtained are important for understanding the fundamental photochemistry of the coordination compounds of iron with polydentate carboxylic acids and can serve as a basis for the use of Fe(III) complexes with natural ligands in the processes of photochemical water purification.

This work was financially supported by the Russian Science Foundation (No. 21-43-00004).

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In situ STUDY AND EVIDENCE OF *N*-HETEROCYCLIC CARBENES BINDING TO THE SURFACE OF PD NANOPARTICLES IN Pd/NHC CATALYSIS

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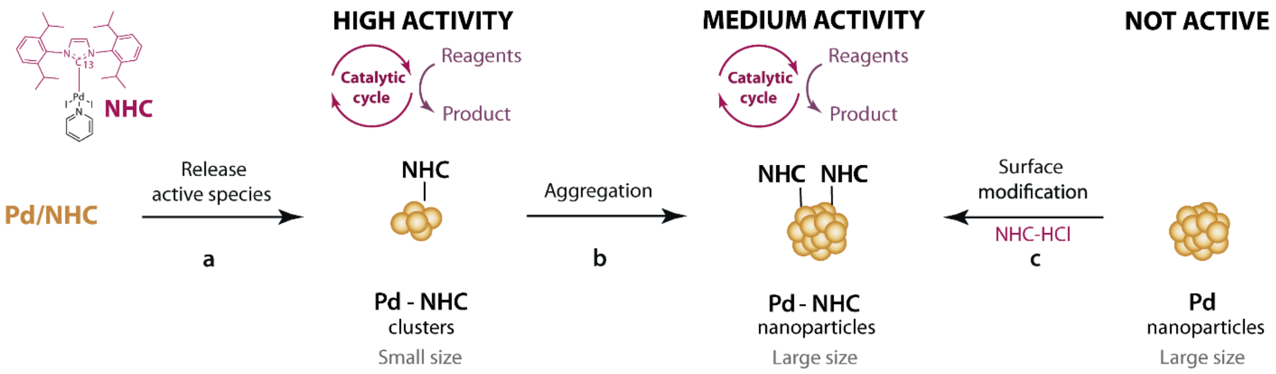
Transformations catalyzed by transition metals such as palladium, platinum, copper, nickel, rhodium, ruthenium, iridium, etc., are widely used in modern organic synthesis to create the carbon skeleton of molecules and introduce various heteroatoms and functional groups into them. Modern research in the field of metal complex catalysis has shown that metal-containing organic reaction media are complex mixtures, which include catalytically active particles of various nature (the so-called "cocktail of catalysts"[1]), as well as inactive forms of metal that can generate active sites or are the final point of catalyst evolution. The ratio of various forms of metal in the system and their role in a specific catalytic process determine the efficiency of the carried out transformation; therefore, obtaining the widest possible spectrum of structural information is an urgent problem, the solution of which will not only reveal the fundamental laws in the behavior of existing catalytic systems, but also allow to predict the properties of the developed catalysts.



Recently, systems based on transition metal complexes with N-heterocyclic carbenes (M/NHC) have been particularly attractive [2-3]. The important role of NHCs released from homogeneous complexes as probable stabilizers of metal nanoparticles and ligands affecting the electronic and steric properties of metal surface active centers has often been suggested but rarely unequivocally confirmed, especially for *in situ* formed metal nanoparticles in catalytic solutions. In this contribution, using a specially developed NMR technique based on ^{13}C labeled NHC ligands, we provide unequivocal evidence for the formation of NHC-ligated catalytically active Pd nanoparticles from Pd/NHC molecular complexes during catalysis. The coordination of NHC through the C(NHC)-Pd bond to the metal surface of the formed in situ Pd NPs was first confirmed by the observation of a Knight shift in the ^{13}C NMR spectrum of the frozen reaction mixture, and also confirmed by the observation of a Knight shift in the spectra of isolated NPs.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 22-13-00286.

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MOLECULAR DESIGN AND SYNTHESIS OF POTENTIAL NIR-FLUORESCENT PROBES BASED ON SPIROPYRAN DYES

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Spiropyrans (SPs) are one of the most interesting classes of organic photochromic compounds [1]. They are characterized by reversible isomerization under activating radiation (usually UV) between the colorless spirocyclic (Sp) and brightly colored merocyanine (Mc) forms. A distinctive feature of SPs is a sharp change in the dipole moment of the molecule and fluorescent properties upon phototransformation (**Figure**). As a result of molecular design and synthesis, new derivatives of indoline spiropyrans with a vinyl-3*H*-indolium fragment were obtained. Structure of SPs was studied by NMR, IR and HRMS methods. Due to the increased conjugation chain, these compounds exhibit photochromic properties and fluorescence in the the biological window range with a maximum at 744, 755 and 748 nm, respectively (**Figure**). Obviously, the introduction of a methoxygroup to the position 8′ justified itself by a red shift of the fluorescence maximum by 29 nm compared to the fluorine-substituted structural analogue [2]. To clarify the possible reasons for differences in the spectral properties, quantum chemical modeling of absorption spectra has been performed in the scope of TD DFT.

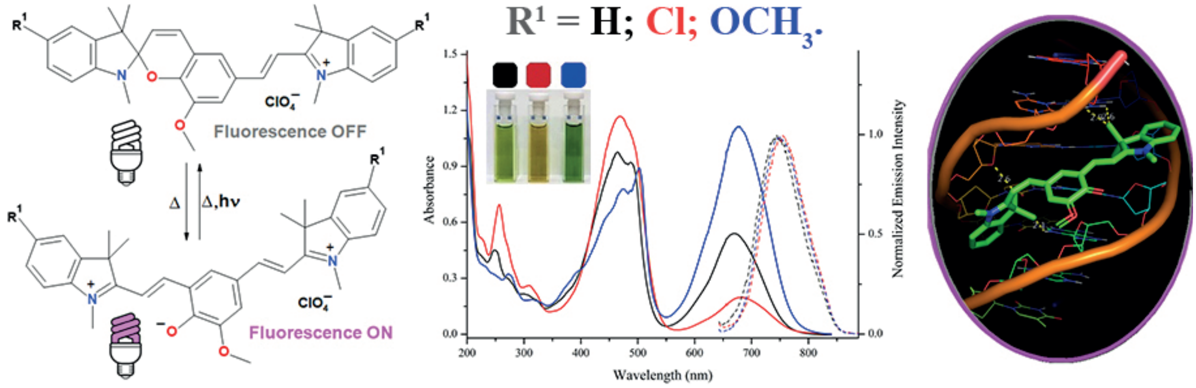

Figure. Phototransformation of SPs, their absorption and photoluminescent spectra, as well as molecular docking with DNA in minor groove mode (more favorable position).

The toxicity of the obtained SPs was studied on biofilms and lux-biosensors. The study showed that SPs do not have a significant effect on biofilms. As a result of studies using lux-biosensors, it can be assumed that compounds can be considered as antibacterial and anticancer agents due to DNA-tropic and prooxidant properties. Non-toxic concentrations are 10^{-8} and 10-7 M. Molecular docking investigation shows that the formation of SP complexes in the minor groove of DNA is energetically more favorable than other types of interactions (Figure). Mc isomers of compounds R1= H, Cl exhibit the highest affinity among all cases. Moreover, in the case of dye R1= H, the difference in energy gain between the Sp and Mc isomers was 1.78 kcal•mol-1, and in the case of R1= Cl, only 0.73 kcal•mol-1. As for R1= OCH3, everything turned out the opposite. The Sp isomer's affinity was higher than the Mc isomer by 2.21 kcal•mol-1. Based on these data, these compounds may be useful for bioimaging of DNA in biofilms without damaging them.

The study was financially supported by the Russian Science Foundation grant No. 22-73-00330, https://rscf.ru/project/22-73-00330/, and carried out in Southern Federal University.

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POTENTIAL USE OF OXOVANADIUM COMPLEXES AS ANTIDIABETIC AGENTS

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Research data from recent decades show that vanadium compounds, in particular organic derivatives, are effective oral insulin mimetics that inhibit lipolysis, reduce blood glucose (BG) levels in animals and in clinical studies, and stimulate insulin secretion in experimental models of diabetes mellitus (DM). Although the mechanisms of the insulinomimetic action of vanadium complexes have not been fully elucidated yet, their ability to increase insulin sensitivity in peripheral tissues and to reduce insulin resistance has attracted significant attention in the context of their potential use in the treatment of type 1 DM, type 2 DM and obesity [1]. The research efforts of developing vanadium-based antidiabetic oral drugs now are focused on the finding of organic ligands or chelators with enhanced properties: to improve target selectivity to block protein tyrosine phosphatase 1B; vanadium complex stabilities and ligand exchanges; to facilitate membrane passages and tissue distributions, etc. Scientific studies carried out at PSPA showed that het(aryl)amides of aroylpyruvic acids (ArPA) can serve as physiologically active ligands for obtaining active complexes with metals.

In order to search for vanadium chelating ligands with certain characteristics (better tolerance, less toxicity, increased uptake by cells, preferably active transporter systems across cell membranes) we carried out a targeted synthesis of oxovanadium complexes (2a-g, 4a-z, 4i-f) based on 4-methiphenylamides (1a-g) ArPA, 2(3)-pyridylamides (3a-z), 2-(5-R-1,3,4-thiadiazolil)amides (3i-f) ArPA. The hypoglycemic activity of the initial derivatives, vanadyl sulfate and the resulting metal complexes was studied in non-linear rats under conditions of alloxan-induced diabetes (at a dose of 170 mg/kg). The derivatives under research, vanadyl sulfate, metformin were administered orally at a dose of 50 mg/kg. The concentration of glucose in the blood of animals was determined by the glucose oxidase method prior to introducing compounds, as well as 30, 120 minutes after it.

The studies have shown that the targeted chemical modification of derivatives of ArPA by the introduction of vanadium (IV) led to a significant increase in hypoglycemic activity in the series of the obtained metal complexes 2, i.e. a marked potentiation of the hypoglycemic effect was noted, compared with the original organic ligands 1 and vanadyl sulfate (figure 1).

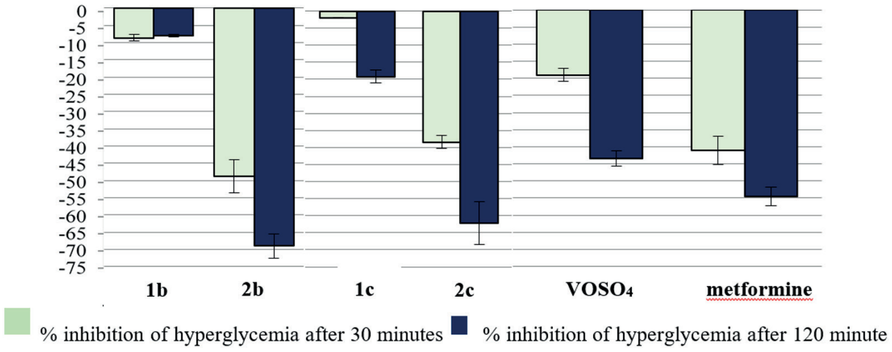

Fig.1 Comparative characteristics of the hypoglycemic action of the most active oxovanadium complexes, vanadyl sulfate and the initial ArPK derivatives.

An appropriate chelator was obtained in the arylamides of aroylpyruvic acids complexes, quite superior to inorganic oxidovanadium salts concerning BG lowering. It was suggested that, their improved potency can be explained by the presence of a fragment of pyruvic acid which is included in normal metabolism, thus contributing to a better orientation of structural fragments at biological targets.

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SYNTHESIS OF SPIROCYCLIC DERIVATIVES OF BARBITURIC ACID BY 1,3-DIPOLAR CYCLOADDITION REACTION BETWEEN AZOMETHINE YLIDE AND MALEIMIDES

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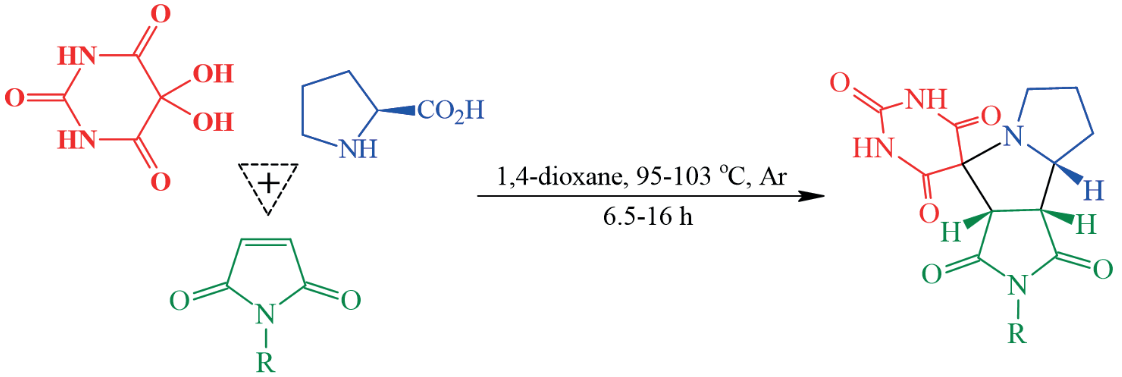
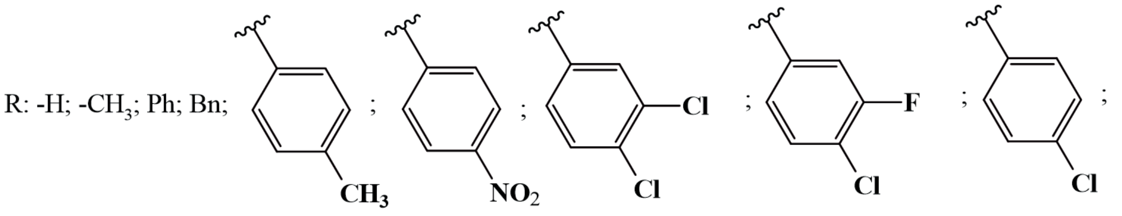
Derivatives of barbituric acid (barbiturates) exhibit a wide range of biological and pharmacological activity, as a result, this class of compounds attracts a lot of attention from researchers. Among barbiturates, it is worth noting their spirocyclic derivatives, which are known to have a sedative effect, anticonvulsant activity and to act as various enzymatic inhibitors, etc. [1]

We present a new method for the preparation of spirocyclic barbiturates with fused cyclic fragments in the course of a *one-pot* 1,3-dipolar cycloaddition reaction. The role of the 1,3-dipole in the formation of the target molecule is played by azomethine ylide, which formed *in situ* from alloxan and *L*-proline. This intermediate subsequently attack a double bond of the corresponding maleimide, which acting as a dipolarophile. Product yields range is 21-37%. The structure of the compounds obtained was proved using NMR spectroscopy, mass spectrometry, and X-ray diffraction analysis.





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SYNTHESIS OF NEW 2,2,4,4-TETRASUBSTITUTE-1,3-DIOXOLANES

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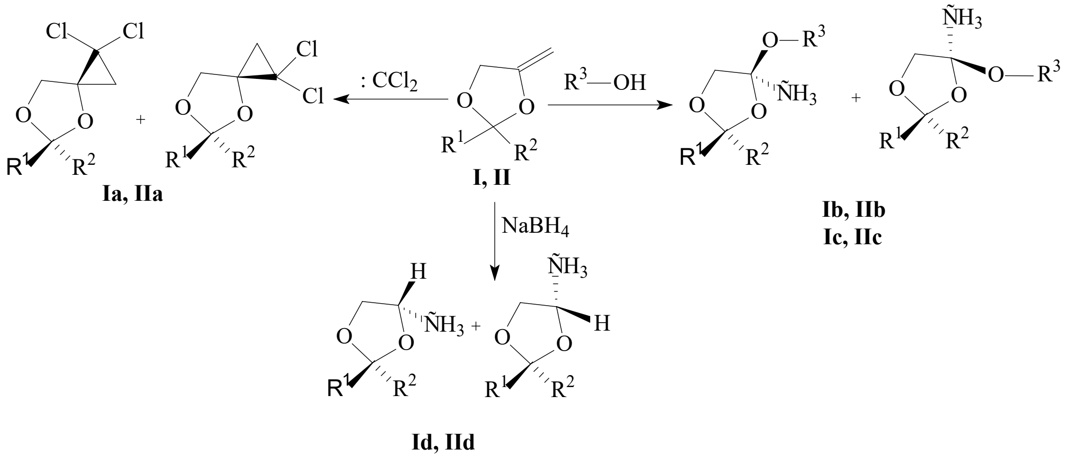
Dehydrohalogenation of 4-halomethyl-1,3-dioxolanes makes it possible to obtain 4-methylene-1,3-dioxolanes (cyclic vinyl ethers) in high yield [1]. These compounds are reactive and are widely used in organic chemistry, in particular, they are used in dichlorocyclopropanation and polymerization reactions. Promising compounds for organic synthesis containing gem-dichlorocyclopropane and cycloacetal fragments have been obtained based on them [2, 3].

New 2,2,4,4-tetrasubstituted-1,3-dioxolanes were synthesized in our work. And we determined that compounds **Ia-d**, **IIa-d** are formed as *syn*- and *anti*-diastereomers in a ratio of 1 : 1.



R^1 = C_2H_5, R^2 = ÑÍ$_3$ (**I, Ia, Ib, Ic, Id**)
R^1= CH_3, R^2= *i*-C_4H_9 (**II, IIa, IIb, IIc, Id**)
R^3 = C_2H_5 (**Ib, IIb**); ÑÍ$_2$–CH=CH$_2$ (**Ic, IIc**)

As a result, cyclic ketals **Ia-d** and **IIa-d** containing a gem-dichlorocyclopropane fragment, alkoxy- and methyl- groups, respectively, were obtained in high yields (80–95%).

Note that the formation of alkoxy derivatives **Ib,c**, **IIb,c** in 80–85% yields was achieved at 5-10°C in presence of cation exchange resin KU-2-8 as an acid catalyst (0.1 g per 0.006 mol of compound **I** or **II**). Protic (pTsOH, H_2SO_4, HCl) and aprotic (BF_3*$(C_2H_5)_2O$, $AlCl_3$) acids stimulate the exothermic destruction of the 1,3-dioxolane ring with the formation of the initial ketones R^1R^2CO, which significantly reduces the yield of target alkoxy derivatives **Ib,c**, **IIb,c**.

The structure of the substituents R^1 and R^2 in the starting compounds **I**, **II** does not significantly affect the result of the reaction – the yields of derivatives **Ia-d** and **IIa-d** are close.

"The work was carried out within the framework of the state task of the Ministry of Education and Science of the Russian Federation in the field of scientific activity, publication number FEUR - 2022-0007 "Petrochemical reagents, oils and materials for thermal power engineering".

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SYNTHESIS AND BIOLOGICAL SCREENING NOVEL SERIES OF PIPERAZINE-SUBSTITUTED PYRANOPYRIDINES SALTS

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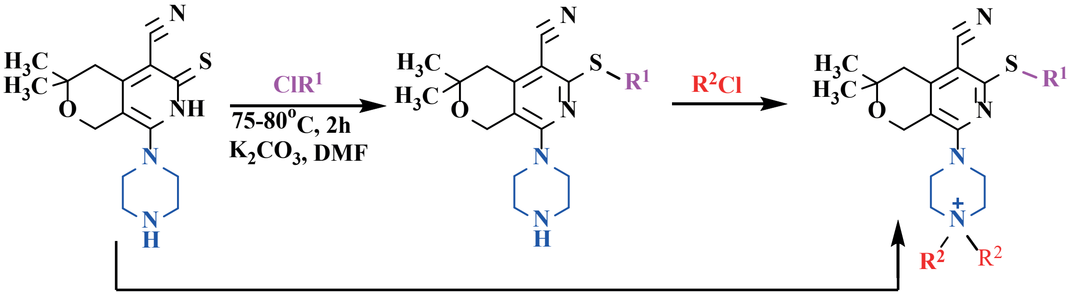
One of the main problems of modern organic, bioorganic chemistry, and medicine is the search for new biologically active compounds with selectively acting pharmacophore groups, which have less toxicity compared to already known drugs. Therefore, it is very important to obtain new partially saturated and unsaturated pyridines and their polycyclic fused analogs, to develop new methods of synthesis, and to study the relationship between chemical structure and biological activity [1].

Based on the fact that functionally substituted piperazines have a wide range of biological activity and have found application in medicine, we have developed a method for the preparation of thioalkyl derivatives of piperazine-substituted pyrano[3,4-c]pyridines, followed by alkylation to the corresponding piperazines salts according to the scheme:



After organic synthesis and describing the physicochemical properties of compounds with NMR spectroscopy, for determination of their possible biological activity was performed *in silico* studies with the “reverse screening method” [2]. Studies indicate that all investigated piperazines can be potentially used for the treatment of atherosclerosis.

Antibacterial activity was tested on gram-positive staphylococci (Staphylococcus aureus 209p, 1) and gram-negative rods (Sh. Flexneri 6858, E. Coli 0-55). The study of the antibacterial activity of the synthesized compounds showed that some of them lack antimicrobial activity. The rest compounds with a piperazine ring are affected by both types of strains in d=10-13 mm.

Thus, the study of the anti-monoamine oxidase activity of some new piperazines has shown that the active compounds can be considered in the future as a potential antidepressant

The study was carried out with the financial support of the Science Committee of the Republic of Armenia within the framework of scientific project No. 20TTSG-1D011.

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SILICAS FOR MODIFICATION OF MEMBRANES BASED ON MICROPOROUS BLOCK COPOLYMERS

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Membranes have been important in analytical chemistry since their discovery in the 1960s, when they began to be widely used as ion-selective electrodes for the determination of cations and anions. To detect the ions to be determined, a membrane composition is required that would ensure fast ion exchange at the interface between the membrane and the solution [1]. Block copolymers (BCs) are promising as sensory membranes. Their properties are largely determined by morphology, which depends on the degree of polymerization of each segment, molecular weight, copolymer polydispersity, and inter-action between segments [2]. The most promising as transparent optical chemical sensors and test methods for the determination of various substances are nanoporous BCs, since they make it possible to visually observe the color change [3]. One of the ways to control the diffusion properties of BCs is based on the directed influence on their supramolecular organization.

Using tetraethoxysilane, polyoxyethylene glycol, and copper chloride, stable to self-condensation cubic and linear polysiloxanes containing polyoxyethylene branches (ASiP-Cu) were synthesized. The effect of copper chloride content on the chemical structure of ASiP-Cu was established. The modifying effect of ASiP-Cu on the sorption characteristics of membranes based on microporous block copolymers (OBC) obtained using 2,4-toluene diisocyanate and block copolymers of ethylene and propylene oxides was studied. A significant increase in the sorption capacity of modified polymers was established. Based on the 1-(2-pyridylazo)-2-naphthol (PAN) analytical reagent and modified microporous block copolymers the test system was obtained. The high diffusion permeability of modified OBC for molecules of organic dyes and metal ions was established. It is shown that the volume of voids and structural features of their internal cavity contribute to the complex formation reaction involving PAN and copper chloride.

Using the modified OBC and the PAN analytical reagent the test system was obtained. The high diffusion permeability of modified OBC for molecules of organic dyes and metal ions were established. It was shown that the volume of voids and structural features of their internal cavity contribute to the complexation reaction involving PAN and $CuCl_2$.

Funding.
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DEALKYLATION IN HALOGENATION OF METHYL-N,N,N-TRIPROPYN-2-YL AMMONIUM BROMIDE

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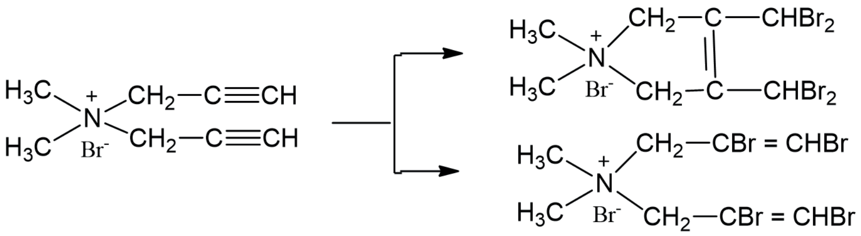
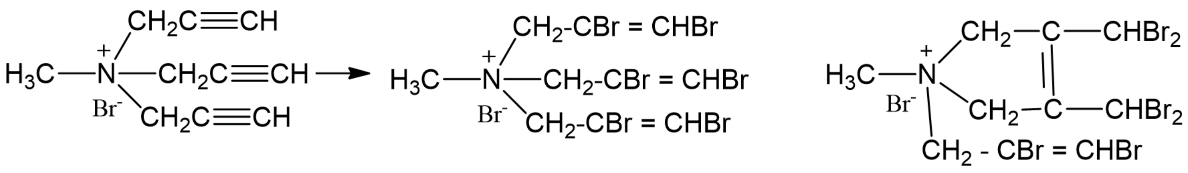
Bromination of ammonium salts containing a triple bond has been studied quite extensively [1, 2]. As a result, products of electrophilic addition to the triple bond were obtained with the formation of trans products. No attachment of two bromine atoms to one terminal carbon atom was observed.

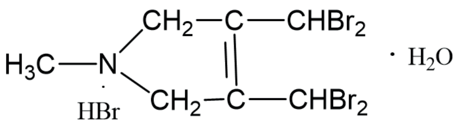
Bromination of dialkyldipropyl-1-ylammonium salts results in both linear addition products and pyrrolinium derivatives, in which both bromine atoms are located at the terminal carbon atoms [3].



The halogenation of methyltripropyn-1-yl ammonium bromide has been studied.



Instead of the expected hexabrome derivative, dealkylation occurs and crystalline hydrate of pyrrolinium bromide is formed.



Dealkylation was observed in [4] in bromination of N,N-dibutyl-N-(4-penten-2-ynyl)ammonium hydrobromide. N-butyl-N-(2,3,4,5-tetrabromopenten-2,4-yl)amine hedrobromide is formed.

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REACTIVITY OF *tert*-BUTYLPEROXYL RADICAL WITH SOME PHENYLTHIAZOLIDINE DERIVATIVES AND PROBUCOL

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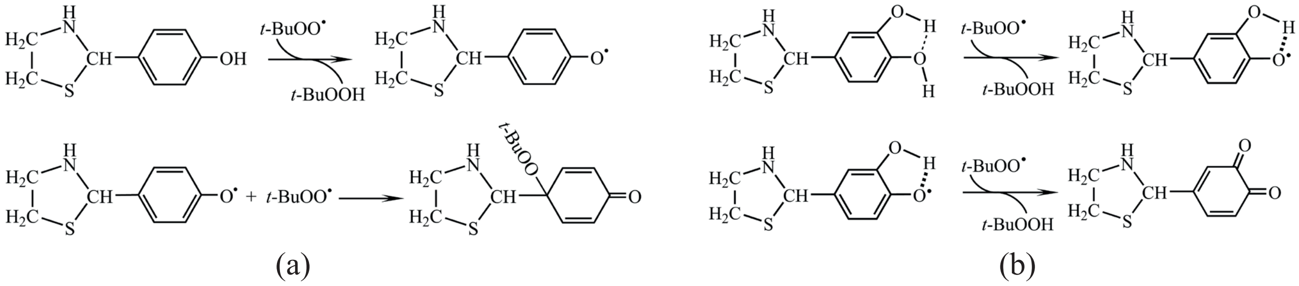
Development of hybrid molecules is a trend of nowadays, that attempts to integrate several pharmacophore fragments with different biological activities in one molecule.

The main objective of the present work is to study the *tert*-butylperoxyl (t-BuOO$^\bullet$) radical reactivity with selected hybrid molecules phenylthiazolidine and its derivatives - 2-phenylthiazolidine (PT), 2-(4-hydroxyphenyl)thiazolidine (HPT), 4-[thiazolidin-2-yl]benzene-1,2-diol (TBD), 2-(3-fluorophenyl)thiazolidine (FPT) and 2-(4-hydroxyphenyl)thiazolidine-4-carboxylic acid (HPTCA). Butylated hydroxytoluene (BHT) and probucol were used as reference antioxidants, the structure of which contains potentially antiradical sites, phenolic OH groups, and in the case of probucol, also sulfide groups. This task was solved by *direct* kinetic measurements using EPR spectroscopy for the reactions of t-BuOO$^\bullet$ with these compounds in lipophilic organic media.

The results of the kinetic-EPR study quantitatively establish that [1]:

- High removal ability of t-BuOO$^\bullet$ peroxyl radical by HPT, TBD, HPTA and probucol was connected with the reaction of hydrogen atom abstraction from phenolic OH group (scheme 1). Under the conditions studied, the antiperoxylradical capacity of these compounds is equal to two for monophenols and catechol derivative thiazolidine, and four for probucol, according to the mechanism of reactions with peroxyl radicals.
- Weaker antiperoxylradical reactivity of phenylthiazolidine derivatives (PT, FPT) was connected with the slower reaction of hydrogen atom abstraction from benzylic C-H bond adjacent to nitrogen atom of thiazolidine ring. This is evidenced by the close values of the rate constants for the reactions of t-BuOO$^\bullet$ radicals with PT and FPT, and with the one for benzylamine.
- Sulfide groups had much weaker participation in antiperoxylradical reactivity of the studied compounds.

It is concluded, that removal of alkylperoxyl radicals by phenylthiazolidine derivatives and probucol may partially account for biological activity of their compounds.



(a) (b)

Scheme 1. A sequence of reactions resulting from a hydrogen atoms transfer from a monophenolic fragment **(a)** and 4-[thiazolidin-2-yl] benzene-1,2-diol (**b**) to a t-BuOO$^\bullet$ radicals.

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APPLICABILITY OF TRANSFERABLE MULTIPOLE PSEUDO-ATOMS FOR RESTORING INNER-CRYSTAL ELECTRONIC FORCE DENSITY FIELDS

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Herein, we have tested the applicability of transferable multipole pseudo-atoms from the University at Buffalo Data Bank for restoring inner-crystal electronic force density fields. The procedure was carried out for the crystal of a uracil derivative and some derived properties of the potential and force fields were compared with those obtained from the experimental multipole model. This procedure was shown to reproduce the force-field pseudoatomic characteristics, such as charge, shape, and volume, and the distinctive features of the quantum potentials along covalent and noncovalent interactions. A detailed orbital-free crystallographic study of the uracil derivative was also performed.

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SOLUTION COMBUSTION SYNTHESIS OF (CoZnFeMnNi)O HIGH ENTROPY OXIDE

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High-entropy oxides (HEOs) are composed of five or more metal oxides and, due to their high entropy, are characterized by an excellent combination of functional characteristics [1]. In particular, they are endowed with high cracking resistance, strength, excellent corrosion resistance, oxidation resistance, controllable magnetism and high catalytic activity. Due to the mentioned properties, these materials can be used in functional coatings, high-speed rotating cutting devices, turbines, as well as energy batteries. There are several methods for synthesizing high entropy oxide nanoparticles, such as flame spray pyrolysis of corresponding metal oxides, hydrothermal synthesis, co-precipitation and sol-gel methods. In this work, the preparation of magnetic, single-phase (CoZnFeMnNi)O HEO powder was performed by energy-saving and eco-friendly solution combustion synthesis (SCS) technology from crystalline hydrates of nitrates of the respective elements, and glycine ($C_2H_5NO_2$) as a complexing and reducing agent. The combustion process can be presented by the following equation:

$$Fe(NO_3)_3 + Co(NO_3)_2 + Ni(NO_3)_2 + Mn(NO_3)_2 + Zn(NO_3)_2 + \frac{25}{2}(\varphi - 1.04)O_2 + \frac{50}{9}\varphi C_2H_5NO_2$$
$$\rightarrow (FeCoNiMnZn)O + \frac{125}{9}\varphi H_2O + \left(5.5 + \frac{25}{9}\varphi\right) N_2 + \frac{100}{9}\varphi CO_2$$

where the parameter φ denotes the fuel to oxidizers ratio.

According to the results, at utilizing 6 mol of glycine, a combustion process is accompanied with a volume ignition and vigorous gas flame (T_c=900°C), resulting to the formation a single-phase, rock-salt structure of (FeCoNiMnZn)O composition. According to XRD pattern (fig.1a), it belongs to the Fm-3m space group with the diffraction peaks at 2θ values 36.53°, 42.38°, 61.32°, 73.37°, 77.19° and 92.10° corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (4 0 0) planes of the rock-salt crystal structure, respectively. According to the results of the SEM analysis, it has a reticulated structure (Fig. 1b), in the nodes of which the presence of individual grains is observed. Moreover, the average atomic composition of elements in the as-synthesized sample is measured to be 57.5% (O), 9.2% (Mn), 9.6% (Fe), 9.9% (Co), 8.8% (Ni) and 5.1% (Zn), respectively, with configuration entropy value of 1.42R, which meets the requirement of high-entropy oxides. Due to the presence of Fe, Ni, Co 3d group ferromagnetic metals it is characterized by clearly expressed magnetic properties. The magnetization increases linearly with the increase in magnetic field, confirming a weak ferromagnetic behavior at room temperature. In addition, low values of coercivity (Hc=215 Oe) and remanent magnetization (Mr=0.32emu/g), classify (FeCoNiMnZn)O HEO as soft magnet.

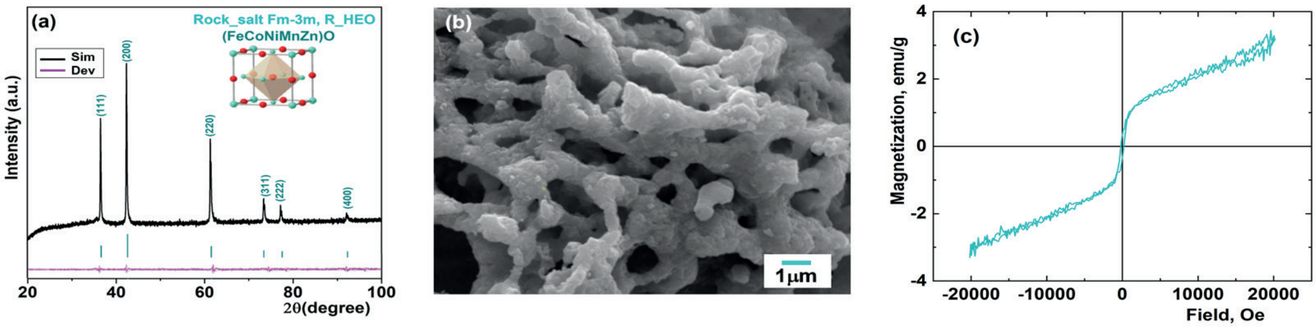

Fig. 1. (a) XRD pattern, (b) SEM micrograph and (c) field-dependence of the magnetization at room temperature of the rock-salt (FeCoNiMnZn)O high entropy oxide

References:

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COMPLEX FORMATION OF COPPER(II) WITH (S)-β-[3-ISOBUTYL-4-(2-METALLYL)-5-THIOXO-1,2,4-TRIAZOL-1-YL]-α-ALANINE IN AQUEOUS SOLUTION

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The complex formation of (S)-b-[3-isobutyl-4-(2-methallyl)-5-thioxo-1,2,4-triazol-1-yl]-a-alanine amino acid (AA1) with copper(II) chloride in aqueous solution has been investigated by means of UV-Vis and FTIR spectroscopy at 25°C.

The data obtained by UV-Vis spectroscopy with using of molar ratio method confirm that the ML2 type complex is formed.

Based on the FTIR data obtained, the structure of the chelate complex has been proposed, in which the copper(II) cation is bound to the oxygen atom of the carboxylate anion by electrostatic interaction, and to the nitrogen atom of the amino group by a covalent bond by the donor-acceptor mechanism. And the octahedral coordination sphere of the copper(II) ion is complemented by two water molecules (fig.1).

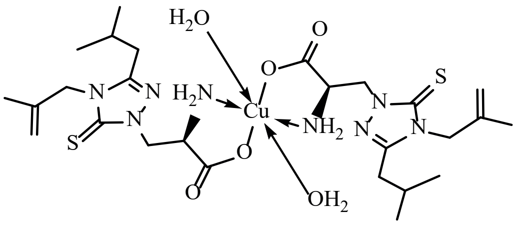

Fig.1. Structure of the complex

Acknowledgments. *The work was carried out in the Laboratory of Physical Chemistry of the YSU Chemistry Research Center with the financial support of the Science Committee of the RA MESCS.*

STUDY OF THE FERTILIZER “MULTIBAR” FOR THE PRODUCTIVITY OF PEPPER VARIETIES

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Introduction: Currently, in connection with the introduction of intensive varieties and hybrids of agricultural crops in production, there is a need to improve the fertilization system as well.

LCF “Multibar” environmentally friendly, non-toxic and non-explosive, non-flammable product, waste-free production. The normal concentration of an undiluted Multibar solution is 2-3 grams per 1 liter of water[1]. Pepper is an important vegetable and popular crop in Armenia. The wide spread cultivation of pepper could be explained by its ability to grow in various climatic zones, high productivity, nutrition value, and by multipurpose utilization of pepper fruits. [2].

Subject and methodology: The research was conducted within 2020-2022 period in the experimental household of Darakert community (the Ararat valley) of the Armenia. The experiments with the fertilizer “Multibar” were conducted over a local selection of sweet pepper sorts - Nataly, Mily, Emily, hot pepper sarts – Haykakan gegecik, Hpart, chili sorts – Gita, Zita, Bucet which is certified in the Armenia. The exsperiment has in three options - 1) non-treated control (I sampls), 2) ammonium nitrate treated (II sampls), 3) “Multibar” processed (III sampls). The seeding of pepper was conducted in the second half of May by the planting plan /90-70/-20cm. Plants were treated with Multibar fertilizer 3 times after planting with a 20-day interval, at a rate of 3g. per 1 liter, and ammonium nitrate 2 times, at a rate of 250 kg per hectare. The experiment was carried out according to the “Methodological regulations of randomized block experimental design” of the World Vegetable Center [3].

Results and Discussion: The number of days to germination- ripening in the studied sweet pepper sorts - was 115- 120 - days (III sampls), was 120-125- days (II sampls), was 125-130 - days (I sampls), the hot pepper sorts – was 87- 90 - days (III sampls), was 92-98- days (II sampls), was 115-120 - days (I sampls), the chili sorts - was 100-105 - days (III sampls), was 110-118- days (II sampls), was 117-126 - days (I sampls). The results of the study of fertilizer studies demonstrated that the yield of the sweet pepper sorts - was 490.5-558.3 - c/ha (III sampls), was 420.8-468.5 c/ha (II sampls), was 290.7- 315.6 c/ha (I sampls), the hot pepper sorts - was 410.9-450.7 - c/ha (III sampls), was 395.8-448.5 c/ha (II sampls), was 260.2-319.5 c/ha (I sampls), the chili sorts - was 225.6-357.3 - c/ha (III sampls), was 220.8-353.5 c/ha (II sampls), was 190.6-234.5 c/ha (I sampls). Similar high data were also obtained in the direction of the average mass of fruits and quality indicators.

Conclusion: According to the obtained results, the new fertilizer "Multibar" provided an increase in both the crop efficiency and fruit quality. Consequently, the new fertilizer "Multibar" is suitable for introducing in the republic and similar regions of the world.

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MEMBRANE MATERIALS BASED ON MODIFIED ORGANOBORON POLYOLS

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In recent years, polymeric membrane materials capable of selective mass transfer have been of interest in the chemical, pharmaceutical, and food industries. The areas of application of such materials are associated with microfiltration, ultrafiltration, dialysis, gas separation, and pervaporation [1]. These technologies are energy- and resource-saving and solve the problems of traditional separation methods. The membranes must withstand the mode of the process, be strong enough, thermally and hydrolytically stable, and not change their properties during operation. There are flat, roll, cartridge, hollow fiber types of membranes [2].

One of the promising materials in this direction are polyurethanes obtained using boric acid amino esters (AEBA). The use of organoboron polyols in the synthesis of polyurethane membranes is associated with the peculiarities of their chemical structure, including high branching, the presence of terminal hydroxyl groups, and the presence of spatially separated ion pairs [3].

Polyurethanes (AEBA-PU) obtained using amino esters of boric acid were studied as vapor-permeable and pervaporative membrane materials. It was found that the introduction of adducts (EM) synthesized on the basis of epoxy resin and monoethanolamine into the AEBA composition leads to a threefold increase in the vapor permeability of polyurethanes obtained on their basis. It is shown that such a significant increase in vapor permeability is due to differences in the macromolecular packing of the corresponding AEBA and AEBA-EM.

Modification of the AEBA structure with the use of an EM adduct leads to a significant decrease in the particle size of AEBA-EM relative to AEBA. A decrease in the size of clusters leads to loosening of their dense packing. Areas of clustering due to associative interactions of hydroxyl groups, together with the hydrophilic nature of polyoxyethylene glycol, create a zone through which water molecules can penetrate.

However, with an increase in the content of the EM adduct, the dependencies cease to be additive due to the fact that, along with the destruction of associative interactions, the EM adduct begins to have an additional effect on the formation of the polymer network. Clustering regions due to associative interactions of hydroxyl groups, together with the hydrophilic nature of polyoxyethylene glycol, create channels through which water molecules can penetrate.

Funding. This work was supported by the Russian Science Foundation (grant No. 19-19-00136).

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HIGHLY FLUORINATED Cu, Co, Mn COMPLEXES BASED ON 1,2,4-TRIAZINE-2-PYRIDINE AND 2,2'-BIPYRIDINE LIGANDS

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Metal complexes based on organofluorine ligands are widely used as materials for organic light-emitting diodes (OLEDs), metal-organic frameworks (MOFs), and polymer materials. In this work, a series of novel Co(II), Cu(II), and Mn(II) complexes containing both aromatic and aliphatic organofluorine species were obtained in 76-90% yields. Structural properties of these coordination compounds derived from pentafluorophenyl-substituted 3-(2-pyridyl)-1,2,4-triazine, 2,2'-bipyridine and hexafluoroacetylacetonate ligands were comprehensively studied using XRD analysis. The spatial characteristics for 3-(2-pyridyl)-1,2,4-triazine bearing pentafluorophenyl moiety at C(5) position as well as its bipyridine analog in relation to ones for the corresponding metal complexes were also studied. The revealed structural features for the elaborated Co(II), Cu(II), and Mn(II) complexes based on 2,2'-bipyridine and 3-(2-pyridyl)-1,2,4-triazine ligands containing organofluorine species could be of particular interest in the design of advanced materials for catalysis, chemosensory, molecular electronics, and other fields of materials science.

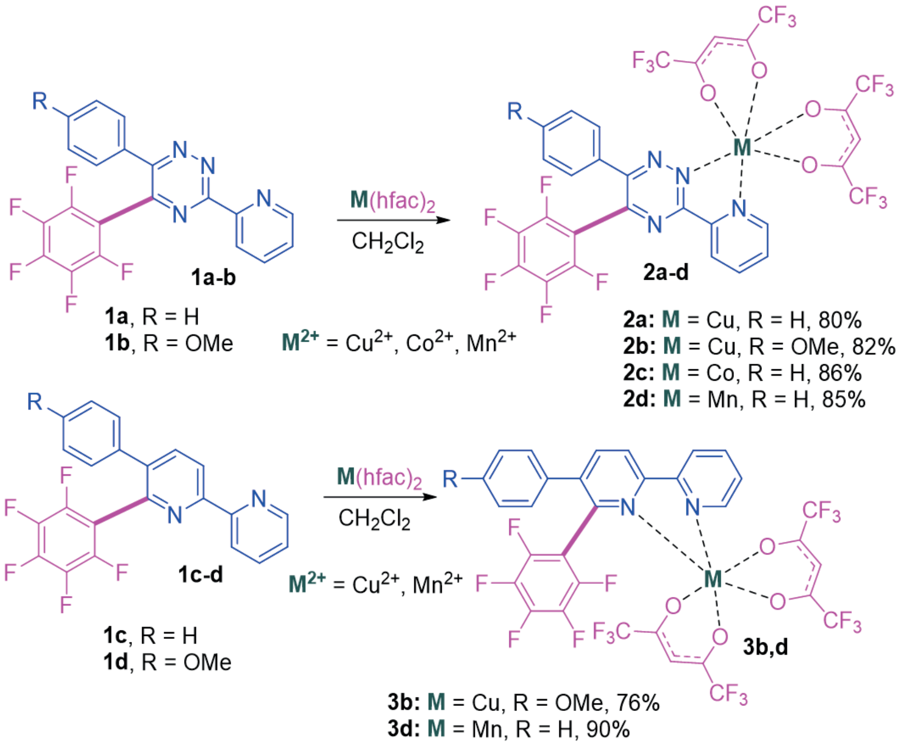

Figure 1. Synthesis of metal complexes

** The study was funded by the Russian Science Foundation (RSF) according to the research project № 20-73-10077, https://www.rscf.ru/en/project/20-73-10077/*

PHOTOPHYSICS AND PHOTOCHEMISTRY OF DIRODIUM ANTICANCER COMPLEX PROSPECTIVE IN PHOTOCHEMOTHERAPY

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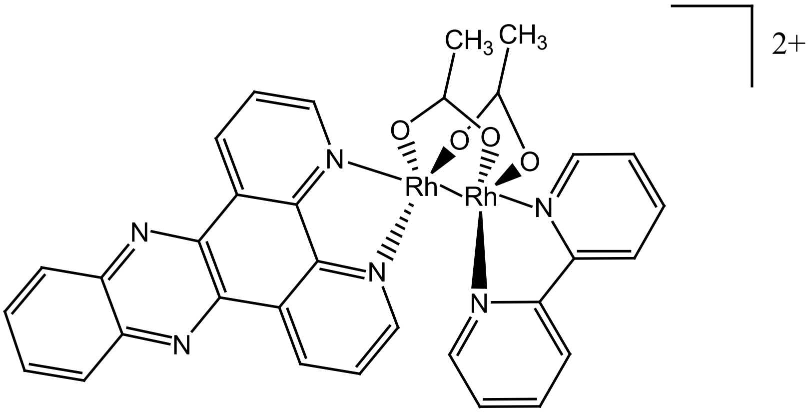
Photochemotherapy (PCT) is one of the most promising methods of anticancer treatment based on the photochemistry of platinum metal complexes. Compared to traditional photodynamic therapy based on triplet sensitizers and formation of singlet oxygen, PCT does not require dissolved oxygen. This is important because many tumors are hypoxic. Several complexes of platinum metals are considered as prospective for PCT; however, their fundamental photophysics and photochemistry are not studied in detail [1].



Complex **1**.

Here we present a case study of photophysics and photochemistry of light-activated anti-cancer complex **1** (*cis*-$[Rh_2(\mu\text{-}O_2CCH_3)_2(bpy)(dppz)]^{2+}$, where dppz is dipyrido[3,2-a:2',3'-c] phenazine). Complex **1** exhibits light-induced cytotoxicity both in the absence and in the presence of dissolved oxygen induced by visible irradiation [2]. Irradiation of **1** in the near UV and visible spectral regions (corresponding to π-π* transitions of dppz) does not cause decomposition of **1**.

Photoexcitation of Complex 1 results in formation of the lowest triplet electronic excited state, which lifetime is less than 10 ns. This time is too short for diffusion-controlled quenching of the triplet state by dissolved oxygen resulting in $^1O_2$ formation. We proposed that singlet oxygen is produced by photoexcitation of weakly-bound van-der-Waals complex $[Rh2\ldots O_2]$, which are formed in solutions. In this case, no oxygen-independent light-induced cytotoxicity of Complex **1** exists. Residual cytotoxicity of deaerated solutions is caused by the remaining $[Rh2\ldots O_2]$ complexes.

The work is supported by the Russian Science Foundation (Grant № 22-33-00248).

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SYNTHESIS OF 1,2,4-TRIAZOLOAZINES AS POTENT BIOLOGICAL ACTIVE COMPOUNDS

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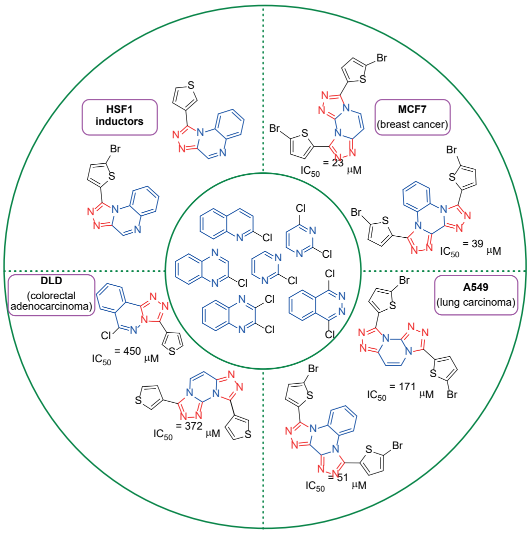
Heterocyclic frameworks serve as fundamental components in the structures of numerous pharmacologically important molecules that participate in diverse biological and biochemical processes [1]. This is evidenced by the fact that a majority of the drugs approved by the US-FDA in 2021 incorporate a heterocyclic fragment as the principal pharmacophore [2]. The inclusion of heterocyclic systems in drug molecules contributes to the modulation of their physicochemical, pharmacokinetic, and pharmacodynamic properties, as well as their toxicity profiles. Derivatives of 1,2,4-triazole and their fused systems occupy a prominent position among the promising compounds in medicinal chemistry. These compounds have demonstrated notable antibacterial, antifungal, anticancer, antiviral activities and also they can be used in the treatment of neurodegenerative diseases.



In our work, a convenient and simple method for the synthesis of a wide range of 1,2,4-triazoloazines from available aldehydes and heterocyclic hydrazines in the presence of hypervalent iodine(III) was demonstrated. The obtained compounds were evaluated against the cancer cell lines MCF7, DLD-1, A549 and as HSF1 inductors. The results were comparable to the activity of the comparable to known drugs. This highlights the potential of these compounds as promising candidates for further study as potential biologically active compounds.

The research was financially supported by the Russian Science Foundation (22-13-00298) and the Ministry of Science and Education of the Russian Federation (FENU-2023-0014).

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ORGANOMETALLIC PRECURSORS FOR NANOSCALE CATALYSTS

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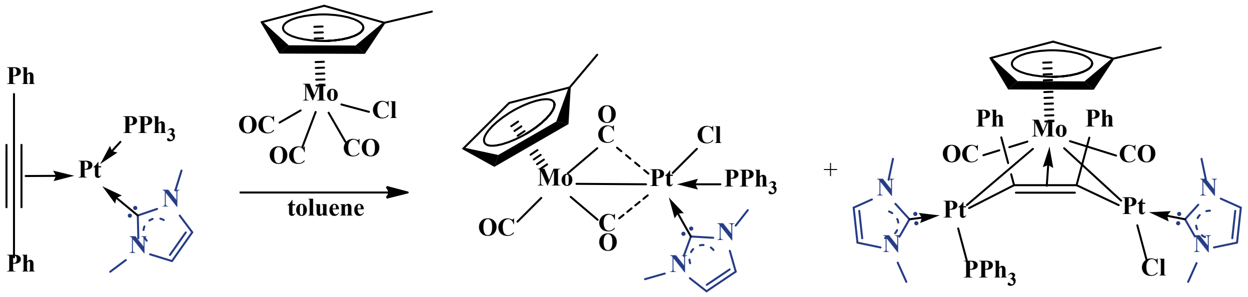
Platinum-based heterometallic complexes are convenient precursors for creating electrocatalysts for direct methanol fuel cells (DMFC) [1]. It has been shown [2] that the PtCo/C, PtMn/C and PtZn/C catalysts synthesized from bimetallic clusters have advantages of application in hydrogen-air fuel cells over a commercial platinum catalyst. N-heterocyclic carbenes (NHCs) can stabilize new heterometallic complexes with different metal ratios due to the strong σ-donor ability of carbene ligands and steric shielding of the metal center [3].

A new platinum carbene complex $(PPh_3)(NHC)Pt(PhCCPh)$ (1) was obtained by the reaction of $(PPh_3)_2Pt(PhCCPh)$ with the 1,3-dimethylimidazolium carboxylate decarboxylation product . The complex exhibits different reactivity depending on the reagents.



A number of binuclear and trinuclear heterometallic complexes of various structures were synthesized on the basis of complex 1 in reactions with $Fe(CO)_5$, $Mn(CO)_5Cl$, $Re_2(CO)_{10}$, $(CH_3)_3SnCl$. Compounds with Pt-Mo, Pt-Sn and Pt-Fe bonds have been used as precursors of electrocatalysts in DMFC.

The work was carried out with the financial support
of the Russian Foundation for Basic Research (grant 19-33-90199).

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AMIDES OF AMPHOTERICIN B AND NYSTATIN A_1: ANALYSIS OF THE EFFECT OF MODIFICATIONS ON THE SELECTIVITY OF ANTIFUNGAL ACTION

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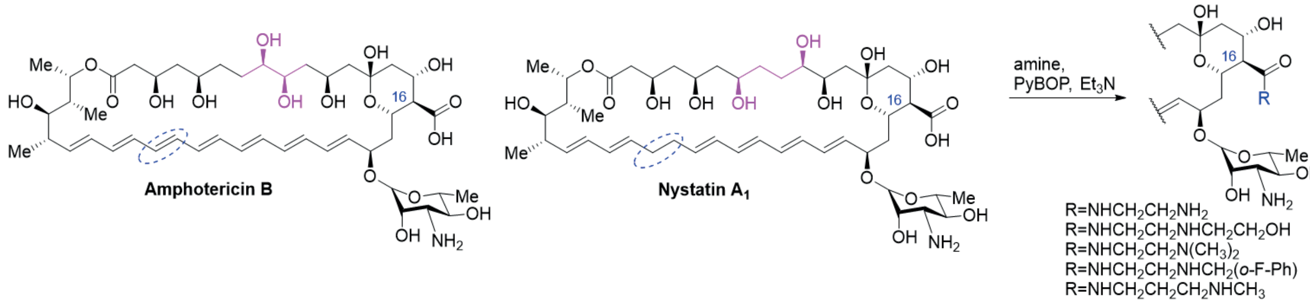
Antifungal polyene macrolide antibiotics (amphotericin B, nystatin A1, natamycin) which have a low rate of resistance emergence, are still widely used in medicine, though their use is limited by nephrotoxicity and very low water solubility. Amphotericin B (AmB) and nystatin (Nys) exhibit biological action through interaction with sterols (especially ergosterol) in the cell membrane and the formation of pores. We present a study of the effects of identical modifications of AmB and Nys on the relation between their structure and properties with the aim to search for new, less toxic semi-synthetic polyenes with increased solubility in water. A new series of amphotericin and nystatin amides were synthesized and studied in terms of their activity/toxicity ratio *in vitro* on cells and on model Erg- and Chol-containing membranes.



Although all modifications led to lacking zwitterionic character, insertion an additional positive charge and disruption of the “salt-bridge” between C16 carboxylic group and amino group of mycosamine, that might decrease toxicity according to known data [1], the exact effect on safety of compounds depend on both polyenes core and amine nature. Thus, the insertion of short ethylenediamine moiety into the AmB and Nys cores led to more active and safe derivatives. However, unlike the situation with AmB derivative, in the case of nystatin this effect could not be explained by increased selectivity to Erg-containing membranes vs Chol-containing ones and might be the result to alteration of polyene-sterol interactions by membrane phospholipids and sphingolipids or decreased aggregation properties might be considered as well. Modification with longer diamines (*N*,*N*-dimethylethylenediamine and *N*-methyl-1,3-propanediamine) have differential effects on the two types of polyenes core – corresponding Nys amides with antifungal activity similar to the parent antibiotic, were not toxic to human embryo kidney cells HEK293 and showed low hemolytic activity, which was well-correlated with increasing selectivity towards Erg-containing vs Chol-containing membranes. In contrast, AmB amides bearing the same moieties proved to be more toxic to kidney and red blood cells, which coincided with a lower ratio of selectivity towards Erg-containing membranes. Long amide chains both lipophilic (2-((2-fluorobenzyl) amino)ethyl)amine and hydrophilic 2-((2-aminoethyl)amino)ethanol led to the most pronounced increase in the permeability of Chol- and Erg-membranes without changing the selectivity for both tested polyene cores, which might be the result of interactions (remained unclear) with the lipid environment. Thus, the design of new structures should take into account not only the affinity for sterols, but also changes in the interaction of polyenes with the lipid environment, as well as the physico-chemical and physico-biological properties of polyenes that affect their self-association in membranes.[2]

This research was funded by Russian Science Foundation, grant number 21-74-20102

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NEW AZAHETEROCYCLIC PYRANO[2,3-F]COUMARINS WITH IMPROVED SOLUBILITY IN AQUEOUS MEDIA

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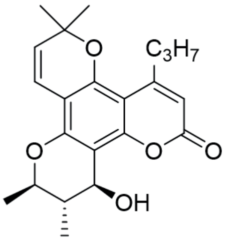
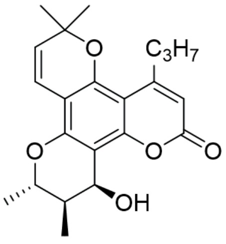
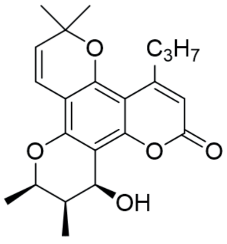
Calanolides belong to the class of tetracyclic compounds active against HIV-1. For example, calanolide was identified as a non-nucleoside reverse transcriptase inhibitor and showed an IC_{50} in the nanomolar range. In addition, calanolide A has shown activity against a wide range of HIV strains, including azidothymidine-resistant and pyridinone-resistant HIV strains. At the same time, the poor solubility of calanolide does not affect any phase of detection. In previously known works, the modification of the pyran ring to obtain 10-bromomethyl-11-demethyl-12-oxo-calanolide made it possible to increase antiviral activity and bioavailability. In this work, we proposed the synthesis of a calanolide containing a free hydroxyl group and a basic nitrogen atom for solubility in water [1].



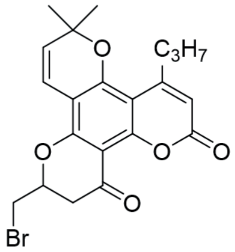
Calanolide A
IC_{50} = 0.1 μM
TI = 200



Calanolide B
IC_{50} = 0.4 μM
TI = 37

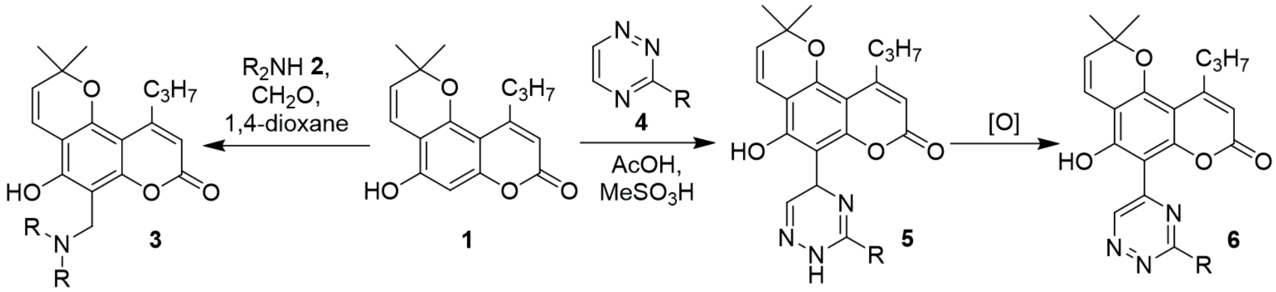


Calanolide C
IC_{50} = -



10-Bromomethyl-11-demethyl-12-oxo-calanolide A
TI > 10256

We found that two methods of synthesis can be used to obtain azaheterocyclic derivatives of pyrano[2,3-f] coumarins, depending on the required substituents in the structure of the resulting products. In the case of the reaction of pyranocoumarin **1** with formaldehyde and secondary aliphatic amines **2** by refluxing in dioxane, Mannich reaction products **3** were obtained in good yields. In the case of the reaction of pyranocoumarin **1** with 1,2,4-triazines **4**, adducts **5** were formed in good yields. Adducts **5** can be subsequently oxidized to products of nucleophilic hydrogen substitution **6**. The resulting azaheterocyclic derivatives showed good solubility and were tested for antiviral activity against HIV-1 cell lines (Scheme 1).



Scheme 1. Synthesis of azaheterocyclic derivatives of pyrano[2,3-f]coumarins

Работа выполнена при поддержке РНФ 21-13-00382

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ACYCLIC CHELATORS FOR RADIOPHARMACEUTICALS

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Radiopharmaceuticals based on radionuclide complexes have become widespread in recent years due to their potential in diagnostic and therapeutic medicine [1]. Although thermodynamic stability and kinetic inertness are key properties of ligand complexes with radiometals, rapid radiolabeling at room temperature is also necessary for short-lived radionuclides. Acyclic ligands are characterized by fast complex formation kinetics; however, often their complexes are not very stable in biological objects. The aim of this work is to obtain two types of acyclic chelators with different chelating groups capable of forming stable complexes with medical metal cations in solution.

Ligands of the first type contain a combination of chelating groups of different nature in one molecule to increase the stability of the complexes formed. In order to obtain such ligands, we developed an original synthesis method, including the hydrolysis of N-substituted amide pyridine-containing azacrown compounds. Ligands of the second type contain a rigid pyridine fragment to reduce the conformational mobility of the ligand (Fig. 1).

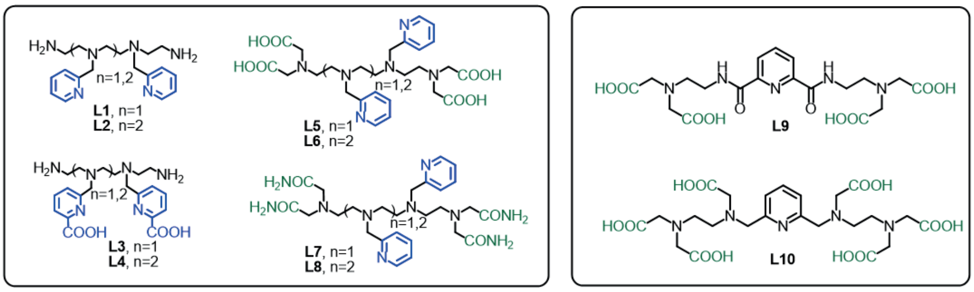

Figure 1. Two types of acyclic ligands

The complex formation of ligands of the second type **L9** and **L10** with metal cations Sc^{3+}, Bi^{3+}, Y^{3+}, Ga^{3+}, Cu^{2+} has been studied by NMR-spectroscopy, mass-spectrometry, and potentiometric titration. It was shown that both ligands form complexes with these metal cations at room temperature. The geometric structure of the complexes was optimized by the DFT-calculation method (Fig. 2).

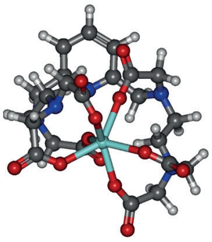

Figure 2. Optimized structure of the Y-**L10** complex

As a result of the studies, it was shown that the **L10** ligand forms stable complexes with Y^{3+}, Bi^{3+}, Ga^{3+}, including in the presence of serum proteins, which makes it promising for use as a component of a radiopharmaceutical.

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

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NEW Co(II) AND Mn(II) COMPLEXES BASED ON (THIA) CALIX[4]ARENES AS POTENTIAL MAGNETIC MATERIALS

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Molecular magnetic materials have attracted great attention over the past decades for their great potentials in high-density information storage device, quantum computer, spintronics and magnetocaloric materials. Unconventional molecular nanomagnets in 1990s, namely single-molecule magnets (SMMs) and single-chain magnets (SCMs), exhibit magnet-type behaviors without long-range magnetic ordering [1]. There is a rich diversity of molecules that exhibit SMM behaviour. Each system has its own unique strengths and limitations for achieving slow relaxation. SMM coordination complexes can be grouped into three classes based on the types of metals in the complexes: *3d*, heterometallic *3d-4f* or *4f* compounds [2].

(Thia)calix[n]arenes due to closely disposed phenolic oxygen atoms can act as versatile ligands for the construction of polynuclear transition metal, rare earth metal and *3d-4f* clusters [3] able to exhibit the single molecule magnet behavior. Moreover, the modification of the lower rim of macrocycle with chelating Schiff base groups may also afford the formation of discrete coordination complexes with attractive magnetic properties both with the luminescence when combined with lanthanoid cations [4].

In this report, we present a strategy for the synthesis of new macrocyclic ligands based on (thia)calix[4]arene bearing salen-type coordinating sites with N,O-donor atoms and their complexes with Co(II/III) and Mn(III). The complexes were obtained in the crystalline phase and studied using single crystal X-ray diffraction, IR-spectroscopy, mass-spectrometry etc. The influence of nature of macrocyclic backbone as well as of the substituents disposed at *ortho* and *para* positions respecting to OH-coordinating group of salen moiety on the formation of obtained complexes will be discussed.

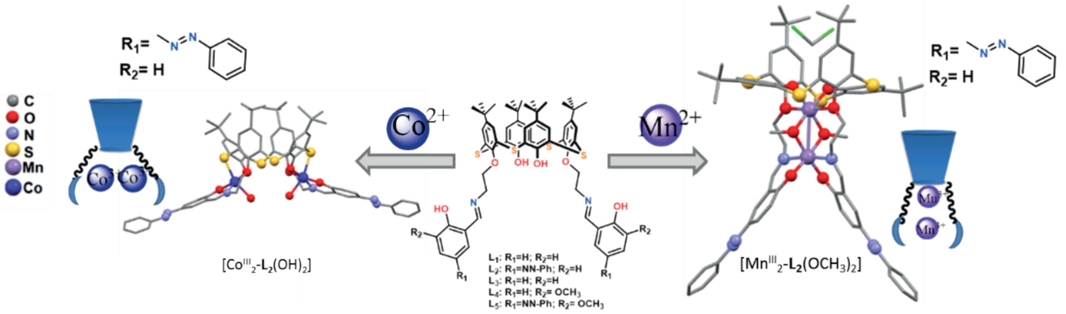

Figure 1. New Schiff base derivatives of (thia)calix[4]arenes for creation of Co (II/III) – and Mn(III) complexes in the crystalline phase.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant № 22-73-10139).

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BINUCLEAR RUTHENIUM COMPLEXES WITH PYRIDONE LIGANDS AS WATER-SOLUBLE ANTITUMOR AGENTS

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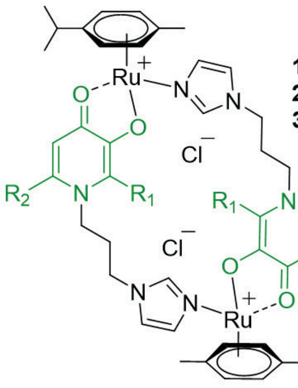
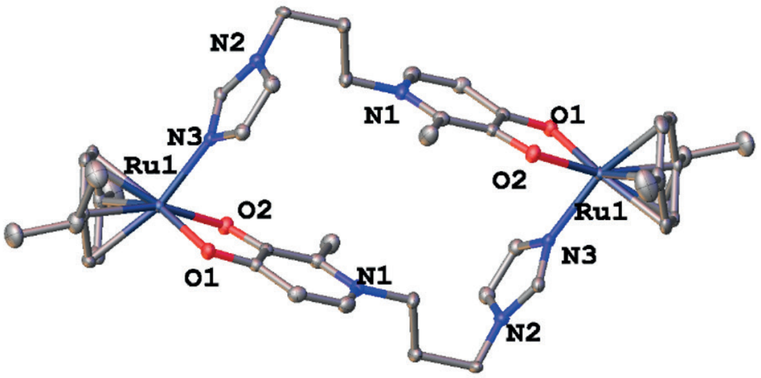
In recent years, ruthenium compounds have become a promising replacement for platinum drugs for chemotherapy of malignant neoplasms. In 2021, BOLD-100 was approved by the FDA as an orphan drug for the treatment of stomach cancer.

The introduction of biologically active organic ligands into the ruthenium coordination sphere makes it possible to adjust the profile of antiproliferative activity and pharmacokinetic parameters, for example, water-solubility of potential drug candidates [1-5]. Within the framework of this work, binuclear complexes of Ru(II) with imidazole ligands containing a fragment of biologically active pyridones maltol, ethylmaltol, and allomaltol were obtained. This work is devoted to the synthesis and detailed physicochemical and biological studies of water-soluble ruthenium binuclear complexes with high antiproliferative activity in *in vitro*.



1: R_1 = H: R_2 = CH_3
2: R_1 = CH_3: R_2 = H
3: R_1 = C_2H_5: R_2 = H



For the obtained compounds, the values of antiproliferative activity were determined in *in vitro* MTT tests on a small library of human cancer cell lines, and structure-activity analysis was carried out, the lead-compounds were selected, for which the ability to induce apoptosis of tumor cells and the caspase activation was studied.

Acknowledgements: This work was supported by RSF project № 23-73-01076

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ORGANIC MODIFICATION OF LAYERED PEROVSKITE-LIKE OXIDES AS A WAY TO OBTAIN HIGHLY EFFICIENT PHOTOCATALYSTS FOR HYDROGEN GENERATION

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Overcoming many global ecological problems caused by the rapid industrial growth and the active use of traditional fuels in the XX–XXI centuries is associated with environmental remediation, the introduction of non-waste technologies and the development of alternative energy sources, including hydrogen. One of the environmentally friendly methods for producing hydrogen is known to be the photocatalytic decomposition of water and organic matter. Among the latter, ion-exchangeable layered perovskite-like oxides deserve special attention as photocatalysts due to their unique structural features being responsible for the efficient separation of photoexcited charge carriers and high chemical activity of the interlayer space towards intercalation and ion exchange. An interesting approach to the modification of layered perovskite-like oxides is the introduction of organic components into the interlayer space, which allows producing hybrid inorganic–organic materials. Despite a wide variety of known perovskite-based inorganic–organic derivatives, until recently, they were almost never investigated as catalysts or photo-catalysts.

Our recent studies [1,2] have shown that oxides $HCa_2Nb_3O_{10}$ $H_2Ln_2Ti_3O_{10}$ and $HLnTiO_4$ (Ln = La, Nd), after organic modification, exhibit magnificent photocatalytic performance towards hydrogen production from aqueous methanol, glucose and xylose, being typical components of plant biomass processing. Particularly, the activity of the organically modified materials exceeded that of the initial protonated oxides up to 117 times, and apparent quantum efficiency reached 40% in the near-ultraviolet range after additional surface platinization. Despite the partial degradation of interlayer organic modifiers upon photocatalysis, the hydrogen evolution rate over the hybrid samples was found to be stable for a long time. The findings described made the creation of organically modified photocatalysts an intriguing and promising research direction.

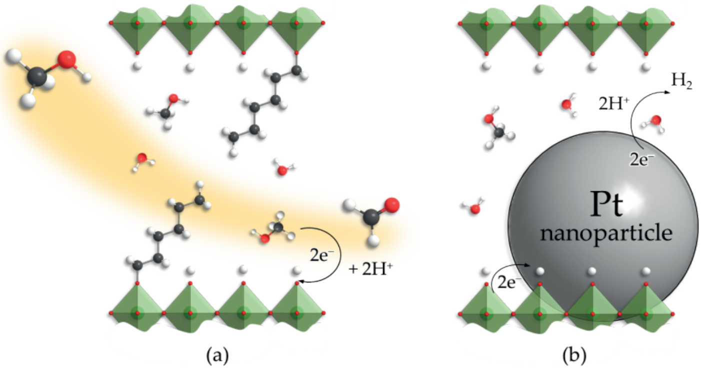

Figure 1. Potential explanations of the photocatalytic properties of inorganic–organic derivatives: increasing of the interlayer reaction zone accessibility (a), reduction of Pt nanoparticles in this zone (b).

Acknowledgements The work was supported by Russian Science Foundation (grant №22-73-10110). Authors are also grateful to Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Materials Research, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics.

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MODIFICATION OF CARBORANES AND METALLACARBORANES: EFFECT OF SUBSTITUENTS

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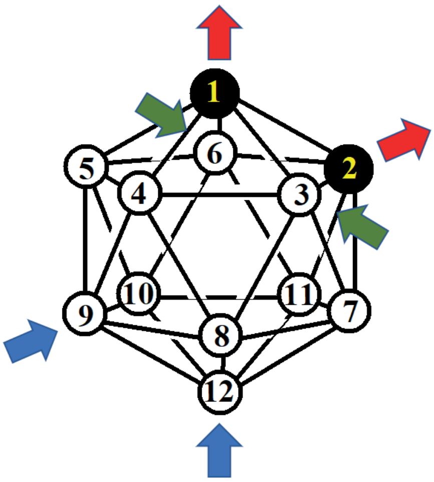
The effect of various substituents at boron atoms in different positions of the *ortho*-carborane cage on its CH-acidity and the electron-withdrawing effect upon substitution at the carbon atom will be considered. The introduction of chlorine atoms to the boron atoms opposite to the carbon atoms (positions 9 and 12) slightly reduces the *CH*-acidity of the carborane cage, whereas the introduction of bromine and, especially, iodine atoms lead to the significant increase in the CH-acidity comparing to the parent *ortho*-carborane. The introduction of halogen atoms to the boron atoms bound to both carbon atoms (positions 3 and 6) results in a significant increase in the CH-acidity which is practically independent on the halogen electronegativity [1].



In *meta*-carborane, the introduction of halogen atoms to the boron atoms most distant from both carbon atoms (positions 9 and 10) leads to a significant increase in the CH-acidity. In this case, as in the case of *ortho*-carborane, there is an inverse correlation between the electronegativity of the halogen atom and an increase in the CH-acidity.

The same trend was observed earlier in the halogen-substituted derivatives of cobalt bis(dicarbollide) $[8,8'\text{-}X_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (X = Cl, Br, I), where the $E_{1/2}(Co^{3+/2+})$ potential decreases in the series H > Cl > Br > I. This is explained by the decrease in the electron-donating nature of the carborane ligands upon the introduction of electron-withdrawing substituents. In this case, iodine is also a more efficient electron-withdrawing substituent than bromine and chlorine [2].

This research was supported by the Russian Science Foundation (21-13-00345).

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MOLECULAR DESIGN AND SYNTHESIS OF CYCLOMETALATED IRIDIUM(III) COMPLEXES WITH N-BENZYLNAPHTIMIDAZOLES AS PHOTOSENSITIZERS

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Cyclometalated Ir(III) complexes can be considered as a stable replacement for Ru(II) complexes and organic dyes in dye-sensitized solar cells (DSSC). However, low extinction coefficients of Ir(III) compounds in the visible area obstruct their widespread using in DSSC. N-benzyl-napht[2,3]imidazoles were chosen as cyclometalated (C^N or antenna) ligands. This type of ligands leads to enhancement of light-harvesting properties compared to N-benzyl-benzimidazoles complexes. 4,4›-dicarboxy-2,2›-bipyridine was chosen as ancillary (N^N) ligands because of its successful application synthesis in the ruthenium(II) dyes and an ancillary ligand with dipyrromethene moiety was chosen in order to improve photophysical properties. (Fig. 1)

The experimental part was carried out in 4 stages. First, C^N ligands were synthesized in 2 steps and characterized by ^{1}H and ^{13}C NMR spectroscopy. After that, dimeric neutral complexes [Ir(C^N)$_2$Cl]$_2$ were obtained from iridium(III) chloride hydrate, from which heteroleptic cyclometalated iridium complexes [Ir(C^N)$_2$(N^N)]+ or [Ir(C^N)$_2$(N^N)] were synthesized.

The resulting complexes were characterized by ^{1}H NMR, HRMS, cyclic voltammetry, absorption and luminescence spectroscopy. For most of the complexes, single crystals were obtained and studied by X-ray diffraction. Analysis of the experimental data revealed clear correlations between the Ir coordination environment and properties of the complexes, which can be useful in creation of effective photosensitizers based on cyclometalated iridium(III) complexes.

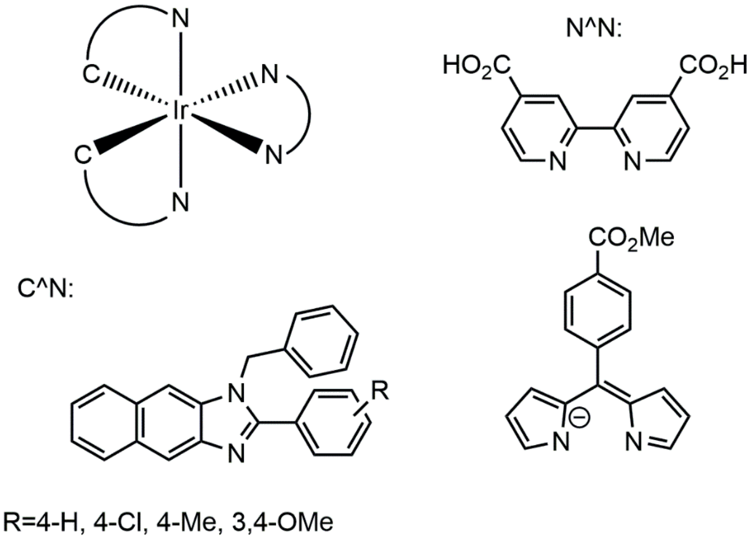

Fig.1. Complexes investigated in this work.

This work was supported by the Russian Science Foundation (grant № 22-23-01171).

RARE-EARTH ELEMENT COORDINATION COMPOUNDS BASED ON β-ENAMINDIONE DERIVATIVES

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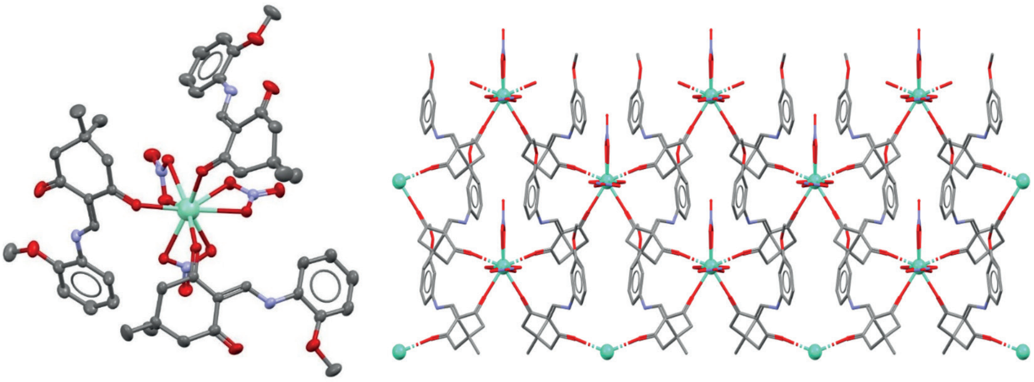
Rare-earth element complexes encourage attention by their luminescent properties as well as coordination chemistry. Due to the shielded *f*-orbitals, there is sharp bands luminescence leading to the pure colour emission. Generally, intensive luminescence is achieved by means of organic compounds used as ligands, which are capable to absorb the light and transfer the energy to lanthanide ion. Different kinds of organic ligands result in large variety of obtained structures as well as coordination polyhedra of the central atom. This work is devoted to the synthesis and investigation both structural features and photoluminescent properties of lanthanide(III) complexes with β-enamindione derivatives. According to the literature data, compounds containing enaminone or β-enamindione moieties are slightly used as ligands for obtaining rare-earth elements complexes. However, they are widely applied as precursors in the organic synthesis [1-4].

The 2-[(phenylamino)methylene]-5,5-dimethyl-cyclohexane-1,3-dione and its methoxy-, methyl- and chloro-substituted derivatives have been made of use for synthesis cooordination compounds. According to single-crystal X-ray diffraction analysis, these ligands exhibit both monodentate coordination mode and bidentate-bridging one leading to the polymers formation (Fig. 1). As a result, the coordination sphere of central ion consists of nine or ten oxygen atoms, while the polyhedron can be related to "muffin"-like or capped square antiprism in case of coordination number equal to 9, as well as to sphenocorona or bicapped square antiprism in case of coordination number equal to 10. Upon photoluminescence investigation, the sensitization is achieved mostly for all europium(III) coordination compounds with chosen ligands as well as in samarium(III) or terbium(III) complexes with some β-enamindione derivatives. The luminescence lifetime of the excited state in coordination compounds increases up to millisecond upon complexation.



a) b)

Figure 1. The structure of mononuclear complex [$SmL_3(NO_3)_3$] with *ortho*-methoxy derivative (a) and polymer compound [$LnL_2(NO_3)_3$]n with *meta*-methoxy derivative (b).

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SINGLET-TRIPLET CONVERSION IN MOLECULAR HYDROGEN ON A HOMOGENEOUS CATALYST IN PARAHYDROGEN INDUCED POLARIZATION EXPERIMENTS

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SABRE (Signal amplification by reversible exchange) belongs to the family of methods for induced hydrogen-parahydrogen polarization of nuclei. Pure parahydrogen potentially contains a huge stock of nonequilibrium polarization, and it can be stored for up to several weeks. One of the problems in PHIP applications is the singlet-triplet conversion in the H_2 molecule (similar to singlet-triplet transitions in radical pairs), which reduces the lifetime of the singlet spin order of H_2 in solution. In the presence of a catalyst, this conversion is significantly accelerated (up to several seconds), which negatively affects the enhancement of NMR signals. The study of this process will make it possible to estimate the lifetime of the singlet spin order H_2 in the systems used in PHIP experiments, and, ultimately, to increase the gain of NMR signals obtained. The study of singlet-triplet conversion in molecular hydrogen on catalysts is also relevant to the problems of liquid hydrogen storage. This is due to the fact that in the liquid state hydrogen completely converts to the singlet state, so it is important to monitor the ortho-para conversion during storage.

Field dependences of the ortho-para conversion rate and free hydrogen signal amplification factor were experimentally obtained for the IrImes (the molecular formula is [Ir(COD)(IMes)Cl]) catalyst. To investigate the influence of different factors on the behavior of the hydrogen conversion rate, we also performed numerical calculations of parahydrogen induced polarization experiments.

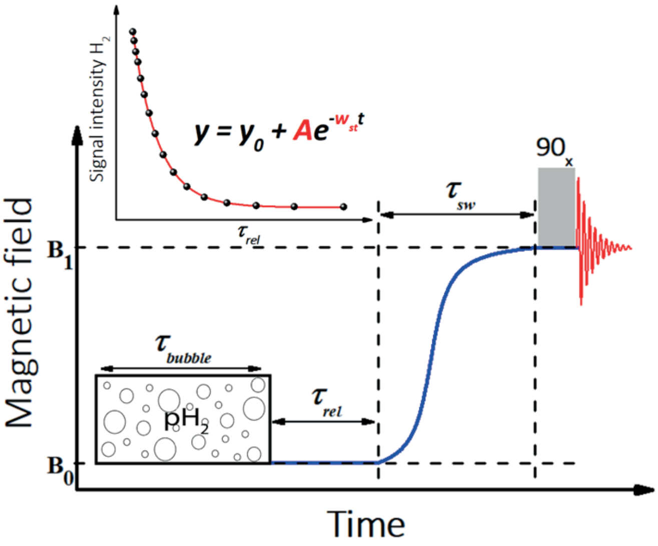

Figure 1. Schematic of experiments to measure the field dependences. τ_{bubble} – time of sample bubbling with parahydrogen (10 s), τ_{rel} – time of varying delay

Acknowledgements. The work was supported by the Ministry of Higher Education and Science of the Russian Federation (Contract No. 075-15-2021-580).

SYNTHESIS OF OPTICALLY PURE (*S*)-2-AMINO-5-(4-((S)-2-AMINO-2-CARBOXYETHYL) PHENYL)PENT-4-YNOIC ACID BY USING SONOGASHIRA REACTION

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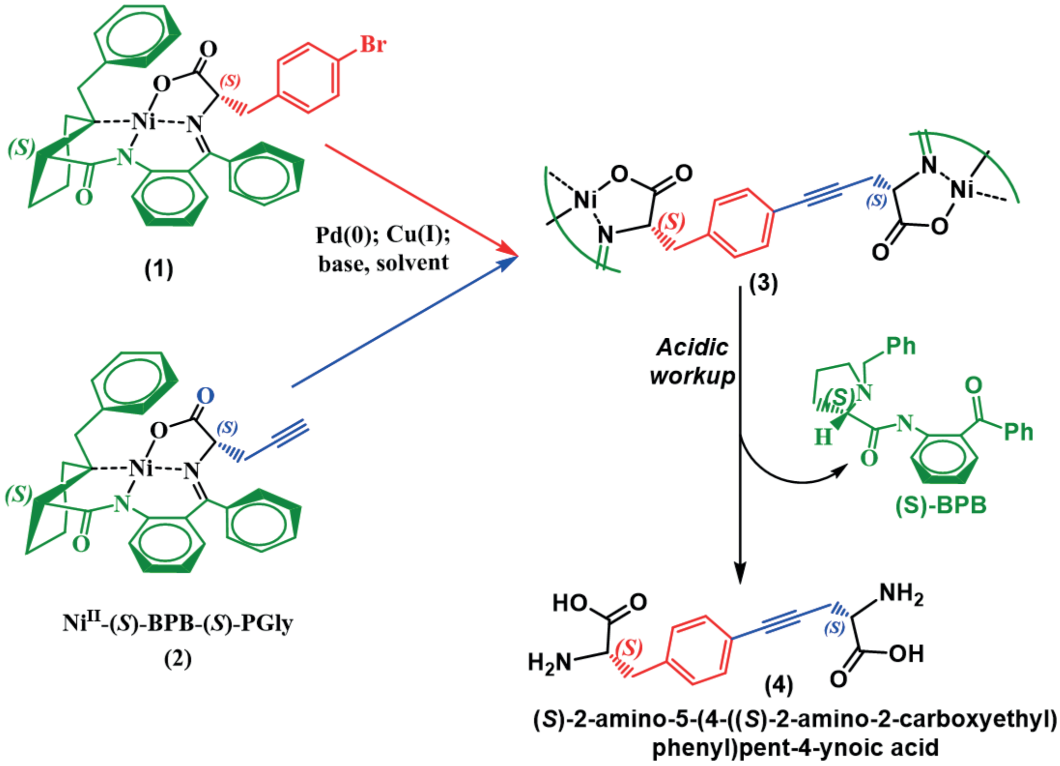
New different-structured enantiomerically enriched (*SS*) amino acids were obtained through the cross-coupling reactions of Sonogashira. As the initial complexes, the Schiff base Ni(II) complexes of the chiral auxiliary (S)-BPB (BPB (N-benzyl proline benzophenone) and amino acids were used. To select the optimal reaction conditions, temperature, bases, catalyst, solwent as well as the ratios of starting substances were investigated.

Scheme



As a result effective way of synthesis novel pure (SS) diastereomer amino acids (ee>99%) was developed.

This work was supported in part by the RA MES State Committee of Science, in the frames of the research project №21T-1D157

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SUPRAMOLECULAR CAGES IN THE CRYSTALLINE PHASE BASED ON SULFONYLCALIX[4]ARENE

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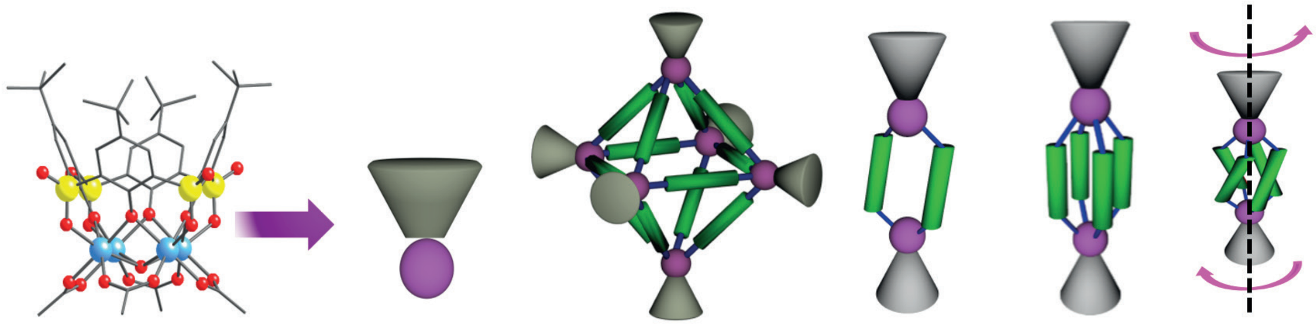
It is known that the macrocyclic platform of thiacalix[4]arene and its oxidized tetrasulfonyl analogue, upon interaction with d-metal cations in the presence of auxiliary co-ligands (as a rule, polytopic carboxyl derivatives), can form polynuclear coordination cages with a given porosity [1]. Such structures can have various useful properties [1]. In addition, calix[4]arenes can be easily modified by introducing various substituents, which makes them attractive linkers for obtaining coordination cages.



In this communication, we will demonstrate an approach [2], which consists in the targeted supramolecular synthesis of polynuclear coordination cages using a three-component system containing sulfonylcalix[4]arene, conformationally flexible succinic acid, or conformationally rigid fumaric acid with d-metal ions (Co^{2+}, Ni^{2+}, Zn^{2+}). As a result, new cages were obtained, the supramolecular motif and the diameter of the inner cavity of which can be tuned by varying the mobility of the hydrocarbon acids spacers, and chiral crystal structures can also be formed.

The work was supported financially by the Russian Science Foundation (project no. 19-73-20035).

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MAGNETO-THERMAL PROPERTIES OF BIOCOMPATIBLE WATER-SOLUBLE NANOCOMPOSITES BASED ON SODIUM ALGINATE AND MAGNETIC NANOPARTICLES

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Nowadays, macromolecules and polymers are used to prepare the nanocomposites with unique physical and chemical properties. For example, nanocomposites with magnetic properties are used as contrast agents in MRI-studies; the magnetic component of compositions for targeted drug delivery; preparations for hyperthermia treatment of pathological foci. The presented work describes the characteristics of a biocompatible non-toxic functional nanocomposites, the significant advantage of which is both solubility in water and sensitivity to the action of a magnetic field.

The sodium salt of alginic acid consists of anionic and hydroxyl groups and being a non-toxic, hydrophilic polyelectrolyte was used as a polymer matrix for creating nanocomposites; maghemite was used as magnetic component of nanocomposites. Since the obtained nanocomposites are potential candidates for hyperthermia application, it is of interest to study their magneto-thermal properties. Solutions of the obtained nanocomposites were testified by alternating magnetic field of different frequencies and amplitudes. It was found that when varying the composition of the composites, there was an increase in local overheating from 5 to 19 degrees. As is known, a local overheating of 3 degrees is sufficient for the manifestation of a hyperthermic effect, which consists in the death of tumor cells.

Thus, biocompatible nanocomposites with controlled magneto-thermal properties were prepared. The effect of the composition of water-compatible magnetic nanocomposites on local overheating due to the action of an alternating magnetic field was demonstrated.

This work was supported by Russian Science Foundation (project 23-23-00156)

CARBAZOLE/FLUORENE-SUBSTITUTED 5-PHENYL-2,2′-BIPYRIDINE D–π–A FLUOROPHORES: PHOTOPHYSICAL DATA, HYPERPOLARIZABILITY AND CT-INDICES.

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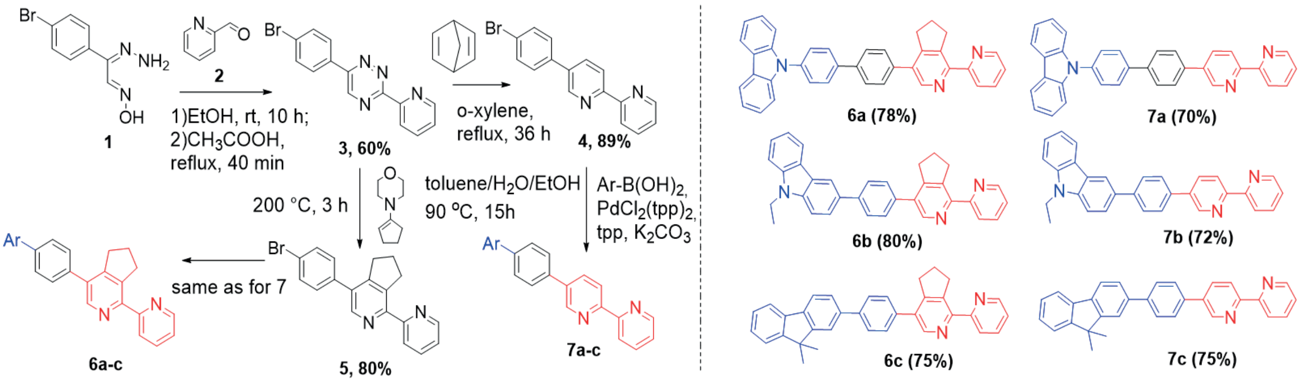
Here we report a new series of D-π-A push-pull fluorophores containing a unified 2,2'-bipyridine domain acceptor with terminal electron donating carbazole/fluorene groups that exhibit good fluorescence performance. All new fluorophores were obtained by *aza*-Diels-Alder reaction and further Pd-catalyzed Suzuki cross-coupling reaction.



All fluorophores demonstrated high fluorescence quantum yields up to 99% and large Stokes shifts up to 10394 cm−1 (157 nm). Due to their remarkable fluorescence capability, two-photon emission cross sections were measured for three dyes using the two-photon fluorescence method. Both experimental studies and calculated charge transfer indices (CT-indices) confirmed the greatest charge separation in carbazole substituted isomers **6a** and **7a**, **6b** and **7b**. *I.e.*, these compounds are very promising ligands for constructing metallic NLO-phores, while fluorene-based fluorophores with a predominant PLICT state can be considered as promising environment polarity sensitive fluorescent dyes and biological probes to detect structural changes in proteins/biomolecular interactions and optical switches.

The research was financially supported by Russian Science Foundation Grant # 19-73-10144-P

CONTROLLED SELF-ASSEMBLY OF CRYSTALLINE MATERIALS BASED ON THE COORDINATION COMPOUNDS OF (THIA)CALIX[4]ARENES AND THEIR FUNCTIONAL DERIVATIVES

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(Thia)calix[4]arenes are versatile molecular building blocks that are widely used in coordination supramolecular chemistry to produce crystalline materials with useful properties such as porosity, single molecule magnet behavior, luminescence, (photo)catalysis, etc. Herein we report on the general approaches for rational design the supramolecular coordination compounds based on (thia)calix[4]arenes and their functional derivatives in the crystalline phase (Figure 1). The factors influencing the self-assembly of coordination polymers, discrete d-/f-metal polynuclear clusters, and supramolecular "cages" based on (thia)calix[4]arenes have been established.[1] The relationship between structure of obtained coordination compounds in the crystalline phase and the observed functional properties has been revealed[2,3].

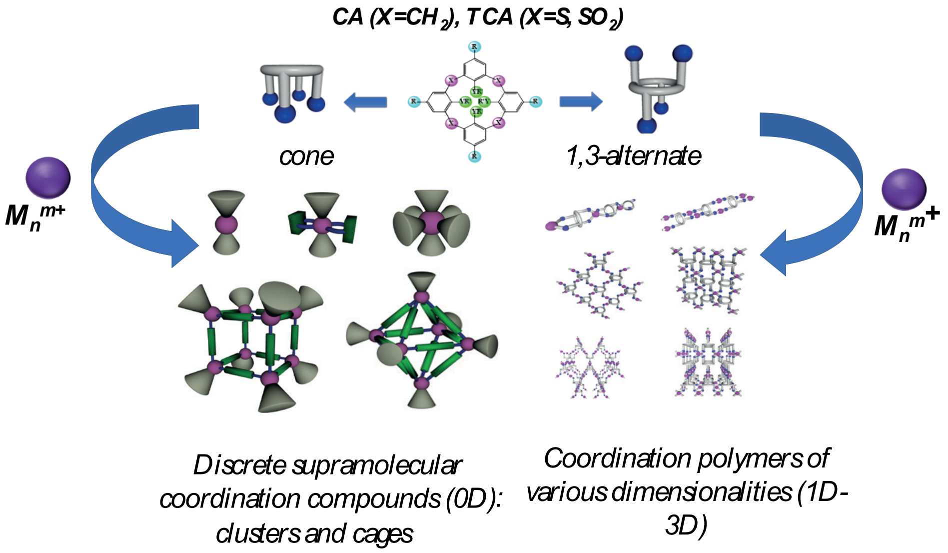

Figure 1. Supramolecular coordination compounds (0D-3D) based on (thia)calix[4]arenes (CA, TCA).

Acknowledgements.This work was supported by the Russian Science Foundation (grant № 19-73-20035).

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF NEW DERIVATIVES OF DITERPENE ACIDS

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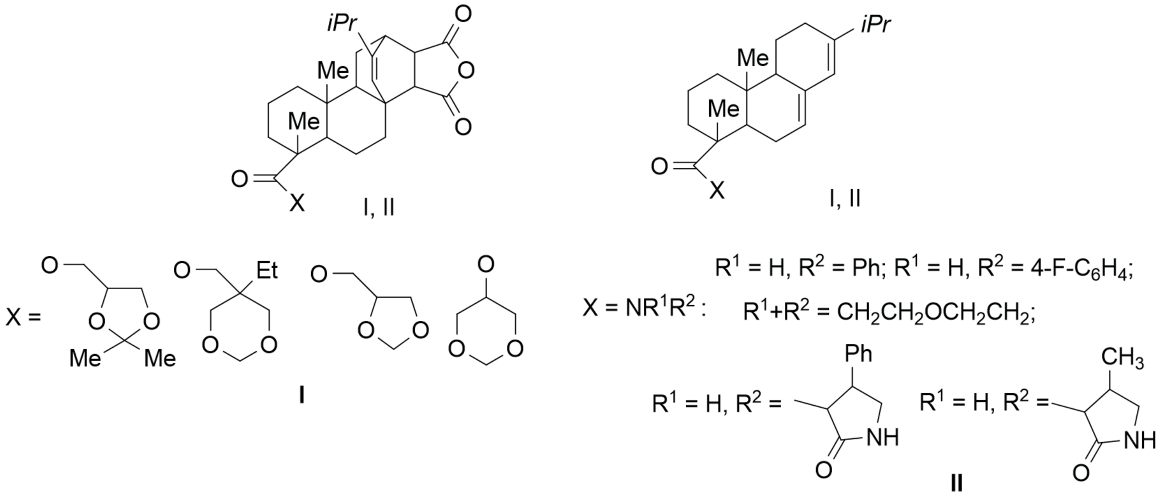
Diterpenic acids, in particular, abietic and levopimaric, are available components of pine resin *Pinus sylvestris L.*, common in Russia, and are used as a basis for the production of a number of biologically active compounds [1]. On the basis of abienic acid (AA) and maleopimaric acid (MPA), we synthesized a series of new heterocyclic amides and esters of types **I** and **II** containing a diterpene moiety (Fig. 1). Conditions have been found that make it possible to obtain these compounds with high outputs.

Pic 1.

Pic 1.



The anticoagulation and antiaggregation activity of AA and MPA amides was studied. The effect of these compounds on the plasma component of the hemostasis system to varying degrees was found. Among the substances obtained, leading compounds have been identified. The report discusses the structure-activity relationship in the series of reactants obtained.

The work was financially supported by the state task of the Ministry of Education and Science of the Russian Federation "Development and creation of low-tonnage products and reagents (corrosion and scale inhibitors, antioxidants, biocides, additives, etc.) for petrochemical processes and purification of aqueous media from pollution, replacing imported substances and materials. Theoretical and experimental approaches (FEUR-2023-0006).

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PHOTOACTIVE N-HETEROCYCLING CARBENE COMPLEXES FOR C-N BOND FORMATION

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Cross-coupling reactions have become fundamental transformations for C-C and C-heteroatom bond constructions [1]. Although their widespread use, they are often carried out at high temperatures. Largely due to the development of photoinduced cross-couplings, also called metallaphotoredox catalysis, some of the reactions are realized under mild conditions [2-5]. The catalytic system commonly used for these chemical transformations consist of two essential partners: a photocatalyst and a metal complex. However, chemists have always sought to simplify the synthesis. According to this, the use of light-absorbing metal catalysts, i.e. single-component catalysts, makes it possible not to use an external photocatalyst and greatly eases the reaction conditions [3]. Besides that, such catalysts in the light-mediated excited state have a unique reactivity and open up the chemical space for new reactions.

In this work, new photoactive palladium complexes were synthesized as single-component catalysts. The obtained complexes consist of a photoactive block, a transition metal, and a N-heterocyclic carbene (NHC)-based binding ligand. In addition, it's catalytic properties can be tuned by varying steric substituents and leaving group. Different members in this transition metal ligand set could be easily prepared by alkylating the corresponding imidazole derivative with photoactive derivatives.

The formation of amides is a central focus in organic synthesis for natural products and drug development [6]. Photoredox induced C-N bond formation is a good and mild way to produce amides. We carried out a photoredox amidation reaction between a benzaldehyde derivative and a secondary amine using novel single-component catalysts. It was performed by irradiation with a 395 nm LED or a household compact fluorescent lamp. As a result, high yield of the target product was achieved.

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CHEMICAL SYNTHESIS OF NUCLEAR SPIN ISOMERS OF ETHYLENE: REVISITED

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In symmetric molecules different sets of rotational levels are allowed for nuclear states of different symmetry leading to the appearance of discrete nuclear spin isomers of molecules (NSIMs). Now, the problem of separating nuclear spin isomers on a scale suitable for practical applications has been solved for only one molecule - hydrogen. This work is devoted to the enrichment of nuclear spin isomers of ethylene via chemical synthesis.

The ethylene molecule has four nuclear spin isomers: A_g, B_{3g}, B_{1u}, B_{2u}. One of the promising methods for enriching NSIMS of ethylene for practical applications is the chemical synthesis method proposed by Zhivonitko et al. [1]. In this approach, ethylene with non-equilibrium distribution of NSIMs was produced via heterogeneous hydrogenation of acetylene with parahydrogen, spin isomer of hydrogen with I=0. To break the magnetic equivalence of ethylene protons and, therefore, study the NSIMs, ethylene was introduced into the electrophilic addition reaction. Also, Zhivonitko et al. investigated interconversion of ethylene NSIMs and showed that the equilibration kinetics is biexponential [1].

In this work, three heterogeneous catalysts (Pd/TiO_2, $Pd\text{-}In/Al_2O_3$, immobilized [Ir(COD)(L)Cl], where L is the P-containing linker on silica gel) with different hydrogenation mechanisms were used. To demonstrate the non-equilibrium ratio of ethylene NSIMs, the hydrogenation products mixture was bubbled through bromine water and the ^1H NMR spectrum was then recorded. For all three catalysts were observed enhanced antiphase signals of 2-bromoethanol, which confirms the non-equilibrium ratio. Moreover, the lineshape of the hyperpolarized signals depends on the ratio of NSIMs of ethylene and is different for all three catalysts. The ^1H NMR spectra of 2-bromoethanol were simulated depending on the ratio of ethylene NSIMs. For each of the three catalysts, the stereospecificity of the hydrogenation was found, at which the simulated NMR spectra fit the experimental NMR spectra. Thus, the method proposed in this work can be used to assess the stereospecificity of hydrogen addition to acetylene over various catalysts.

To study the interconversion between NSIMs of ethylene in the gas phase, we stored ethylene in a syringe for a certain period of time. It was found that even when ethylene was stored in a syringe for 1 hour, the polarized signals from 2-bromoethanol was observed when ethylene was bubbled through bromine water, which indicates a non-equilibrium ratio of ethylene spin isomers. Thus, we observe that the equilibration time of nuclear spin isomers exceeds T_1 (in experimental conditions T_1 is about 300 ms) by many orders of magnitude, which confirms the presence of long-lived states. To understand the mechanism of ethylene isomer equilibration, we analyzed the shape of the polarized signal from 2-bromoethanol in ^1H NMR spectra recorded for different periods of ethylene storage in a syringe. Based on the modeling of experimental spectra under the assumption of partial equilibration of nuclear spin isomers, it was found that during 30 second of storage, ethylene isomers are balanced within the same spatial symmetry classes (g and u). With further storage (more than 30 s), interconversion between isomers of classes *g* and *u* occurs. Thus, we can conclude that the short part of the biexponential corresponds to the interconversion of isomers within classes *g* and *u*, and the long part of the biexponential corresponds to the interconversion of isomers between classes *g* and *u*.

Acknowledgements: This work was supported by Russia Science Foundation (grant 21-73-10105).

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CARBOXYMETHYL CYCLODEXTRIN ENSEMBLES ON CATIONIC LIPOSOMES AS CAPACIOUS NANOCONTAINERS FOR HYDROPHOBIC MOLECULES

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Liposomes are spherical bilayer lipid vesicles that have long of utilization as nanocontainers in drug delivery. However, the capacity of such nanocontainers towards hydrophobic molecules is small and rarely exceeds several percent. To solve this problem, a method has been proposed in this work to modify the liposome surface with molecules with additional affinity to hydrophobic compounds.

Carboxymethy lcyclodextrins (CMCDs) are small biocompatible cyclic polysaccharides with sizes less than 1 nm. Internal structure The CMCD cavities allow the formation of "guest-host" complexes with aromatic fragments of bioactive molecules. Modification of the liposome surface using CMCDs can significantly improve the capacity of the liposomal nanocontainer with respect to hydrophobic molecules.

As a central core for the adsorption of CMCD, we propose to use liposomes formed from a mixture of the electroneutral lipid dioleoylphosphatidylcholine and the cationic lipid dioleoyl trimethylammonium propane (DOTAP) with the molar fraction of DOTAP 0.3. While the carboxyl groups of CMCD provide electrostatic adsorption on the surface a lipid bilayer containing cationic groups, additional stabilization of complexes can be achieved due to hydrophobic interactions of CMCD with the lipid bilayer. The interaction of liposomes with CMCDs and the compositions of the resulted complexes were studied using laser microelectrophoresis, dynamic light scattering, conductometry, IR-scpectroscopy and Langmuir-Blodgett techniques. The ability of complex nanocontainers to incorporate hydrophobic molecules was studied using UV-Vis spectrophotometry. As model bioactive molecules the phenolphthalein and curcumin were studied. Nanocontainers were visualized using atomic force microscopy. It has been established, that cationic liposomes can accumulate on their surface several hundred CMCD molecules, and an increase in the size of the liposome leads to an increase in the maximum possible number of CMCD molecules. It is important to emphasize that colloid-stable systems can be formed using different ratios of CMCD and DOTAP molecules in a wide range. It has been demonstrated that cationic liposomes modified by CMCD are capable of including hydrophobic molecules of bioactive compounds in an amount about 10 times exceeding the capacity of individual liposomes for these compounds

The cytotoxicity of the formed nanocontainers was studied by MTT test with the following results. The positively charged complexes of CMCDs and cationic liposomes as well as complexes with curcumin demonstrated high cell viability in wide range of concentrations up to 2 mg/ml.

This work was supported by Russian Science Foundation (project 22-23-00723)

SYNTHESIS OF NEW MACROCYCLIC LIGANDS AS COMPONENTS OF RADIOPHARMACEUTICALS

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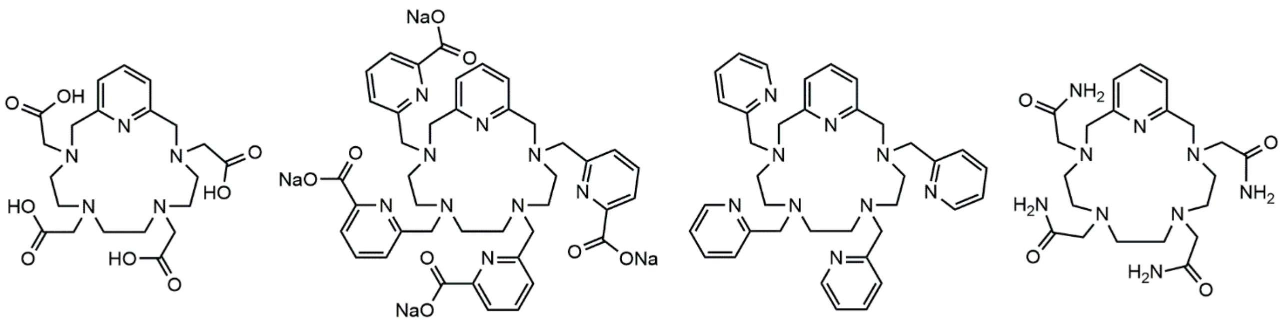
One of the advanced methods for the treatment and diagnosis of oncological diseases is the use of radiopharmaceuticals. There are strong complexes of ligands with radionuclide ions, sewn to a vector biomolecule. Currently, there are no chelators that meet all the requirements for them, so the development 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. The rigidity of the ligand, which affects the rate of complexation and the stability of the resulting complex, is due to the presence of a pyridyl fragment in the structure; the ability of the chelator to bind ions of certain metals is carried out due to the introduction of various chelating groups into the composition of the azacrown ether.

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. At the next stage of the work, the complexing properties of the obtained chelators with cations for medical purposes were studied. The complexing properties of ligand **1** were studied with Pb^{2+} and Bi^{3+} cations by NMR spectroscopy and mass spectrometry. The ability to complex formation was studied by NMR spectroscopy and mass spectrometry, as well as the efficiency of labeling chelators **1** and **4** with Ga^{3+} and Lu^{3+} cations. The complexing properties of chelator **2** with Cu^{2+}, Pb^{2+}, Bi^{3+} were studied by mass spectrometry. The ability of ligand **3** to bind Pb^{2+} and Cu^{2+} cations was studied by mass spectrometry and spectrophotometric titration.

It was shown that the resulting ligands form complex compounds with the studied metals at room temperature. Compound **1** forms complexes with a rigid structure with Pb^{2+}, Bi^{3+}, and also binds Ga^{3+} and Lu^{3+} stronger than **4**, which makes it relevant for further study as a ligand for radiopharmaceuticals. The obtained stability constants for **3** with Pb^{2+} and Cu^{2+} are not high enough to speak about the prospects of using this ligand as a component of radiopharmaceuticals.



1 **2** **3** **4**

Scheme 1. Target macrocyclic ligands

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

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INFLUENCE OF BENZIMIDAZOLE LIGANDS STRUCTURE ON THE COMPOSITION, REACTIVITY AND PHOTOPHYSICAL PROPERTIES OF CYCLOMETALATED IRIDIUM(III) COMPLEXES

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Cyclometalated iridium (III) complexes have gained massive attention mainly due to the outstanding photophysical properties and possibility to widely tune those by structural variation of ligands. To develop effective emitters or light-harvesting dyes one needs clear understanding of the impact of incorporating various groups into the ligands structure on the corresponding complexes properties. Such concepts could be developed via analysis of the series of compounds in which gradual tuning of the ligands is accessible. For this purpose, benzimidazole scaffold is perfectly suitable, as it has several points of functionalization and great variety of ligands is easily accessible.

In this work we have synthesized and investigated photophysics of bis-cyclometalated iridium(III) complexes with 2-arylbenzimidazoles as cyclometalated ligands and β-diketonates as ancillary ligand. We have shown that the use of bulky N-coordinated fragment in cyclometalated 2-aryl-N-phenylphenanthro[9,10-d]imidazoles in combination with aromatic β-diketones dramatically enhanced the reactivity of the corresponding iridium(III) complexes[1]. Tailoring the π-system of the cyclometalated ligands leaded to formation of stable strongly absorbing diketonate complexes which were successfully applied as photosensitizers in solar cells[2]. Precise incorporation of substituents in both benzimidazole and diketonate ligands allowed to govern the excited state localization that improved photosensibilization efficiency.

Moreover, it was shown that the involvement of rigid 2-(9-anthracenyl)-*N*-phenylbenzimidazole into iridium(III) chemistry (with appropriate optimisation of reaction conditions and variation of additional ligands) yielded a straightforward way to both an unprecedented *mono*-cyclometalated square pyramidal Ir(III) complex and an interesting *non*-cyclometalated species stabilized by intramolecular π-stacking. These compounds go beyond the usual iridium(III) chemistry being interesting not only from the crystallographic point of view, but also as a basis to create complexes of new composition and structure with potentially new properties.

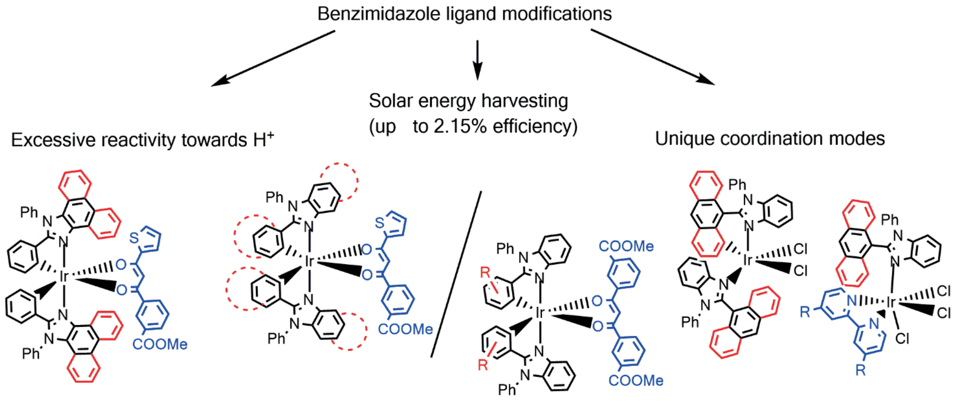

Fig.1. Series of the compounds investigated in this work.

This work was supported by the Russian Science Foundation (grant № 22-23-01171).

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DEVELOPMENT OF NEW ANTIMICROBIALS CIRCUMVENTING DRUG RESISTANCE

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One of the main problems of modern antimicrobial chemotherapy is the low effectiveness of existing drugs against resistant bacterial strains [1]. This causes an urgent need to constantly update the arsenal of antibacterial drugs by searching for new natural products or obtaining semi-synthetic/synthetic antibiotics with improved chemotherapeutic properties.

Our research was focused on a chemical modification of natural antibiotics to create new derivatives potent against resistant strains of pathogens. Semi-synthetic derivatives of well known classes of antibiotics, namely, polyenes, aminoglycosides, macrolides and glycopeptides were designed, synthesized and evaluated. In particular, a new direction of chemical modification of aminoglycoside kanamycin A by 6”-position was investigated and a series of its semi-synthetic derivatives was obtained [2]. Synthetic works on the chemical conjugation of the macrolide antibiotic azithromycin with chloramphenicol and metronidazole resulted in hybrid antibacterial substances. A series of new water-soluble natamycin amides were obtained and studied: a number of compounds showed advantages over the parental molecule for the creation of antifungal drugs for the treatment of systemic mycoses [3]. Optimization of the glycopeptide antibiotic eremomycin yielded to flavancin, a semi-synthetic derivative which is up to 256 times more active *in vitro* than the «gold standard» vancomycin against sensitive and glycopeptide-resistant strains of Gram-positive bacteria.

Taking together, new directions of chemical modification of natural antibiotics have been developed giving the promising prototypes of antibacterial drugs which are capable of overcoming the mechanisms of antibiotic resistance.

Research of the laboratory was preformed with the financial support of the Ministry of Science and Higher Education of the Russian Federation

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PYRAMD: A PYTHON-BASED *ab initio* MOLECULAR DYNAMICS SOFTWARE

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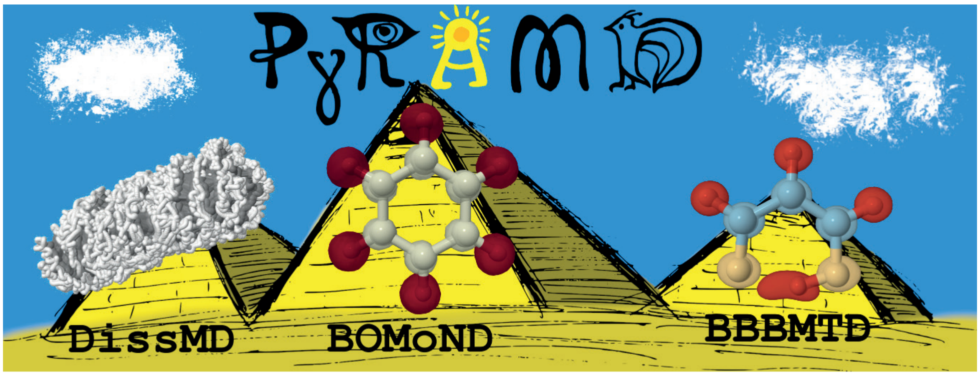

Here, we present PyRAMD, an *ab initio* (AI) molecular dynamics (MD) package [1]. It is designed to provide AIMD and AIMD-based simulations of molecular systems using external quantum-chemical (ORCA [2]) and semi-empirical (xTB [3]) packages. PyRAMD consists of three parts of software: BOMoND, BBBMTD, and DissMD.

BOMoND is used for the *NVE* and *NVT* Born-Oppenheimer MD (BOMD) simulations. Currently, Berendsen's and Andersen's thermostats are available. A unique feature of the BOMoND is the simplified Wigner sampling (SWS) routine for generating initial conditions [4]. It allows an introduction of the nuclear quantum effects at the simplicity of the Maxwell-Boltzmann sampling. Also, it can be combined with Andersen's thermostat.

BBBMTD is a metadynamics (MTD) driver for reactions involving bond cleavage. It uses a new reparametrization of the MTD bias potential as the Bohmian quantum potential [5]. The simulations can be augmented by the Berendsen thermostat and artificial spherical constraining potential to prevent the dissociation of weakly bound clusters.

DissMD is an augmented BOMD driver for simulating the mass spectra of molecules upon photoexcitation with lasers. It uses ideas of the QCEIMS approach [6] with reformulated models for excitation, internal conversion, and fragmentation [7]. DissMD can also be used to trace the Coulomb explosion properties [8].

Various examples of the PyRAMD applications, including benchmarking of the new MD-based methods, will be provided [4,5,7,8]. Visualizing software for nuclear motions, CubeTheMD [9], will also be presented.

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INVESTIGATION OF THE RADIOLYTIC STABILITY OF NEW EXTRACTION SYSTEMS BASED ON CROWN ETHERS SELECTIVE TO RADIOGENIC CESIUM AND STRONTIUM

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Among a great variety of supramolecular compounds, crown ethers and their derivatives have established themselves as promising extractants for the needs of radiochemical industry. As it is known crown ethers possess good complexing properties in relation to cations of alkaline and alkaline-earth elements, and their ability to extract strontium-90 and cesium-137 has found application in processing of high level waste (HLW). Therefore, the radiolysis of crown ethers under γ-radiation has been actively studied. Also an important point in the development of new extraction systems is the study of radiolysis products of the diluents themselves, and their effect on the stability of the extractant molecules [1, 2].

In this work we studied the radiolytic stability of extraction systems based on 4,4’(5’)-di-tret-butyldibenzo-18-crown-6 (DTBDB18C6) and 4,4’(5’)-di-tret-butyldicyclohexano-18-crown-6 (DTBDCH18C6) in the fluorinated diluents bis(2,2,3,3-tetrafluoropropyl) carbonate (BK-1) and bis(2,2,3,3-tetrafluoropropoxy)methane (FN-1) - fluorinated alcohol-telomer derivatives H(CF2CF2)nCH2OH (n = 1). Irradiation of dry crown ethers and their solutions, including those in contact with water and nitric acid (3 mol/l HNO_3) solutions, has been carried out. Radiolysis products were identified by chromato-mass spectrometry and mechanisms of their formation under the action of irradiation were proposed. Researches were carried out on chromato-mass spectrometer “MaXis”, Bruker Daltonik GmbH (Germany), (ESI-QTOF). To confirm the experimental data, the most likely radiolysis pathways and decay products were modelled using DFT methods.

The effect of irradiation on the extraction ability of the crown ethers was studied [3]. Extraction systems based on crown ether DTBDCH18C6 have been found to be more stable with respect to radiolysis and continue efficient extraction of strontium from nitric acid solutions even at an absorbed dose > 700 kGy. The organic phases in contact with nitric acid solutions retain their extraction capacity to a greater extent than those irradiated in contact with water. Systems based on crown ether DTBDB18C6 are less stable to γ-irradiation and in some cases are quantitatively nitrated by nitric acid prior to irradiation, followed by fragmentation during radiolysis.

The study was supported by the Russian Science Foundation (project № 20-13-00143). Scientific research was performed using the equipment of the Research Park of St. Petersburg State University «Center for Magnetic Resonance» and «Center for Chemical Analysis and Materials Research».

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CONSTRUCTION OF *N*-CONTAINING HETEROCYCLIC SYSTEMS FROM ISOQUINOLINE DERIVATIVES USING [3,3]-SIGMATROPIC REARRANGEMENTS

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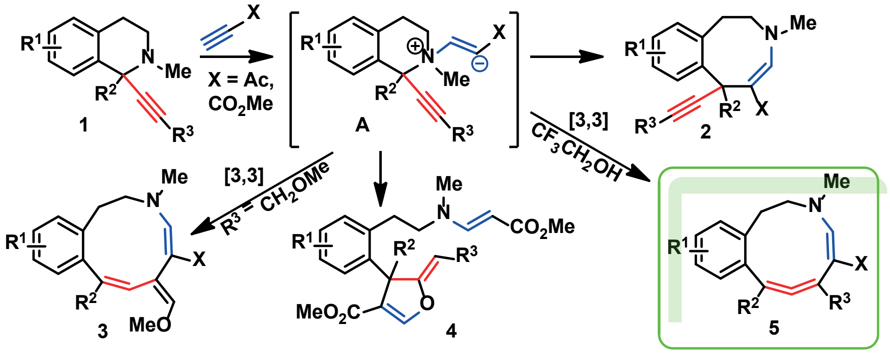
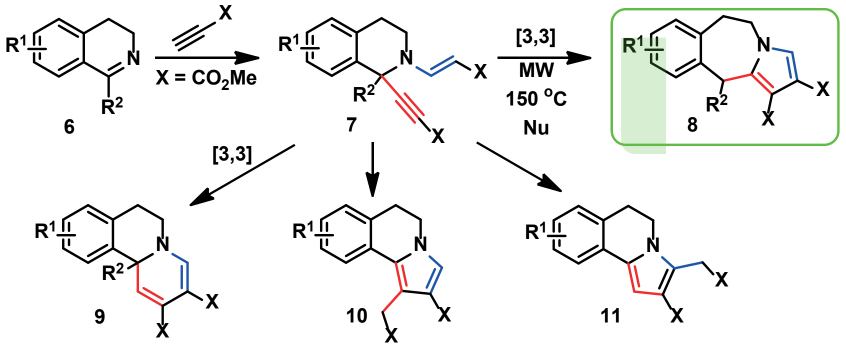
One of the convenient and efficient methods for constructing complex molecules are [3,3]-sigmatropic rearrangements [1]. Among these, *N*-propargyl-aza-Claisen reaction is the most interesting, which proceeds via the formation of allene intermediates [2].

Exploring the synthetic limitations of these transformations, a spectrum of products has been obtained from isoquinoline derivatives **1**, including benzazocines **2**, 6-ylidene decorated benzazecines **3**, substituted furans **4**, and azacyclic allenes **5** [3–6]. The reaction conditions are quite mild since the driving force of the process is a charge-accelerated rearrangement of the zwitterionic intermediate resulting from the Michael addition of isoquinoline **1** to the terminal alkyne in protic solvents.



The rearrangement of 1-ethynyl-2-vinylisoquinolines **7** requires higher energy costs to proceed tricyclic compounds: pyrrolobenzazepines **8**, pyridoisoquinolines **9**, and pyrroloisoquinolines **10**, **11**. In this case, the formation of products also strongly depends on substituents of the isoquinoline core and on solvents.



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COPPER(I) AND SILVER(I) PYRAZOLATE COMPLEXES: SUPRAMOLECULAR ORGANIZATION AND PHOTOLUMINESCENCE

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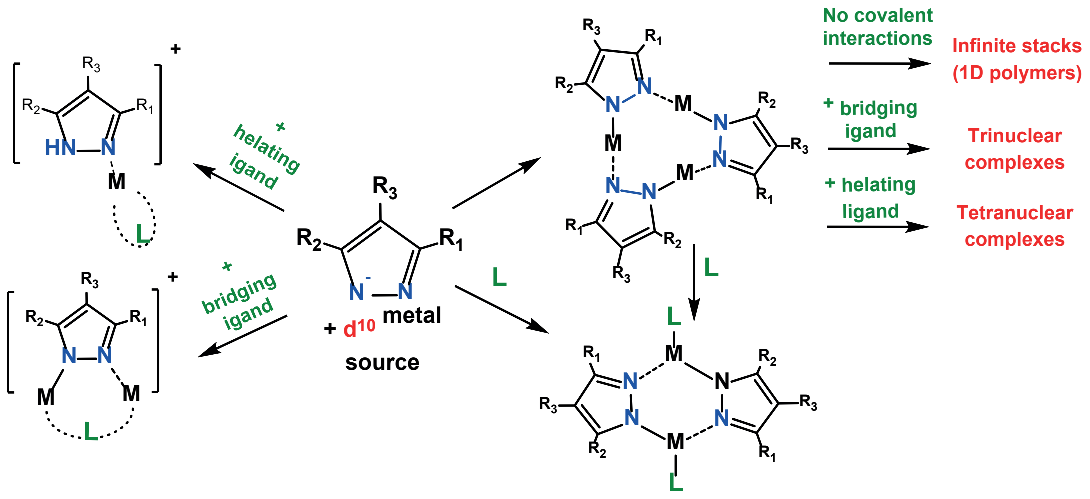
Intermolecular non-covalent interactions play an important role in coordination chemistry. Hydrogen, halogen bonding, and π–π stacking interactions lead to the formation of supramolecular aggregates of organic compounds determining their properties. Metal complexes with organic ligands allow the formation of other types of intermolecular forces such as metal–metal (M-M) or metal–π (M–π) interactions. Designing complexes based on metal-involved interactions are of constant interest in the past decades. Their ability to form coordination/supramolecular aggregates determines the properties and practical applications such as catalysis, gas sensing, molecule recognition, and photoluminescence. Group 11 metals form macrocyclic compounds with pyrazole of general formula $[MPz]_{n,}$ where n depends on the type of substituents in the pyrazolate ligand and on a metal atom. Copper(I) and silver(I) form with pyrazole di-, tri-, and tetranuclear complexes or polymers.[1] Macrocyclic copper(I) and silver(I) pyrazolate adducts represent an important class of coordination compounds used in numerous fundamental areas, such as acid-base chemistry, metallophilic bonding, supramolecular assemblies.[2] Pyrazolate anions can serve as bridging bidentate ligands binding with metals in a different fashion to give complexes of different structures(Scheme 1).



Here we report syntheses, structures and study of luminescent properties with theoretical insight of the group 11 metal pyrazolate adducts.[3-5] Variation of ligand structure and metal atoms leads to the compounds possible to emit the light in a wide spectral range.

This work was supported by Russian Science Foundation (grant № 19-73-20262)

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PHOTOINDUCED ELECTRON TRANSFER FROM RUTHENIUM (II) IMIDAZO-1,10-PHENANTHROLINE COMPLEXES TO SEMICONDUCTOR NANOPARTICLES FOR GAS SENSORS PERFORMANCE

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In this work, a series of imidazo[4,5-f][1,10]phenanthroline-containing ligands and their monoruthenium(II) and heterobimetallic complexes were synthesized (Fig. 1 left). These complexes are capable of photo-induced electron transfer to the conduction band of some semiconductor materials (Fig. 1 right). Such photosensitization process will reduce the operating temperature of semiconductor gas sensors and thus reduce their energy consumption.

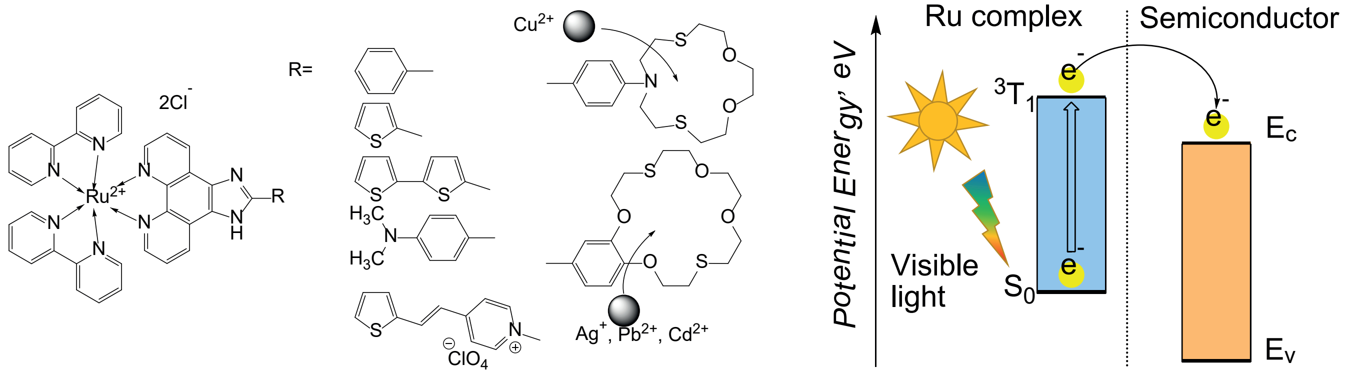

Figure 1. left: Structures of synthesized complexes; **right:** photoinduced sensitization in a hybrid semiconductor-dye material

We have shown that energies of HOMO and LUMO of complexes were suitable for electron transfer from excited state to the conduction band of SnO_2 and In_2O_3. LUMOs of synthesized complexes are of triplet nature with a high lifetime sufficient for electron transfer. Modification of the surface of nanoparticles of SnO_2 and In_2O_3 with Ru(II) complexes gave hybrid organic-inorganic materials that were studied as sensitive elements for gas sensors to NH_3, NO_2 and NO. Hybrid sensors appeared to have reproducible sensory signal in the presence of analyte gases at room temperature in air under periodic illumination with visible light LEDs. Some materials were able to determine NO_2 and NO within 0.25–2 ppm at room temperature under illumination with red LED. The MPC of the daily dose of NO is 2.6 ppm. Second cation in heterobimetallic complexes helped to control affinity of the surface towards one or another gas, which resulted in improven selectivity of gas analysis.

Acknowledgements.
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PHOTOELECTRICAL PROPERTIES OF VANADYL ETIOPORPHYRIN-III IN THIN FILMS: VTE *vs* SPIN-COATING

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Complexes of several transition metals with etioporphyrin ligand (MEtioP) are naturally occurring semiconductors, stability of which has been proven by nature itself. The solid films can be obtained not only by dry but also by wet techniques since their solubility is higher than that of related synthetic dyes like phthalocyanines. An interesting feature of etioporphyrins is the positional isomerism of peripheral Me/Et groups, which determines different packing motifs in a solid [1]. The problem of dealing with a complex that has a certain substitution pattern is therefore important. There are two ways to solve it: selective organic synthesis and, more laborious, isolation of the porphyrin fraction from heavy petroleums with subsequent separation. In both cases, careful characterization of thin films composed of target compounds will be required.

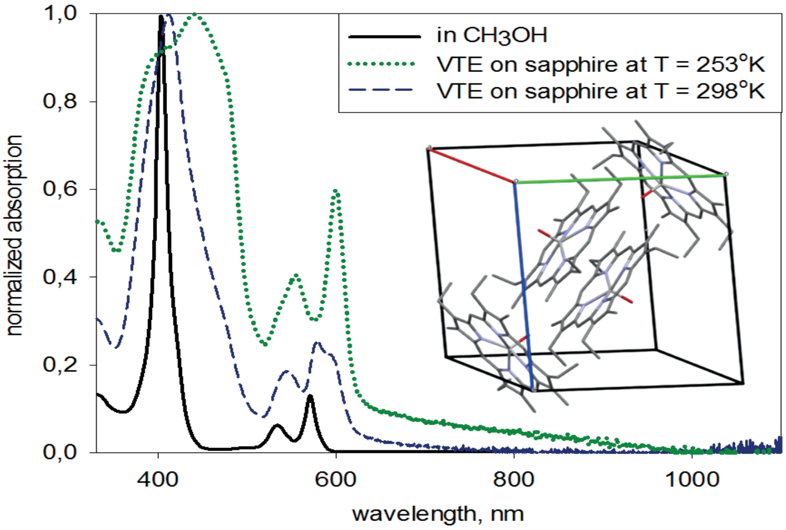

Figure. 1. Normalized electronic absorption spectra of VOEtioP-III in solution and thin films deposited on sapphire at different temperatures. Inset: unit cell based on single-crystal X-ray experiment.

Earlier, we studied the aggregation effects of Ni- or CuEtioP-I,II,III films and output parameters of photovoltaic cells based on them [2]. In this work, VOEtioP-III thin films were deposited on various functional substrates by either vacuum thermal evaporation (VTE) or solution (spin-coating, drop-casting) deposition techniques – Figure 1. Aggregation leads to large bathochromic shifts and broadening of bands despite “sandwich” (thus H-type) arrangement of molecules in dimers. Photoelectrical measurements were carried out in lateral and vertical geometry to assess the anisotropy of currents leaking through the molecular layer. The dependence of the current-voltage characteristics on the substrate temperature (for VTE) or solution chemistry (for wet-processed films) was traced. The results are discussed in terms of different supramolecular organization in the VOEtioP-III films grown in a non-equilibrium process.

This work was supported by RSF grant no. 20-13-00285.

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SYNTHESIS OF (4-AMINO-1H-INDOL-6-YL)PHOSPHONIC ACID DERIVATIVES

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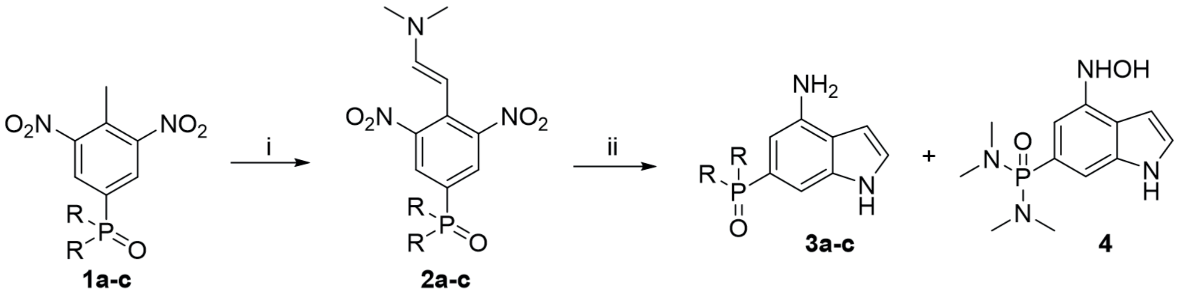
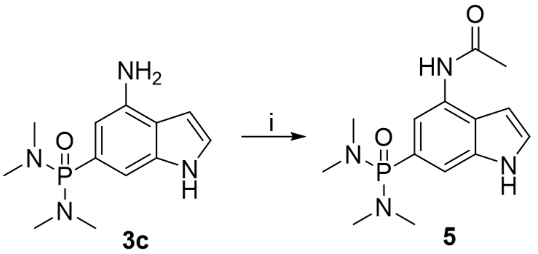
A convenient methodology for the synthesis of previously unreported (1H-indol-6-yl)phosphonic acid derivatives has been described. Reaction of (4-methyl-3,5-dinitrophenyl)phosphonates (**1a-c**) with dimethylformamide dimethyl acetal (DMF DMA) leads to the respective enamines (**2a-c**) that can be readily converted into indoles by the Batcho–Leimgruber synthetic protocol. Proper choice of reducing agent for the reductive cyclization of intermediate enamines allows to selectively obtain (4-amino-1H-indol-6-yl)phosphonates (**3a-c**) without N-hydroxiindol impurities (**Scheme 1**).



R = OMe (**a**); OEt (**b**); NMe_2 (**c**)

Scheme 1. Reagents and conditions: (i)DMF DMA, toluene, 80 °C; (ii) H_2, Pd/C (10%), EtOAc, rt.

The reaction of compound **3c** with 1 eq. of Ac_2O in dichloroethane in the absence of a base proceeded regioselectively affording solely N-{6-[bis(dimethylamino)-phosphoryl]-1H-indol-4-yl}acetamide (**5**) in 65% yield. Product **5** showed an excellent activity against *Candida albicans*.



Scheme 2. Reagents and conditions: (i) Ac_2O, DCE, reflux.

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AMMONIZATION OF CARBONYL COMPOUNDS: ROLE OF SOLVENT LIES IN THE NATURE OR IN THE NUMBER OF TS CENTERS?

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The ammonization reactions of carbonyl compounds occurring in solutions lead to the formation of secondary organic aerosols (SOA) [1], and these reactions are the key for the formation of valuable N-containing heterocycles. Recent studies [2] have shown that modeling of these processes without the involvement of solvent molecules leads to high energy barriers, and also revealed that the solvent played a key role in decreasing the energy barrier for hydrogen transfer processes.

In this work, the catalytic role of the solvent nature was compared with the number of centers in the transition states of the reaction of acetaldehyde and glyoxal with ammonia [3]. The effect of molecules of water, methanol and ethanol, formic and acetic acid, and ammonia on the energy barriers of reaction stages was considered. The catalytic effect of the solvent was considered in the following types of reactions: ammonization of carbonyl compounds, dehydration of aminoalcoholes, cyclization of N-heterocycle, and proton transfer.

The key role in lowering the energy barriers of the ammonization and dehydration stages is played by the number of transition state centers involved in the transfer of a hydrogen atom, and not by the nature of the molecule included in these TSs. The formation of a geometrically favorable 7-centered transition state with the participation of solvent molecules for the proton transfer stage significantly reduces the magnitude of energy barriers regardless of the nature of the catalyzing molecule.

The energies of the optimized structures in terms of Gibbs free energy in the solution were used to construct the potential energy surface (PES). The Gibbs free energy calculations for each structure in a solution consisted in the optimization of the geometry and calculation of the frequencies of this structure at the B3LYP/6-311(d,p) level of theory taking into account the PCM solvation using the Gaussian'09 program package and recalculating the obtained thermochemical data using the freely available GoodVibes script developed by Paton and Funes-Ardoiz [4]. The search for TSs was carried out by the Quadratic Synchronous Transit method (QST2).

This study was supported by the Tomsk State University Development Programme (Priority2030).

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FUNCTIONALIZATION OF SINGLE-LAYER MoS_2 NANOFLAKES WITH PORPHYRIN-BASED SURFACE-ATTACHED MOFs FOR PHOTOCATALYTIC APPLICATIONS

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Functionalization of two-dimensional materials with organic molecules is among the most extensively developing areas of materials chemistry. Fabrication of hybrid materials from 2D semiconductors such as dichalcogenides of transition metals is particularly important for the applications exploiting donor-acceptor interactions between components to initiate charge/energy transfer. These materials might be broadly useful for catalysis, photocatalysis, selective chemical sensing and organic electronics.

Nanodispersed dichalcogenides exhibit a number of useful properties such as optical transparency and strong luminescence. By combining these inorganic semiconducting matrices with potent organic chromophores, it is therefore potentially possible to imitate a synergy of components properties by light-induced energy transfer between them. Porphyrins are especially interesting organic components for this purpose because of their photochemical and receptor properties providing them both sensing and photocatalytic activity. However, the integration of 2D dichalcogenides into organized architectures that orchestrate their functioning remains a challenging issue.

In this work, we use a novel method of liquid phase exfoliation in the saturated solution of 2-methylimidazole to obtain chemically pure ultra-thin MoS2 nanoflakes [1]. These nanoflakes were functionalized by porphyrin molecules through coordination bonding with zinc acetate metal clusters using self-assembly method. The integration of components was confirmed using XRD and fluorescent spectroscopy methods. Obtained material was characterized with Raman and fluorescent spectroscopy, scanning electron microscopy and nitrogen adsorption methods. Photocatalytic activity of a hybrid material was studied on a model reaction of 1,5-dihydroxynaphthalene (DHN) photodestruction. The mechanism of this process was investigated through photoluminescence and MALDI-TOF mass spectrometry. Self-assembly strategy, described in this work, can be extended to a wide variety of porphyrin complexes for obtaining such hybrid materials without covalent pre-functionalization of the particle surface.

Acknowledgements: This work was supported by the Russian Science Foundation (project No 23-73-00095)

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AGGREGATION INDUCED EMISSION OF BISSTYRYL DYE COMPLEXES WITH CUCURBIT[7]URIL

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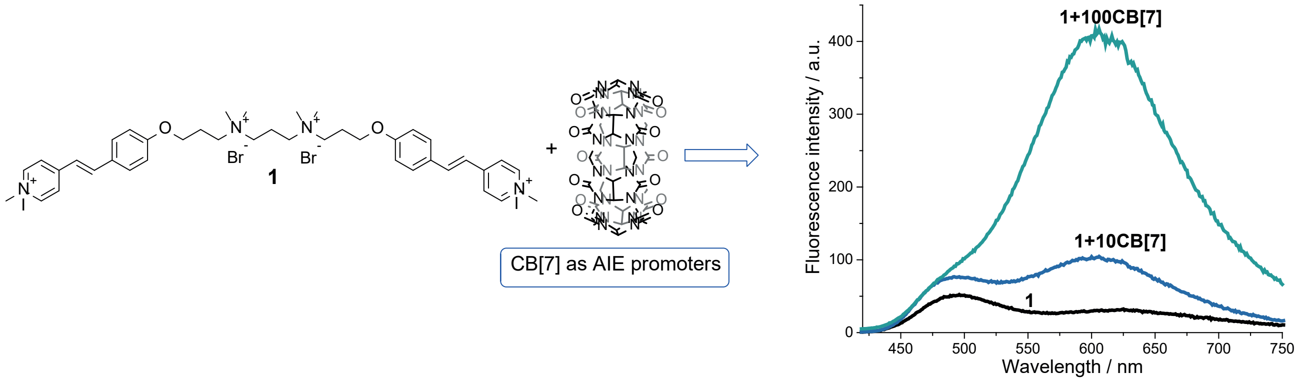
AIE (aggregation-induced emission) refers to a phenomenon characterized by the “turn-on” or enhancement of fluorescent emission during the aggregation process of certain organic molecules. One of effective strategy to induce AIE is through the restriction of intramolecular rotation of the molecule. The approach presented in this work utilizes macrocyclic receptors, specifically cucurbit[7]uril (CB[7]). It is well-known that macrocyclic hosts impose structural confinement on the included chromophoric guest molecules, effectively suppressing nonradiative relaxation processes associated with molecular movements and vibrations. As a result, this confinement leads to improved luminescence quantum yield and longer lifetime of photoexcited states[1,2].



Scheme 1. Structure of bisstyryl dye **1**; fluorescence spectra resulting from the addition of CB[7] to an aqueous solution of bisstyryl dye **1**.

Herein, we report the combination of these two ideas and show that encapsulation of polyaminic bisstyryl dye **1** inside the cavity of cucurbituril CB[7] promotes AIE through the formation of the host–guest adduct (Scheme 1).

This work was supported Russian Science Foundation (№ 23-23-00594).

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SYNTHESIS AND STUDY OF MANGANESE-CONTAINING PHOTOCATALYSTS BASED ON $Na_2La_2Ti_3O_{10}$ LAYERED OXIDE

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Photocatalytic decomposition of water and organic substrates under the action of sunlight is currently attract the attention of researchers due to the possibility of obtaining environmentally friendly hydrogen fuel. However, most of the known photocatalysts do not show activity under visible radiation, but are active only under ultraviolet. One of the well-known classes of photocatalysts is layered perovskite-like oxides in the structure of which there is a sequential alternation of two-dimensional blocks (layers) with a perovskite structure, with layers with a different type of structure (interlayer space).

It is known that $Na_2La_2Ti_3O_{10}$ compound and corresponding protonated form $H_2La_2Ti_3O_{10}$ exhibits photocatalytic activity under ultraviolet radiation, but are inactive under visible radiation. This work is devoted to the development of a procedure for the synthesis of layered perovskite-like titanates of the composition $Na_2La_2Mn_xTi_{3-x}O_{10}$ and its corresponding protonated forms with the degree of substitution of Ti for Mn in the range from 0.1 to 1.0, capable of absorbing radiation in the visible region of the spectrum.

The compounds were synthesized by high-temperature solid state reaction. The optimal synthesis conditions were selected by varying the temperature, duration and number of calcination steps, and an excess of Na_2CO_3. Single-phase samples were obtained, which was confirmed by X-ray diffraction. It was found that the Mn-containing oxides are isostructural to the Mn-free compound, manganese is predominantly introduced into the central octahedron of the perovskite block. The data obtained by DRS indicate a decrease in the band gap and the appearance of light absorption in the visible region of the spectrum when manganese is introduced into the oxide structure. However, photocatalysts under ultraviolet, visible, and simulated sunlight in aqueous solutions of 1% (mol.) methanol and 10% (mol.) formic acid using Pt as a cocatalyst showed a decrease in the efficiency of photocatalysis when replacing titanium cations with manganese cations.

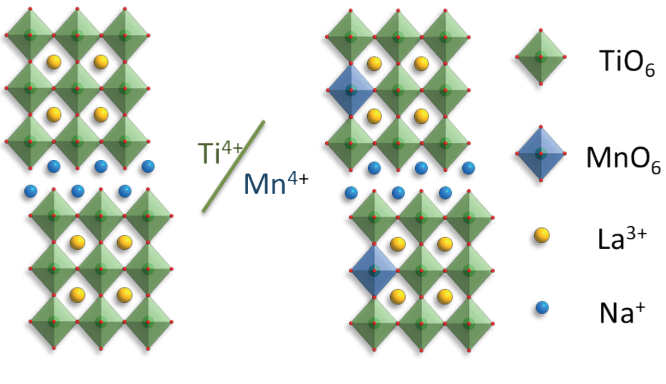

Figure 1. The schematic structure of $Na_2La_2Ti_3O_{10}$ and $Na_2La_2Mn_xTi_{3-x}O_{10}$ compounds

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HIGH TEMPERATURE KINETICS OF COBALT OXIDE REDUCTION BY HYDROGEN

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Many works have been devoted to the kinetics of cobalt formation from cobalt oxides, in which hydrogen was mainly used as a reductant [1] and process patterns were studied in a relatively low temperature range (mainly 200-900 °C). In this work, the reduction of cobalt oxide (II) by hydrogen, under temperature conditions of 900-1250 ° C, was studied. The choice of the temperature rang is conditioned by the reduction of cobalt oxide with organic reducing agents (e.g. polystyrene) in the combustion mode, which take place in the temperature range of 800-1200 °C [2]. The experiments were carried out by electrothermography method; cobalt wires (ESPI Metals, 3N purity 99.9%) with a diameter of 100 µm was used as raw materials. They, were preliminary oxidized in air (T=1320 °C, t=10 s), as a result of which a 6-8 µm thick oxide layer was formed on the metal surface (Fig. 1a). It was found that the reduction reaction proceeds with a well-defined induction period, followed by a sharp self-acceleration of the process. As a result, the conversion degree – time kinetic curves have an S-shaped appearance. As can be seen from the fig. 1b, the interaction of cobalt oxide with hydrogen begins on the entire surface of the sample. As a consequence, a compact metal shell comprising reduced cobalt is formed on the oxide layer from the initial stages of the process. This ring gradually grows towards the metal core during the reduction process and merges with the metal core at the end of the process.

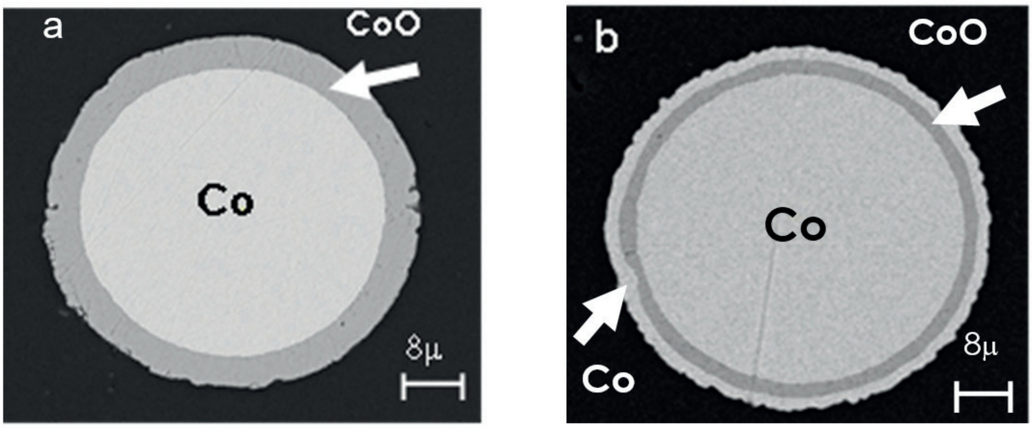

Fig. 1 SEM micrographs of the cross section for the oxidized (a) and partially reduced (b) cobalt wire

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SYNTHESIS OF NEW DERIVATIVES OF THIENO[2,3-*d*]PYRIMIDINE ON THE BASE SUBSTITUTED 1,4-BENZODIOXANYLTHIOPHENE

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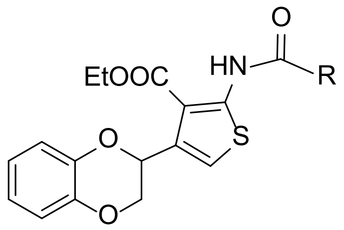
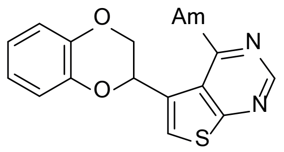
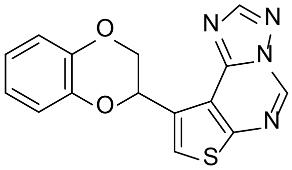
1,4-Benzodioxane derivatives containing a substituted thiophene ring are of interest as potential pharmacological active compounds, since they combine in their structure two pharmacophoric heterocycles present in the composition of a wide range of drugs [1].

In the present work we present synthesis of target heterocyclic amides with ethoxycarbonyl substituent in the 3-position of thiophene ring. The key compound - ethyl 2-amino-4-(1,4-benzodioxan-2-yl)thiophene-3-carboxylate was prepared under the Gewald reaction conditions from 2-acetyl-1,4-benzodioxane[2].

In continuation of our studies the new tetra- and pentacyclic compounds were synthesized. By heating the above mentioned aminoester with formamide was isolated 5-(1,4-benzodioxan-2-yl)thieno[2,3-*d*]pyrimidin-4(3*H*)-one , which was treated with phosphoryl chloride to produce 4-chloro derivative. The latter reacted with various amines to afford target thienopyrimidines. From 4-hydrazinyl derivative by Dimroth rearrangement thienotriazolopyrimidine was obtained [3].







The purity of the synthesized compounds was checked by TLC,
and their structure was proved by IR and ^{1}H and ^{13}C NMR spectra.

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CATALYSTS FOR THE COUPLING OF THIOLS TO DISULFIDES BASED ON METAL COMPLEXES WITH PHTHALOCYANINE SULFONIC ACIDS

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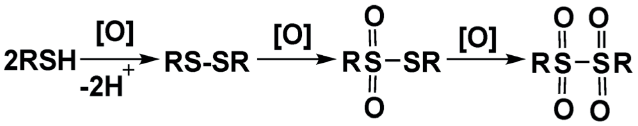
Disulfide compounds of tetraalkylthiuram exhibit valuable properties in terms of synthetic or biological processes [1] . They are used as components of a drugs for the treatment of alcohol addiction and human immunodeficiency [2]. Also, disulfides are known to be used for enhancing ADAM10 upon diagnosis of Alzheimer's disease [3]. Tetramethylthiuram disulfide (TMTD) has to be marked among large amount of disulfiram derivatives.

Synthesis of TMTD is easily performed via liquid-phase oxidation of N,N-diethylcarbamodithiolate (DTC) within alkali medium in presence of catalyst [4-5], although there are difficulties regarding oxidation process control. The use of inorganic catalysts leads to formation of mixed oxidation products and the process takes form according to Scheme:



$$\mathrm{2RSH} \xrightarrow[-2H^+]{[O]} \mathrm{RS\text{-}SR} \xrightarrow{[O]} \mathrm{R}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{-SR} \xrightarrow{[O]} \mathrm{R}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{-}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{R}$$

Applying metal complexes of organic macroheterocyclic ligands, for example phthalocyanines, as catalysts increases selectivity of the process and allows use of air oxygen as oxidant [6]. It helps to avoid harsh conditions of reaction and hence increases purity degree of the final product.

Present study shows the immobilization of tetrasulfo-substituted iron (FePc), cobalt (CoPc), and zinc (ZnPc) phthalocyaninates on the silica surface and the use of the resulting hybrid materials as catalysts for the thiol coupling process. The catalysts were synthesized by the sol-gel technology by co-hydrolysis of tetrasulfo-substituted *d*-metal phthalocyanines with tetraethoxysilane. To slow down the polycondensation process and increase the degree of fixation of the phthalocyanine dye, triethylamine was introduced into the system with gradual addition.

The catalytic activity of the materials was measured in the oxidative coupling reaction of DTC in TMTD, as well as 2-mercaptoethanol. In each process, high activity was shown by the material with the inclusion of CoPc. The introduction of perhydrol into the system led to an increase in the rate of the process by an order of magnitude due to the appearance in the system of an additional direction for the formation of RS• radicals (an increase in reactive oxygen species) and their recombination.

$$\mathrm{C_2H_5S^{\bullet}+C_2H_5S^{\bullet} \rightarrow C_2H_5S\text{-}SC_2H_5}$$

$$\mathrm{C_2H_5S^{\bullet}+HO^{\bullet} \rightarrow C_2H_5S\text{-}OH \xrightarrow{C_2H_5SH,pH>8,4} C_2H_5S\text{-}SC_2H_5+H_2O}$$

This work was supported by Russian Science Foundation (project 22-73-10158)

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C-H ARYLATION OF [1,2,4]TRIAZOLO[5,1-C][1,2,4]TRIAZIN-4(1*H*)-ONE WITH ARYL DIAZONIUM

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Currently, the development of new etiotropic drugs with antiviral effect is one of the urgent tasks for medicinal chemistry and organic synthesis because of the active evolution and spread of viral diseases. There are many ways to design such molecules, one of which is the strategy of directed modification of known scaffolds included in existing drugs.

Azoloazine derivatives are azaheterocyclic compounds possessing a wide range of biological activities, particularly the antiviral effects. One of the representatives of this class is Triazavirin, a synthetic analogue of purine nucleoside bases, which is widely used in the treatment of influenza, acute respiratory infections, and COVID-19.

The present work deals with the development of a new synthetic technique for the directed chemical modification of azoloazine substrates. This method includes the interaction of azoloazine **1** with diazonium salts generated *in situ* by the action of isopropyl nitrite on aromatic amine **2** in the presence of copper (II) acetate as an oxidant and calcium carbonate as a base. Finally, 6 new arylated azolotriazines **3** have been isolated in the yields of up to 74%.

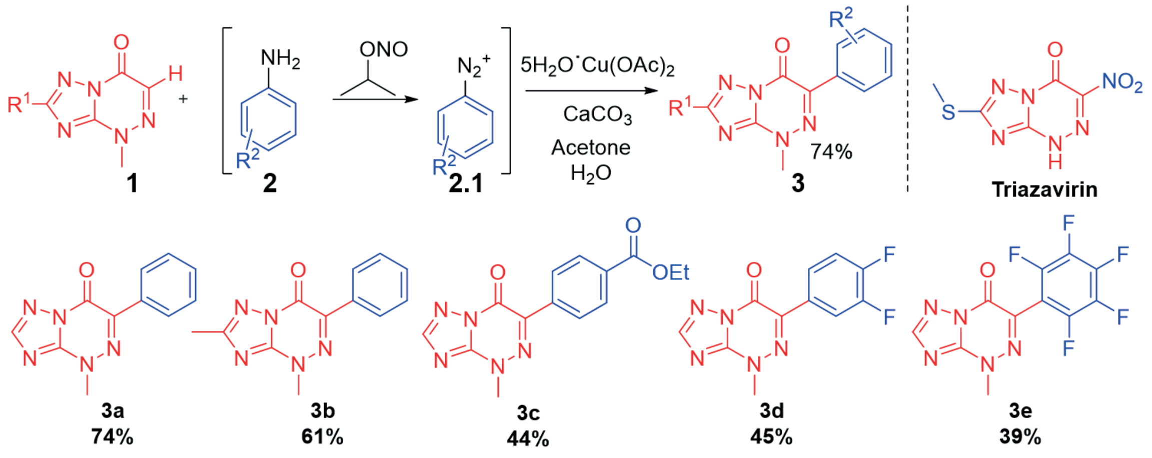

Figure 1. Arylation of [1,2,4]triazolo[5,1-c][1,2,4]triazin-4(1*H*)-one by *in situ* generated diazonium salt

It’s worth noting that the anti-viral properties of obtained compounds will be investigated soon.

The study was funded by Russian Foundation for Basic Research (RFBR)
according to the research project № 20-53-55003

BIS(CALIX[4]ARENES) HAVING PHOTOREACTIVE AZOBENZENE OR STILBENE LINKERS

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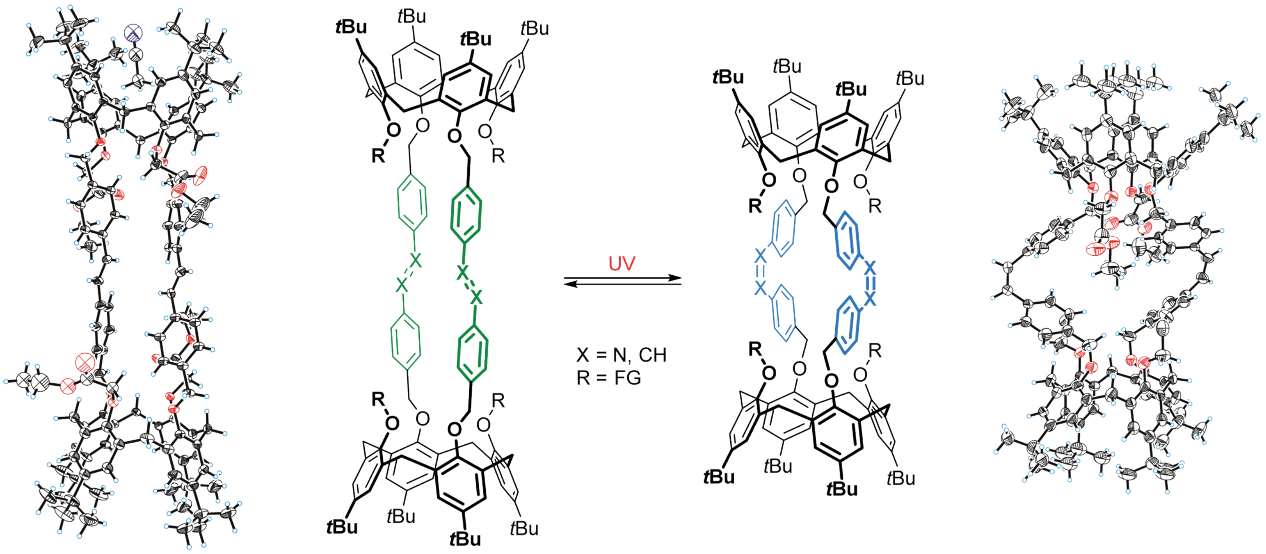
Photosensitive bis(calixarenes) of photo-variable length were prepared by a direct distal alkylation of parent calix[4]arene tetrols with (*E*)-4,4′-bis(bromomethyl)azobenzene or (*E*)-4,4′-bis(bromomethyl)stilbene using potassium carbonate as a base. Alkylation of four remaining phenolic OH-groups in two calix[4]arene macrorings allowed further derivatization of the biscalixarene cores. When exposed to soft UV light, the (*E*)-azobenzene-derived bis(calixarenes) underwent stepwise isomerization of both linkers from the (*E*)- to the (*Z*)-form, resulting in shrunken (*Z*,*Z*)-bis(calixarenes) as the major products. These (*Z*,*Z*)-bis(calixarenes) are thermally unstable and can be stretched back into their (*E*,*E*)-shape upon heating. Photo-shrinking of an (*E*)-stilbene-containing bis(calixarene) was achieved in the presence of 1,2-benzanthracene as a photosensitizer and the stable (*Z*,*Z*)-isomer of the bis(calixarene) was separated. Upon irradiation, the (*E*)-stilbene-linked bis(calix[4]arene) with no additional functional groups in its structure undergoes an intramolecular [2 + 2]-cycloaddition, which occurs much faster than *E*-to-*Z* isomerization and results in a mixture of isomeric biscalixarene cyclobutanes with *rtct*- and *rctt*-configurations.



The X-ray diffraction data as well as the results of quantum-chemical calculations, show that *E*/*Z*-isomerization of two azobenzene or stilbene linkers enables longitudinal shrinking/stretching of the bis(calixarenes), while maintaining the tail-to-tail arrangement of the calix[4]arene macrorings and their co-axiality. Along with the change in the molecular length, the shrinking/stretching affects the shapes of the internal cavities of the bis(calixarenes), as well as the arrangement of the functional groups, thus showing the applicability of the azobenzene-/stilbene-linked bis(calixarenes) as cores for the design of photoswitchable host molecules and larger assemblies capable of sophisticated supramolecular interactions controlled by light.

The study was supported by the Russian Science Foundation
(Grant No. 22-23-00584, https://rscf.ru/en/project/22-23-00584/)

PHOTOCATALYTIC ACTIVITY OF TiO_2 DOPED WITH WO_3 IN THE DECOMPOSITION REACTION OF METHYLENE BLUE UNDER VISIBLE LIGHT IRRADIATION

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Considering that clean water is becoming one of the strategic resources in the modern world, water purification from toxic industrial effluents is one of the urgent tasks of environmental protection and human health. One of the ways to neutralize these compounds is photocatalytic oxidation or oxidative degradation by air or oxygen without of any consumable materials. Currently, paired (doped) photocatalysts are widely used, which are activated due to the ability to absorb the energy of visible light.

Photocatalysis is a “green technology”.

Proceeding from this, recently the priority direction of our research is the synthesis of composite photocatalysts based on photosensitive nanomaterials capable of being activated under the influence of photoradiation simulating sunlight. For this purpose, we synthesized composites based on titanium dioxide doped with various amounts of tungsten trioxide (TiO_2 / WO_3). The photocatalytic activity of the composites was investigated in the degradation reaction of the organic dye methylene blue (MB).

Photocatalysts were prepared by wet impregnation of titanium dioxide nanopowder with ammonium paratungstate, followed by calcination at 500°C. The composites were characterized by XRD, SEM, and DRS methods.

The diffuse reflection spectra obtained for TiO_2 and TiO_2/WO_3 in the range of 200-800 nm, showed that TiO_2, with a band gap of 3.2 eV, is able to absorb light in the UV region (up to 400 nm). The doping of WO_3 to TiO_2 expands the light absorption region of the composite, including the visible range of the light, up to 555 nm. Therefore, it can be expected that the doped TiO_2/WO_3 photocatalyst will be photoactive in the visible light region, at least in the range up to 555 nm. This assumption was experimentally confirmed when the aqueous solution of MB was irradiated under visible light (380-800 nm, xenon lamp Dr-1000) in the presence of the TiO_2/WO_3 photocatalyst, as well as bare TiO_2 and just MB without photosensitizers for various time intervals. It has been found that the dopping of WO_3 in TiO_2 leads to a significantly higher photocatalytic activity of TiO_2/WO_3 compared to bare TiO_2. In particular, 89.8% of MB were removed during 30 minutes under visible light exposure. The conversion of MB under visible light irradiation in the presence of bare TiO_2 is 14-18%. In order to determine the role of WO_3 in the photocatalytic reaction of MB decomposition, this reaction was also studied in the presence of composite SiO_2/WO_3 based on non-semiconductor SiO_2. It is shown that MB is removed from an aqueous solution as a result of adsorption on the SiO_2 surface ($S=300m^2/g$), the reaction of photocatalytic decomposition of MB does not proceed. Consequently, the high photocatalytic efficiency of the TiO_2/WO_3 composite is explained by the synergistic effect. Calculations of the band gap Eg (photon energy) of the TiO_2/WO_3 photocatalyst showed that doping of TiO_2 with WO_3 reduces the band gap of the photocatalyst to 2.2 eV, which results to ability of composite to absorb energy in the range of 280-555 nm. It is obvious that the ability to absorb both ultraviolet and visible light contributes to a significant increase in the photocatalytic properties of the doped TiO_2/WO_3 photocatalysts. Under photoradiation in this wavelength range of light, almost complete decomposition of MB in an aqueous solution is achieved in just 10 minutes. The data obtained show that the TiO_2/WO_3 photocatalyst can be effective in the treatment of wastewater containing MB.

PYRROLINE DERIVATIVES AS A NEW TYPE OF N-DONOR LIGANDS: INTERCORRELATION BETWEEN STRUCTURAL AND ELECTRONIC STRUCTURE OF LIGAND AND ITS COMPLEXES

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One of the most promising directions in modern medical chemistry is the study of the biological activity of the metal coordination compounds with organic ligands already used as drugs. This interest is due to a very wide range of their medical applications.

In this work the coordination of pyrroline derivatives by a number of essential metals – copper, zinc and silver - was investigated.

Pyrrolidine derivatives are one of the most attractive classes of heterocyclic compounds from the point of view of their biological activity. The structural fragment of pyrrolidine is part of many well-known biologically active compounds [1,2], both natural (among the most famous are the alkaloid nicotine and the proline amino acid) and synthetic. According to the literature data [3] the pyrrolidine and pyrroline cycles belong to the most common heterocycles in the structure of drugs. They have been proposed as anticancer drugs, compounds for the treatment of mental and neurophysiological disorders such as Parkinson's and Alzheimer's diseases, somastatin receptor inhibitors, modulators of glutamate receptors etc [4]. Thus, the use of arylpyrrolidines as ligands for the synthesis of various metal-containing biologically active compounds is of great interest.

Pyrroline and pyrrolidine derivatives prevail among natural compounds and are actively used as medicines. For example, the pyrroline cycle is part of vitamin B12, being coordinated to the cobalt ion by an electron lone pair of a nitrogen atom. However, systematic studies of coordination compounds with these heterocycles as ligands have not been carried out.

Here we report on reactions of copper, zinc, iron and silver salts of phenyl-substituted pyrrolines bearing para-chloro, para- and meta-hydroxy, para-oxymethyl and para-oxyethyl substituents at the phenyl ring. Both complex salts [5] and coordination compounds of molecular and polymer structures were obtained. All compounds were obtained in the form of single crystals, for which molecular and crystal structures were established by X-ray analysis. The dependence of the structure of the final product on the substituent in the para-position of the benzene cycle was found for copper complexes. The structure of zinc and silver complexes synthesized by now is mainly determined by the configuration of the metal ion.

This research was funded by the Russian Science Foundation, grant number 23-13-00374

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STUDY OF SELECTIVE NITRIC OXIDE SORPTION INTO ROBUST BLATTER RADICAL-DECORATED MATERIALS BY EPR SPECTROSCOPY

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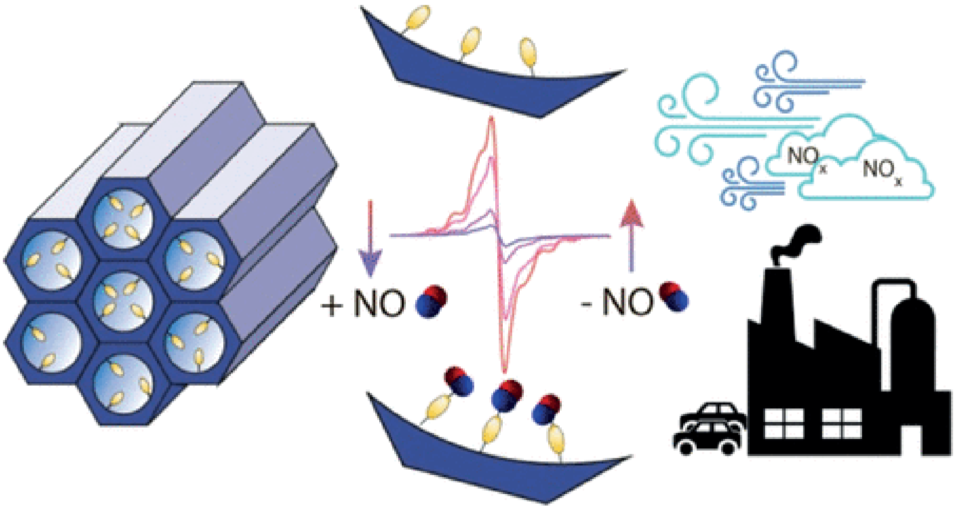
Ecology problems such as air pollution come to the fore nowadays. One of the most widespread toxic waste gases is NO_x mixture. The main source of NO_x is combustion process and emerging gas mixture consists mainly of NO (over 70%). Selective sorption is a perspective route for NO removal from fuel gas. Accordingly this field is attracted interest of the scientific community and industry.

Various porous materials such as metal-organic frameworks (MOFs) and organosilica materials have established themself as perspective sorbents. Furthemore these materials are promising sorbents because of the ease of surface functionalization and tailoring morphology. Introduction of paramagnetic sites into materials also makes them promising sorbents of paramagnetic gases.

Electron paramagnetic resonance is a suitable and convenient spectroscopic technique for monitoring radical centers behavior during paramagnetic gas sorption and desorption.

Thus, in this work we studied sorption of nitric oxide. We used several materials in order to compare sorption properties of robust materials: Blatter radical - containing silicas, xerogels and SBA-15, and MOF-808. As a result, we demonstrated for the first time that Blatter radical-containing materials are able to interact with NO forming diamagnetic product. We showed that sorption properties of such paramagnetic materials are significantly different and depends on the synthesis conditions and structural features. We obtained record value of selective sorption capacity for xerogels equals to 0.5 mmol/g. We studied desorption by heating up to different temperatures and monitoring numeric change of radical centers by EPR. Quantitative EPR analysis of radical content during repetitive sorption/desorption under optimal condition revealed high stability of sorption capacity for radical based xerogels over 5 cycles. At the same time, reactivation of the Blatter radical – containing SBA-15 upon evacuation and heating at moderate temperature (240 ºC) can restore up to ~90% of the radicals. Selective capturing of nitric oxide from flue gas model mixture by radical containing xerogel was approved by EPR spectroscopy.



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EFFECT OF ALKALI METAL ON SORPTION CAPACITY OF LITHIUM CONTAINING SORBENT

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Since the beginning of the industrial revolution, global greenhouse gas emissions have increased and the greenhouse effect has become more and more severe. Climate change has become a major issue to be faced. According to statistics, CO_2 is the main greenhouse gas, accounting for more than 70% of the world's greenhouse gases, with the rest being methane, nitrous oxide and various fluorinated gases. Mitigating the effects of global climate change is one of the most important challenges of our time. At the Climate Action Summit held on September 23, 2019, it was announced that 77 countries, 10 regions and over 100 cities have committed to achieving net zero carbon emissions by 2050. The development of zero and low carbon energy generation technologies to address these challenges is the main goal of these pioneer countries. Carbon capture, use and storage (CCUS) technologies are a key way to address this challenge, especially as fossil fuels will continue to play an important role in global energy consumption. Capturing and separating CO_2 from large volumes of flue gases is still costly and consumes a lot of energy; therefore, it is invaluable to develop efficient adsorbents for relatively concentrated streams in order to reduce the overall cost of the adsorption process. At present, in particular, there is no ideal sorbent for post-combustion capture from large point sources due to various disadvantages associated with either low CO_2 capture capacity, or selectivity under real pressure conditions, or high cost, slow kinetics, and sensitivity to moisture. Consequently, research is focused on developing improved sorbents with lower regeneration energy, high adsorption/desorption rates, and better stability for cost-effective adsorption performance.

Li_4SiO_4 has been extensively researched as a CO_2 sorbent, especially due to its high theoretical trapping capacity, good stability over several trapping/desorption cycles, and lower regeneration temperatures compared to other sorbents, such as CaO. These characteristics are crucial when it comes to industrial applications.

In this work, silicon oxide obtained from rice husks was used to obtain Li_4SiO_4. The sorption capacity of Li_4SiO_4 for carbon dioxide has been studied. Adsorption was carried out at a temperature of 500°C, desorption at 750°C, the sorption capacity of Li_4SiO_4 was 24%. Li_4SiO_4 was promoted with potassium and sodium oxides; the study of the sorption capacity of sorbents showed that, compared with sodium, promotion with potassium oxide leads to a significant increase in the sorption capacity (36 %) of the sorbent.

The work was supported by the Ministry of Science and Higher Education of the Republic of Kazakhstan within the framework of the scientific project No. AP1486903 Scientific and practical aspects of the development of sorbents and catalysts for capturing and methanation of greenhouse gas carbon dioxide.

EFFECT OF PREPARATION METHOD ON THE ACTIVITY OF $LaNiO_3$ IN THE DRY REFORMING OF METHANE

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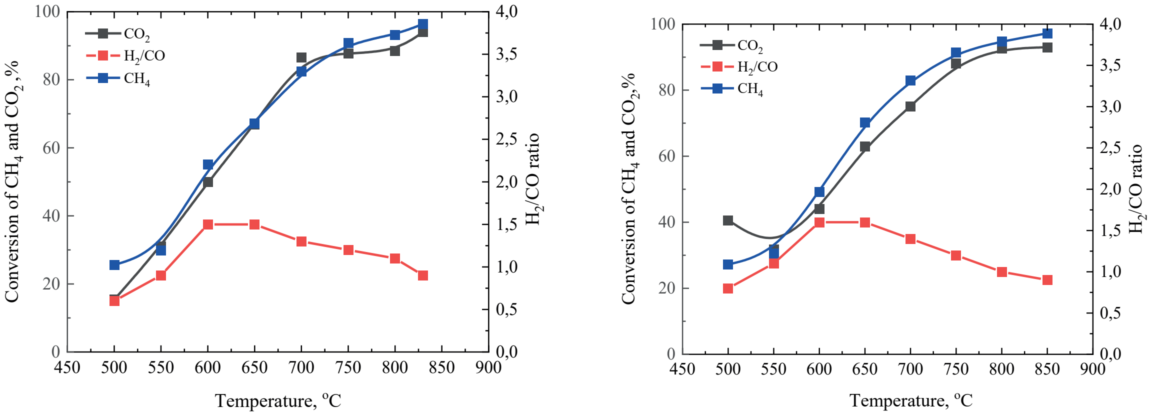
In recent years, when the negative impact of the greenhouse effect has become more and more obvious, reducing global greenhouse gas emissions has become an important task for all countries of the world. Dry reforming of methane (DRM) has been widely studied as one of the potential ways to produce synthesis gas from two greenhouse gases (CH_4 and CO_2) and can reduce the emission of these gases. Many traditional metal/support catalyst systems, although highly active, are deactivated in for several hours due to deposition of coke on the surface or sintering of active metal clusters. To overcome these difficulties and withstand the extreme operating temperatures of DRM, active metals can be incorporated into crystalline oxides such as perovskites, pyrochlores, hydrotalcites and hexaaluminates. These metal-containing oxides, after the reduction of the active metal, give a finely dispersed active catalyst.

The purpose of this work is to study the effect of catalyst preparation methods on their catalytic activity in the DRM process. The synthesis of catalysts based on $LaNiO_3$ was carried out by the sol-gel and solution combustion methods using a dispersing agent. The synthesized catalysts were tested in the conversion of a model mixture (CH_4+CO_2) in the reaction of greenhouse gas utilization under the conditions: T= 500-830°C, W=1000 h^{-1}, CO_2:CH_4 ratio =1:1. The results obtained are shown in Figure 1 a, b.



a-$LaNiO_3$ catalyst, ZG method

b- $LaNiO_3$ catalyst, SC method

Influence of reaction temperature on the activity of $LaNiO_3$(ZG) and $LaNiO_3$(SC) catalysts in the DRM

The results showed that the perovskite catalysts $LaNiO_3$(ZG) and $LaNiO_3$(SC) show good activity in the utilization of greenhouse gases to synthesis gas in the temperature range T=500-830°C. The highest conversion of methane and carbon dioxide is observed on the perovskite $LaNiO_3$ catalyst prepared by the solution combustion method, under the reaction condition: T=850°C, W=1000 h^{-1} and CO_2:CH_4 in the initial reaction mixture=1:1, the conversion of methane is 97,2 and carbon dioxide 93%.

The work was supported by the Ministry of Science and Higher Education of the Republic of Kazakhstan within the framework of the scientific project No. BR18574084.

LANTHANIDE CHELATE NANOPARTICLES FOR LUMINESCENCE APPLICATIONS

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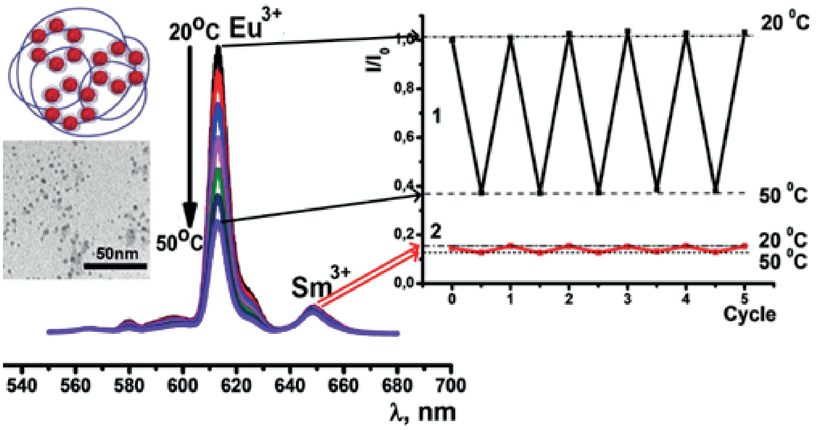
Luminescent lanthanide complexes have long attracting researchers due to their excellent optical properties. They are widely used as building blocks for luminescent nanomaterials for application in biomedical analysis, medical diagnosis, and cell imaging[1, 2]biomedical imaging, drug delivery, etc. However, these novel nanomaterials have to be carefully designed to ensure that the unique properties conveyed by each component, i.e., lanthanide ions and nanoparticles, are maximized and not negatively affected by one another. In this Forum Article, the main advances in the design of lanthanide-based nanoparticles will be discussed, with the first part focusing on the design of gadolinium(III. Long luminescence lifetimes, sharp characteristic emission bands, and large Stoke's shifts allow getting rid of biological background autofluorescence, which is of great importance when biomedical experiments are conducted.



The wide applicability of lanthanide complexes in fluorescent sensing of residual amounts of drugs, including antibiotics, in water or biological fluids is well-known[3, 4]. In this regard, the synthesis of new lanthanide complexes, where ligand-to-metal energy transfer is enough for sensitizing lanthanide-centered luminescence, and ligand-metal coordination bonds are tight enough for the safe conversion of the complexes into water-dispersible nanomaterial with high lanthanide-centered luminescence is a challenging scientific task.

The applicability of the developed aqueous colloids as nanosensors will be demonstrated by their luminescent reply on ceftriaxone, which is the third generation of cephalosporin antibiotic widely applied in treating of such socially relevant bacterial infections as meningitis, pneumonia and many others as well as fluoroquinolones antibiotics, glyphosate and temperature [5-7].

Acknowledgement. The authors thank the Russian Science Foundation (grant 22-23-00853) for financial support. RZ and AD thank the Kazan Federal University Strategic Academic Leadership Program (PRIORITY-2030) for support.

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CRYSTALLIZATION-INDUCED STEREOCHEMICAL TRANSFORMATIONS OF 15-EN-STEVIOL AND DIHYDROSTEVIOL

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Progress in crystal engineering has led to the accumulation of a large amount of information about supramolecular associates formed in a complex way through classical hydrogen bonds or a wide range of other intermolecular interactions. Basic descriptors of stereochemistry (concepts of an asymmetric center, configuration) are not enough to describe such structures. Consideration of such systems urgently requires the use of concepts formed in classical dynamic stereochemistry to explain the special spatial aspects of chemical reaction behaviors and of the predominately forming one of possible stereoisomers - the concept of prochirality, the notion of prostereogenic grouping, and the corresponding prostereoisomerism descriptors.[1] This suggests the emergence of a new field - dynamic supramolecular stereochemistry.

In this work, the need for such an approach is demonstrated in the study of crystallization of 15-ene and dihydrosteviols. It is established that polymorphism is characteristic of these substances. The variety of crystal phases, as well as the transitions between them, were studied by DSC, single-crystal and powder XRD. The one-, two- and three-dimensional system of hydrogen bonds formed by supramolecular diastereomers molecules, the appearance of which is associated with the asymmetry of the hydroxyl oxygen atom, was detected in the crystal forms of 15-en and dihydrosteviols.

Acknowledgements.
The work was carried out with the financial support of the RSF (grant 22-13-00284)

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ETHERIFICATION OF ORTHOPHOSPHORIC ACID IN THE SYNTHESIS OF POLYURETHANE IONOMERS

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The synthesis of ionomers, which are polymeric materials with a small number of ionic groups, is a promising way to create new functional materials. Functional ionic groups are used to influence such properties of polymers as the glass transition temperature, size and distribution of domain supramolecular structures in the continuous polymer phase, miscibility of polymers, rheological characteristics, and to improve the mechanical properties of polymers [1-2]. The ionic fragments are generally incorporated into these polymers as cationic, anionic, or zwitterionic particles in various concentrations.

In [3-4], orthophosphoric acid aminoethers (AEPA) were synthesized by the interaction of triethanolamine (TEOA), OPA and polyoxypropylene glycol (PPG). Such a relative content of the initial reagents was used when all three hydroxyl groups of triethanolamine and one hydroxyl group of PPG could potentially be consumed for the esterification reaction. The main branching center of AEPA is the tertiary amine, and phosphates perform the function of subsequent branching centers.

In this paper, the mechanism of the esterification reaction of orthophosphoric acid (OPA) catalyzed by tertiary amines with polyoxypropylene glycol has been studied. It was found that when using triethylamine, complete esterification of OPA occurs, accompanied by the formation of polyphosphate structures and branched OPA esters terminated by hydroxyl groups in EPA. When triethanolamine is used as a catalyst, incomplete esterification of OPA with polyoxypropylene glycol occurs, as a result of which a part of phosphate anions remain unreacted in the composition of ortho-phosphoric acid aminoesters (AEPA) formed here. In this case, the hydroxyl groups of triethanolamine are fully involved in the OPA esterification reaction, but the catalytic activity of the tertiary amine weakens due to a decrease in its availability in the branched structure of AEPA. The kinetics of the catalyzed TEOA and TEA reaction of OPA esterification with polyoxypropylene glycol has been studied. It has been established that triethanolamine occupies a central position in the structure of AEPA. The physicochemical properties of AEPA synthesized in a wide temperature range and the ratio of the initial reagents, as well as the physico-mechanical properties of polyurethane ionomers obtained on their basis are investigated.

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DFT STUDY ON THE EFFECT OF HYDROXYL GROUPS ON THE STRUCTURE AND REACTIVITY OF 2-METHYLQUINOLIN-4-OL DERIVATIVES

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Quinolines and their derivatives, particularly hydroxyquinolines, exhibit biological activity, which depends on their structural features [1]. In this report, we present a theoretical study on the effect of hydroxyl groups on the structure and properties of 2-methylquinolin-4-ol derivatives. The quantum chemical calculations for geometry optimization and vibrational frequency analysis in the gas phase were carried out on the DFT/B3LYP/6-311+g(d,p) level, using Gaussian 09 program package. Full geometry optimization along with vibrational frequency calculations characterize the structure corresponding to the minimum of the potential energy surface. The bond length, bond angle, total energy, and dipole moment of 6-[(4-dimethylaminobenzyliden)amino]-2-methylquinolin-4-ol (C1) and 6-[(2,4-dihydroxybenzyliden)amino]-2-methylquinolin-4-ol (C2) were determined. Parameters characterizing kinetic stability, chemical activity, optical polarizability, and chemical hardness/softness of the compounds (the energy gap, HOMO, and LUMO electron orbitals) were also calculated. The optimized structure of C1 and C2 are presented in Fig. 1.

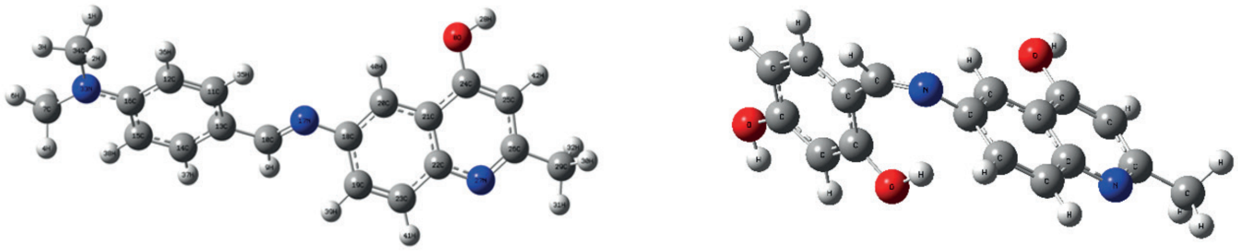

Fig. 1 Optimized structure of C1 and C2.

When the energy gap is small, the molecule is highly polarizable and has high chemical reactivity. Based on the analysis of the obtained results, C1 (Eg = 0.1386 eV) is a highly polarizable and chemically reactive molecule compared with C2 (Eg = 0.1539 eV) due to the effect of hydroxyl groups. Because C2 (ELUMO = -0.0659 eV) is more negative compared with C1 (ELUMO = -0.0446 eV), therefore C2 exhibits high electrophilicity.

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IMDAF APPROACH IN THE SYNTHESIS OF EPOXYISOINDOLES CONTAINING (THIO, SELENO)UREA MOIETY

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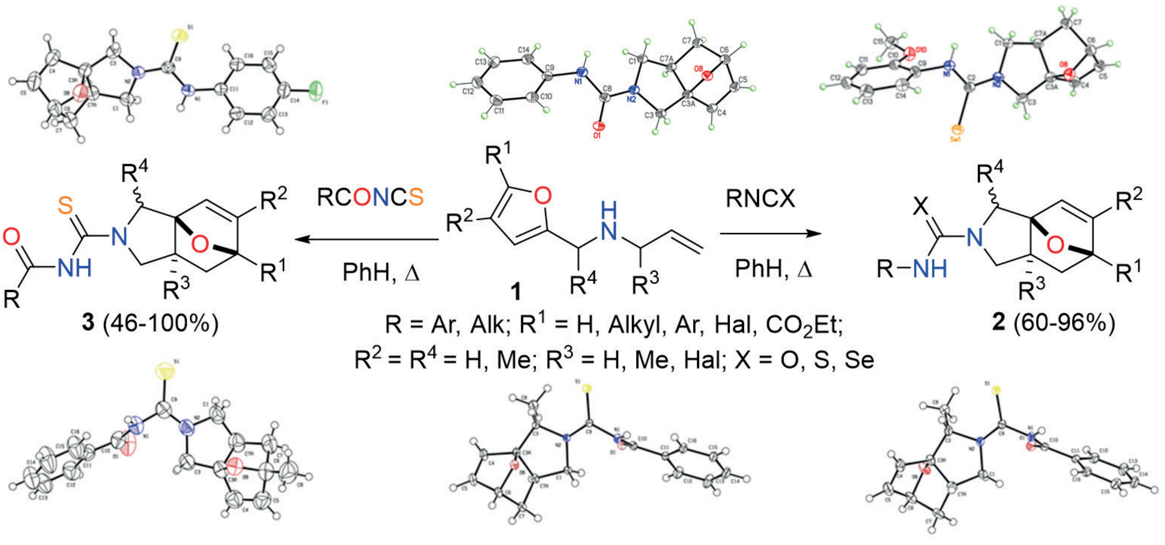
Research in the field of derivatives of urea, thiourea, selenourea occupy a huge niche in organic, pharmaceutical and medicinal chemistry, since a huge number of drugs, dietary supplements, auxiliary compounds used in industry containing the skeletons of these molecules are known. A literature analysis shows that since 1990 the number of publications on the synthesis, study of the properties and use of urea, thiourea, selenourea steadily increasing. The (thio,seleno)ureas attract attention due to their high antitumor activity and acceptably low cytotoxicity. They are used as broad spectrum antimicrobial and antibacterial agents. Thio- and selenoureas are effective scavengers of superoxide radicals, selenoureas act as effective antioxidants, showing low cytotoxicity for some human cells. The importance of (thio)ureas as pesticides, fungicides and bactericides has long been known. In particular, 1,1-dimethyl-3-arylureas such as *fenuron*, *isoproturon*, *chlorotoluron*, *methoxuron*, *monouron* and *diuron* are known as urea herbicides widely used in agricultural practice.

The proposed project is based on the tandem reaction of nucleophilic addition / intramolecular [4+2]-cycloaddition of furylallylamines [1] under the action of alkyl-, aryl- and aroylisothiocyanates, isocyanates and isoselenocyanates.



It was shown that refluxing allylfurfurylamines **1** with the corresponding alkyl-, aryl- and aroylthioisocyanates, isocyanates and isoselenocyanates in benzene for 6-8 hours leads to the formation of epoxyisoindolyl(thio,seleno)ureas **2,3** in moderate to high yields (46-100%). The *exo*-cycloaddition reaction proceeded stereoselectively with the retention of the substituent R^3 configuration in products **2,3**. Selected isoindolones displayed antibacterial and antifungal activity.

This work was supported by the Russian Science Foundation (RSF) (project №. 22-73-00127).

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MOLECULAR STRUCTURE OF TETRAPYRROLE MACROCYCLES PROMISING FOR ORGANIC ELECTRONICS

Zhabanov Yu.A., Eroshin A.V., Otlyotov A.A., Kuzmin I.A.,
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The increasing interest in metal complexes of porphyrins, porphyrazines and their analogues is due to the fact that these compounds demonstrate examples of their successful application for gas-phase transport in order to obtain films for various purposes, up to the formation of films of high-temperature superconductors. Their distinctive feature is that they not can only be used as volatile components for deposition of a metal layer on the surface of a semiconductor, but also exhibit outstanding semiconducting properties. Structural studies of complexes with metal ions can make it possible to analyze the influence of the nature of the metal atom on the electronic and geometry structure of ligands, to obtain information about the nature of the chemical bond between the metal and the ligand and to identify trends in changes in the covalent and ionic components of bonding. No less important is information about the effect of peripheral substituents on the structure of the macrocyclic complex, as well as on the volatility of these compounds. The identified trends is important for predicting the behavior of these compounds, both in gas and in solution, allowing judging by the nature of substituents of the increase or decrease in volatility and solubility, without additional experiments.

In this work, an experimental and theoretical study of the geometric and electronic structure of molecules of tetrapyrrole macrocycles was carried out in order to establish and theoretically explain the general patterns in their structure, as well as expand reference information. For a comprehensive study of the structure and energetics of macroheterocyclic compounds, a complex of theoretical and experimental methods was used. Studies of sublimation processes of 21-oxa-5,10,15,20-tetraphenylporphyrin, 21-thia-5,10,15,20-tetraphenylporphyrin, 21,23-dithia-5,10,15,20-tetraphenylporphyrin were carried out by mass spectrometry using a Knudsen effusion cell, which made it possible to determine the thermal stability and the possibility of congruent evaporation of these substances in order to establish the prospects for their use in MO CVD technologies. The structure of free molecules of octaethylporphyrin, its complex with palladium, and 21-thia-5,10,15,20-tetraphenylporphyrin, which, according to mass spectrometry data, can be congruently transferred to the gas phase, was determined by gas electron diffraction. Electron diffraction studies are of particular importance due to the fact that the resulting molecular structure is free from collective interactions characteristic of X-ray and neutron diffraction, which makes it possible to establish with high reliability the fine details of the geometric structure of molecules necessary for reliable prediction of gas-phase processes used in modern micro- and nanoelectronics, as well as in optoelectronics.

An important component of the studies carried out is the theoretical determination of the geometric and electronic structure of macroheterocyclic compounds using high-level quantum chemical calculations, which made it possible to determine the effect of substituents on the structure and spectral properties of these compounds. Quantum-chemical calculations for a number of metal complexes with macroheterocyclic ligands were performed: Fe(II) complexes with porphyrin and tetrabenzoporphyrin; vanadyl and titanyl complexes with porphyrazine, perchlorinated and perfluorinated porphyrazine, tetrathia-2,3,5,10,12,13,15,20,22,23,25,30,32,33,35,40-hexadecaazaoctaphyrin (C40N20H16S4) and its complex with Cu ($Cu_4C_{40}N_{40}H_{12}S_4O$), Al(III) complex with 3′-(p-cyclohexyl)phenoxyphthalocyanine and axial ligand –Cl. Additional calculations of the binding energies of dimeric heteroporphyrins, 21-oxa 5,10,15,20-tetraphenylporphyrin, 21-thia-5,10,15,20-tetraphenylporphyrin, 21,23-dithia-5,10,15,20-tetraphenylporphyrin were carried out.

This work was supported by the Russian Science Foundation grant 21-73-10126.

VAPOR DEPOSITION PROCESSES: HOW CAN THE THERMODYNAMICS OF METAL-ORGANIC PRECURSORS PROMOTE THE CREATION OF ADVANCED MATERIALS?

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Volatile metal-organic compounds are involved as precursors for producing functional film materials by gas-phase processes, such as chemical or physical vapor deposition. To optimize the technological deposition conditions, knowledge about the vapor pressure and thermodynamics of sublimation or vaporization of the precursor used is indispensable. Together with the thermal behavior in the condensed phase (thermal stability, phase transitions), these data determine the evaporator mode in the reactor, allowing precise control of the amount of substance fed into the deposition zone at a certain temperature. Obviously, the experimental conditions for the volatilization of complexes with various metals and ligands vary significantly. Moreover, as a rule, thermodynamic data for the same precursor, obtained by different methods and in different labs, also differ considerably in vapor pressures, melting temperatures, as well as the interrelated enthalpies of sublimation, vaporization, and fusion. As a result, we are faced with a data pool (see fig.1) which cannot be compared, rationalized, or favored, and deposition experiments are inevitably carried out under empirically determined conditions.

In focus of this contribution, there is a general algorithm for diagnosing data on the thermodynamics of solid-gas, liquid-gas, and solid-liquid phase transitions for metal β-diketonates which are the most-known precursors. It is based on “structure-property” correlations and the group additivity principles [1,2]. The approach has been developed and tested for a number of metal *tris*-β-diketonates [3–5].

The financial support of the work was provided by the Russian Science Foundation and the Government of the Novosibirsk Region (project no. 22-23-20182)

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COORDINATING ABILITY OF 3-ARYLIDENE-1-PYRROLINES IN REACTIONS WITH COPPER(II) NITRATE

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Pyrrolidine derivatives are one of the most important and widespread classes of heterocyclic compounds. Its importance is emphasized by a number of new antiviral and anticancer drugs that have appeared in the pharmaceutical market in recent years. Unsaturated analogues of pyrrolidine derivatives, known as 3-arylidene-1-pyrrolines [1], demonstrate anti-cancer and anti-tuberculosis activity as well as the ability to inhibit the formation of bacterial biofilms. The introduction of 3-arylidene-1-pyrrolines as N-donor ligands into the coordination sphere of vital metals makes it possible to obtain fundamentally new compounds, the range of possible applications of which includes biologically active compounds, magnetic materials and precursors for further modification of the organic fragment.

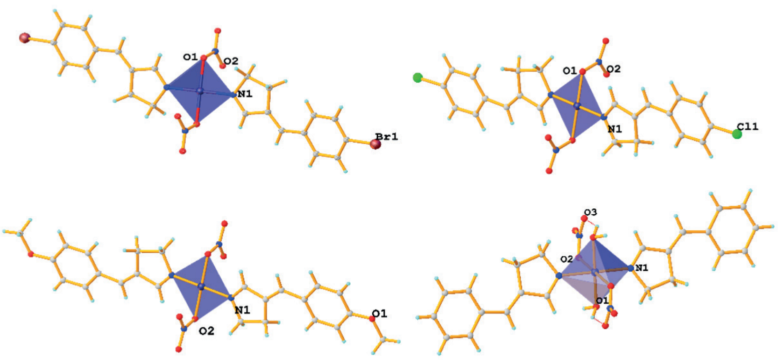

Fig. 1. Structure of the obtained copper(II) complexes in crystals

This work aims to study the coordinating ability of 3-arylidene-1-pyrroline derivatives with different substituents in the benzene ring in reactions with copper(II) nitrate and the structural features of the resulting compounds.

Acknowledgements. This research was funded by the Russian Science Foundation, grant number 23-13-00374

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AZAD Pharma AG was founded in 2000 in Switzerland by entrepreneur and philanthropist Mihran Baronian. The mission of the company is dedicated to develop and offer generic APIs and Finished Products with unique processes and formulations as to provide customers with the opportunity for an early market entry and, subsequently, a beneficial position in the market. Teams of experienced chemists, formulators and regulatory experts are responsible for assuring the products and the documentation are of the highest standards, and that the requirements of all regulators are met. The head office located in Switzerland as well as the offices in Armenia, Canada and China ensure the company's presence in all markets around the world.

AZAD Pharmaceuticals LLC was founded in 2004 in Armenia. The company introduces generic APIs in the CIS countries, Georgia, Ukraine and Iran and is a good platform to present European products in the region. Moosmann Pharmaceuticals LLC, which has been operating within AZAD Pharmaceuticals LLC since 2019, is engaged in the registration and marketing, as well as the import and sales of high-quality cost-effective medicinal products in Armenia and Georgia.

In 2015 an R&D lab was established within AZAD Pharmaceuticals LLC in order to strengthen the company's own capabilities in the field of API R&D. The main goal of the laboratory is the development of non-infringing pathways for the commercial scale synthesis of generic oncological, ophthalmological, antiviral and antibacterial APIs as well as iron deficiency medicines, highly demanded on the global pharmaceutical market. Based on the results obtained a number of international patents were filed and several APIs are produced based on the technologies developed in the laboratory.

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