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Ivanovo State University of Chemistry and Technology
G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences
Institute of Macroheterocycle compounds ISUCT
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БОРИС ДМИТРИЕВИЧ БЕРЁЗИН – ОСНОВАТЕЛЬ ИВАНОВСКОЙ ШКОЛЫ ПОРФИРИНОВ И ФТАЛОЦИАНИНОВ

Berezin D.B.

БОРИС ДМИТРИЕВИЧ БЕРЁЗИН – ЭТАПЫ НАУЧНОЙ ДЕЯТЕЛЬНОСТИ

Belykh D.V.

PHEOPHYTIN *A* AS THE STARTING COMPOUND IN THE PORPHYRINS SYNTHESIS

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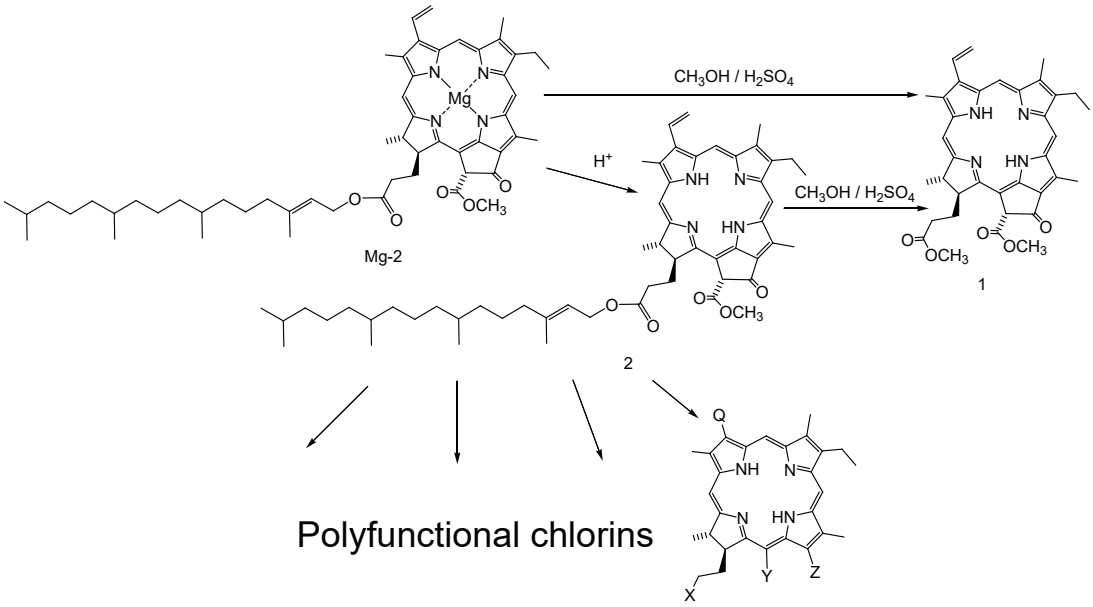
Chlorophyll a and its derivatives are convenient starting materials for the synthesis of macrocyclic compounds for various purposes (medical photosensitizers, diagnostic drugs in oncology, etc.). Due to a number of reasons related to stability and availability when preparing from chlorophyll-containing raw materials (primarily spirulina), methylpheophorbide *a* **1** and its immediate derivatives (pheoforbide *a*, pyropheophorbide *a* and its methyl ether, chlorine e_6 trimethyl ether). The pheophytin *a* **2** molecule has a similar reaction centers, therefore many chlorins derived from **1** can be obtained from **2**, and obtaining from **2** can be beneficial in terms of the number of stages. The possibility of pheophytin *a* **2** obtaining from spirulina with a minimal amount of impurities makes it possible in many cases to consider **2** as an acceptable or even more advantageous alternative **1**. A fragment of phytol in the substituent at position 17 in molecule **2** can influence the conditions for carrying out reactions similar to transformations **1** and their result. In addition, the phytol fragment can act as a reaction center itself in some cases. All this must be considered when planning and carrying out the synthesis of macrocyclic compounds based on **2**.



Scheme 1

This report analyzes the literature data on the chemical transformations of pheophytin *a* **1** from the point of view of the possibility of its use in the synthesis of macrocyclic compounds.

Bender Timothy P.

BORON SUBPHTHALOCYANINES AND SUBNAPHTHALOCYANINES FOR ORGANIC PHOTOVOLTAICS: THEIR AMBIENT STABILITY, THE MIXED ALLOYS AND THEIR SEPARATION, DERIVING THESE MATERIALS FROM BIO SOURCES AND THEIR PATHWAY TO COMMERCIAL PRODUCTION

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For some time, our group has been focused on the design, synthesis and application of derivatives of boron subphthalocyanines (BsubPcs). Our focal point has been and continues to be equally between the basic chemistry of BsubPcs and their application in organic photovoltaics (OPVs)/solar cells. More recently, we have taken an equal approach to extended pi-conjugated derivatives of BsubPcs, boron subnaphthalocyanines (BsubNcs); BsubNcs being unique and beneficial materials for OPV application.

We have recently shown that BsubNcs actually become randomly chlorinated during their synthetic preparation and actually then form a mixed alloy composition of chlorinated materials, which we have designated as Cl-ClnBsubNcs. The mixed alloy composition is unique, and has been determined to be a mixture of 24 (more or less) chlorinated BsubNcs despite being a mixture that uniquely forms single crystals. The formation of single crystals is enabled by the chlorine atoms occupying vacancies within the solid state structure, the vacancies being the so-called "bay position" of the BsubNcs structure. After establishing the correlation of electrochemical characteristics and OPV performance for Cl-ClnBsubNcs, we have also recently shown that phenoxylated versions of ClnBsubNc are also a mixed alloy and applicable in BHJ OPVs also as electron accepting materials. We have also shown that Cl-ClnBsubNcs can be equally applied as electron donating materials in OPVs have the same performance correlations to the amount of chlorination present. We have also shown that BsubNcs are equally stable within an OPV in the ambient environment compared with BsubPcs. This accumulation of properties led us to consider how to separate the alloyed mixtures and how to prepare pure BsubNcs.

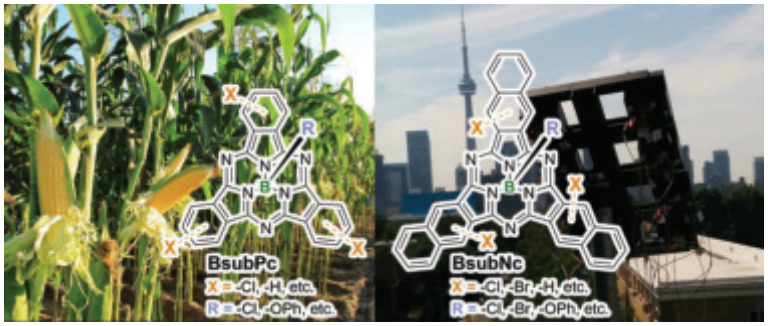

Fig.

During this presentation I will describe a chemical pathway to enable the separation of the mixed alloys of BsubNcs. We found that not all 24 (more or less) isomers can be separated, yet this process has enabled a more detailed electrochemical characterization and correlation to amount of halogenation. I will also describe a chemical pathway to pure BsubNcs, avoiding halogenation/chlorination in the bay position. This pathway enables a detailed characterization of a pure BsubNc including its electrochemical properties. Finally, if completed by the presentation time, I will also describe a new identified chemical pathway to BsubPc from bio source. Using bio sources, every carbon atom of the BsubPc is from a renewable non-petroleum source and is inherently scalable to industrial production scale.

Co-authors/investigators will be identified during this presentation.

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Islyaikin M.K.

VOYAGE FROM HEMIPORPHYRAZINE TO HEMIHEXAPORPHYRAZINE. SYNTHESIS, PROPERTIES, APPLICATION

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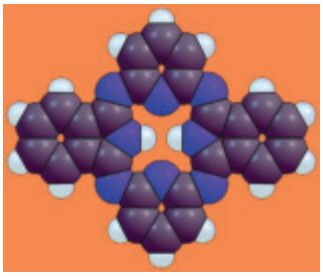
Macroheterocyclic compounds (Mcs) of A_mB_n types, where A – subunits derived from aromatic diamines, B – pyrrole containing fragments and m and n are within 1–4, attract much attention last decade [1–3]. The various approaches to the synthesis elaborated for now allow to drastically modify macroheterocyclic framework by a task-oriented way, introduce the substituents on periphery of polycyclic molecules and embed the atoms of metals in coordination cavities what result in a large number of molecular architectures.



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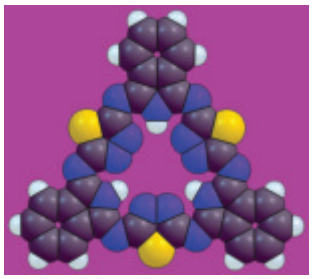

2

In this talk main accent was made on hemiporphyrazines (ABAB, **1**) and hemihexaphyrazines (ABABAB, **2**). New aspects of their synthesis, structure particularities, study practically useful properties as well as various aspects of their applications are under consideration [4, 5].

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Grin M.A.

MODIFIED NATURAL CHLORINS FOR DIRECTED TRANSPORT IN TUMOR OF DIFFERENT GENESIS

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Molecular therapy is one of the new directions of drug treatment (pharmacotherapy) of cancer. As a type of molecular medicine, targeted therapy blocks the growth of cancer cells by interfering with the mechanism of action of specific key molecules required for cancerogenesis and tumor growth, rather than simply preventing the reproduction of all rapidly proliferating cells.

Currently, there are two approaches to increasing the tropicity of chemotherapy drugs and, in particular, photosensitizers (FS). Creating conjugates of FS with vector molecules allows active targeting of tumor cells. Another approach to increasing the selectivity of accumulation is the immobilization of active pharmaceutical substances on nanoparticles of various nature, which provides passive targeting, including the extravasation of loaded nanoparticles from defective tumor vessels and their retention in the interstitium due to an impaired lymphatic drainage system of the tumor (EPR effect).

The purpose of this work was to direct the functionalization of natural chlorins and bacteriochlorins by attaching biologically active molecules to the periphery of the macrocycle, or immobilizing the pigment on iron oxide nanoparticles to create photodynamic agents of targeted action.

To achieve this goal, the regioselective introduction of the PSMA ligand into the 3-, 13-, 15-, 17- positions of the macrocycle of natural chlorins and bacteriopurpurinimide for targeted photodynamic therapy of prostate cancer was carried out. Aminoamides of chlorin e6 containing spacers of different lengths, with folic acid for active targeting of cells with overexpression of folate receptors were obtained. Noncovalent complexes based on bacteriopurpurinimide derivatives with magnetite nanoparticles are proposed for combined therapy and diagnostic methods in oncology.

The study of photoinduced cytotoxicity on HeLa cells with overexpression of folate receptors showed that the length of the spacer between the pharmacophore and the folic acid molecule is essential for the efficiency of internalization into tumor cells. It was found that a compound containing the spacer of eight methylene units between the macrocycle and the folic acid residue has the highest activity.

A study of the specific activity of conjugates based on bacteriochlorophyll a and chlorophyll a derivatives with a ligand for PSMA in different positions of the macrocycle on cell lines with overexpression of PSMA and in the absence of antigen showed that the introduction of PSMA ligand into different positions of the macrocycle significantly affects the efficiency of photosensitizers. The most active was the 13-substituted chlorin e_6.

It has been shown that the developed method of obtaining iron oxide nanoparticles loaded with bacteriopurpurinimide allows the photodynamic activity of the pigment to be maintained, combining it with the possibilities of diagnosing oncological diseases using magnetic resonance imaging (MRI).

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REGIOISOMERIC EFFECT ON PORPHYRINOIDS: SYNTHETIC MODEL, PHOTOPHYSICAL PROPERTY AND APPLICATION

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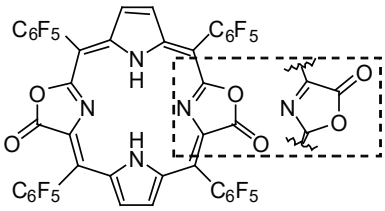

The photophysical properties of naturally occurring chlorophylls depend on the regioisomeric nature of the β-pyrrolic substituents.[1] Such systems are the "gold standard" by which such effects are judged. However, simple extrapolations from what have been learned with chlorophylls may not be appropriate for other partially reduced porphyrinoids. Here we report the synthesis of a series of cis/trans-porphodilactones[2] (cis/trans-**1**) and related derivatives (*cis/trans* **2–5**) designed to probe the effect of regioisomeric substitution in porphyrinoids that incorporate degrees of unsaturation through the β-pyrrolic periphery that exceed those of chlorophyll.[3] Being able to fine-tune the electronic features through control of regioisomeric effects may allow for the production of chromophores optimized for a certain applications or better control over NIR lanthanide sensitization[4] and triplet annihilation-based upconversion[5] as well as the related biological studies.

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COMPARISON OF PHOTODYNAMIC ACTIVITIES OF MOLECULAR OXYGEN AND PORPHYRINS

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An idea that low level laser therapy results from direct excitation of oxygen molecules by laser radiation attracts growing attention of medical community as an alternative of classic PDT with porphyrin photosensitizers. This paper is devoted to testing of this idea based on experimental analysis of the rates of singlet oxygen generation upon photosensitized and direct laser excitation of O_2 dissolved in aerated organic solvents and water. As a result, the main absorption maxima of monomeric oxygen molecules were found at 1273 and 765 nm. Absorbance (A) and molar absorption coefficients (ε) corresponding to these maxima and relative intensities of vibrational absorption bands were estimated. The ε_{1273} was shown to vary in the range $(1.5–5)\times10^{-3}$ $M^{-1}cm^{-1}$ having minimal value in water. The ε_{765} varies within $(0.5–1.1)\times10^{-3}$ in solvents lacking heavy atoms, having the maximal value in water. As a result, the ratios $\varepsilon_{1273}/\varepsilon_{765}$ changed from (4–10)/1 in organic solvents and to 1.5/1 in water. This suggests that the use the 765 nm lasers for oxygen excitation in aqueous and biological systems is more rational than application of the 1273 nm laser emission, because having similar efficiency dark red radiation corresponds to the most transparent spectral region of biological tissues and causes minimal heating of water. Under laser radiation at 630 nm ($\leq$ 500 mW/cm^2) corresponding to the absorption maximum of oxygen dimols no reliable singlet oxygen generation was observed in aerated solvents. This fact suggests that biological activity of the red light is probably not connected with direct oxygen excitation and might be due to metal-free porphyrins, which are always present in living cells in nanomolar concentrations. Validity of this proposal is analyzed based on photosensitizing activity of porphyrins and its dependence on concentration and structure of porphyrins, excitation wavelengths and nature of environment. More detailed information can be found in refs. [1–3].

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MOLECULAR STRUCTURE, CONFORMATION AND ACID-BASE PROPERTIES OF THE FREE BASE CORROLES

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The corroles constitute the group of contracted tetrapyrrolic compounds lacking one *meso*-carbon atom in which two adjacent rings (pyrrole and pyrrolenine) are bound directly through a C_a-C_a bond. To provide the aromatic stabilization of tetrapyrrolic macrocycle upon its contraction the Hückel ($4n + 2$) rule for the number of π-electrons must be fulfilled. This is maintained by the increase in the number of pyrrole rings at the expense of a pyrrolenine. Thus, the contracted corrole macrocycle consists of three pyrrole and one pyrrolenine ring rather than two pyrrole and two pyrrolenine rings in the free base porphyrin molecules. Reduction of the core size due to the macrocycle contraction and the increase in the pyrrole proton number (there are three protons in the core now) are two intrinsic features which ultimately promote nonplanar macrocycle distortions in free base corroles. As a result, the corrole macrocycle achieves a nonplanar conformation with pyrrole rings tilted out of the macrocycle mean plane, even if sterical strains from peripheral substituents are absent. It is worth to note that reducing the distance between the adjacent pyrrolic nitrogen atoms favors the formation of an intramolecular hydrogen NH…N bond, which acts as an opposing force to the forces promoting nonplanar macrocycle distortions.

Another characteristic feature of the free base corrole macrocycle is the substantial deviation of the positions of the pyrrole hydrogen atoms from the respective pyrrole planes. These displacements correspond to the pyramidalization of the pyrrole nitrogen atoms and imply that they acquire some sp^3 character. The degree of displacement has been earlier suggested to relate to the macrocycle acidity, i.e. the higher the pyramidalization, the higher the acidity of a given corrole macrocycle. The differences in pyramidalization of the pyrrole nitrogen atoms for the two tautomers of 10-(4,6-dichloropyrimidinyl)-5,15-dimesitylcorrole were used to account for the experimentally observed acidity difference between these tautomers.[1,2] Stability of the free base and de(protonated) species in solution need to be considered in the context of the molecular conformation of molecules and electronic effects of the substituents. Such an analysis will be the subject of the lecture.

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ANTITUMOR AND ANTIMICROBIAL PHOTODYNAMIC THERAPY – YESTERDAY, TODAY AND TOMORROW

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Photodynamic therapy (PDT) with the appropriate photosensitizer (PS) of the first, second or third generation is a very promising option for treating many nonmalignant and neoplastic superficial processes [1–3]. For many cases it allows to achieve the total inactivation of atypical cells or killing of multiresistant pathogens causing superinfections which become a rapidly growing and alarming problem for many countries [3]. Both the antitumor and antimicrobial effects of PDT are known to based on three non-toxic components: photosensitizer, visible light, and oxygen [1–3]. However, taken together they initiate a cascade of photochemical reactions leading to formation of highly reactive oxygen species (ROS). The antitumor action of PDT contains three inter-related mechanisms [1]: a direct cytotoxic effect on tumor cells, damage to the tumor vasculature and an inflammatory reaction of tissue leading to an extended immune response that it is very important for a long term tumor control [3]. The photodynamic inactivation of pathogen microflora exploits only the first effect. However, this easily repeatable procedure is a well-established tool for inactivating both planktonic bacteria and their biofilms, various fungi and viruses. Unfortunately, despite its potential and the growing body of knowledge on this modality, it is underutilized in the domestic clinic. Being included in the Program of state guarantees for the provision of high-tech medical care this efficient technique very slowly penetrates into everyday practice.

The goal of this report is twofold. First, it will provide comprehensive information about the history of PDT, its mechanisms and the examples of the most recent preclinical and clinical studies with photosensitizers of the first, second or third generation. Second and general, it will highlight new ways and efforts which appear to be important to tackle the current limitations of PDT and extend its efficacy to make it the first-line modality to treat cancer and multiresistant superinfections.

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CARBAPORPHYRINOIDS – A QUEST FOR MACROCYCLIC SURROUNDINGS IN ORGANOMETALLIC CHEMISTRY

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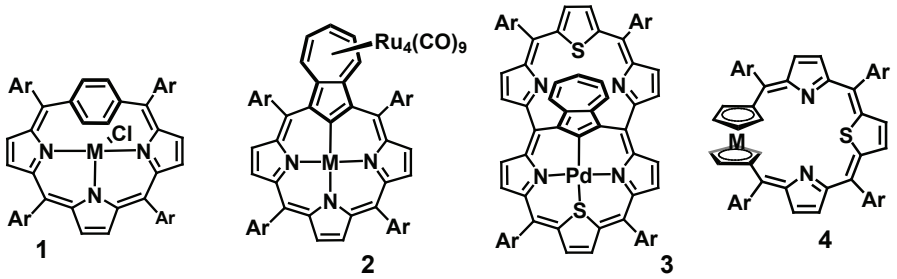
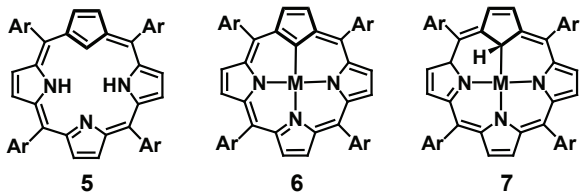
Redesign of archetypical porphyrin frame, introducing of CH unit(s) in place of one of the pyrrolic nitrogen atoms, created an original class of macrocycles - carbaporphyrinoids, which reveal fascinating properties in terms of their electronic structure, aromaticity and their potential ability to bind metal ions. Carbaporphyrinoids realize the specific concept of macrocyclic ligand construction by fusing the structural frame of porphyrin and carbon donor(s), introduced by appropriately chosen moieties, including ferrocene and ruthenocene.



The entrapment of metal ions in a coordination core of carbaporphyrinoids creates an efficient protection of the metal-carbon bond and allows to stabilize extremely rare oxidation/electronic states in organometallic environments. These macrocycles enforce the specific intramolecular reactivity, skeletal rearrangements and frequently exotic coordination architectures: **1** - **7**. For instance the azulene moiety of azuliporphyrinoids provides the suitable π-surface to bind the ruthenium cluster in a unique three-dimensional structural design of **2**. Noticeably, palladium(II) azulene-bridged A,D-dithiahexaphyrin **3** undergoes transformations into *meso*-linked carbaporphyrins. Metallocenoporphyrinoids **4** demonstrate a hitherto unknown facet of porphyrinoid aromaticity, namely the possibility of including a d-electron subunit in π-electron conjugation pathways. The contraction *p*-phenylene – embedded in *p*-benziporphyrin **1** – to cyclopentadiene, mediated by transition metal cations produced complexes of 21-carbaporphyrins **6**.



Incorporation of a cyclopentadiene moiety into the *meso*-tetraarylporphyrin framework, using 1,3-bis(arylhydroxymethyl)ferrocene as a synthon, resulted in the rational synthesis of *meso*-tetraaryl-21-carbaporphyrin **5**. The molecular design preserves all essential virtues of the original tetrapyrrolic architecture of *meso*-tetraarylporphyrin, including the perfect match between the ionic radii of inserted metal cations and the size of the macrocyclic (CNNN) core, and steric protection provided *meso*-aryl substituents as shown in **6**. The protonation of the inner core reveals an adjustable(trigonal versus tetrahedral, **6** vs. **7**) geometry.

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METAL PORPHYRIN BASED MOLECULAR MATERIALS WITH PHOTOINDUCED ELECTRON TRANSFER AND MAGNETOCALORIC ACTIVITY

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The work represents synthesis and characterization of porphyrin complexes promising in material chemistry with both coordination activity towards pyridyl-substituted fulleropyrrolidine to develop donor-acceptor systems with photoinduced electron transfer (PET) and magnetocaloric effect at the temperature close to room. The first group complexes are a porphyrin-ligated transition metal ion with axially coordinated by the pyridyl group fullero[60]/[70]pyrrolidine in which an electron donor and an electron acceptor role belongs respectively to the macrocycle and the fullerene moiety. The self-assembly in organic media (parameters and mechanism), stability, and optoelectronic properties were described [1–7] for In^{III}, Mn^{III}, Co^{II}, Mo^{V}, and Re^{V} complexes of substituted porphyrins/phthalocyanines to establish the chemical structure – functionality relation.

New paramagnets based on axially coordinated metal porphyrins magnetocaloric behavior studied in collaboration with V.V. Korolev's scientific group was observed using two strategies. Namely, a paramagnetic ion coordinated by an aromatic porphyrin/phthalocyanine macrocycle or the one with ferromagnetic coupling unit in the molecular structure was under investigation. Magnetocaloric effect in lanthanide complex comparable with the one in polycrystalline gadolinium (1.4 K at the magnetic induction 1 T) and giant magnetocaloric effect in paramagnets based on *d* metal porphyrin (2.1 K at the magnetic induction 1 T) was achieved.

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THE CONCEPT OF NANOSTRUCTURING OF MACROHETEROCYCLIC COMPOUNDS AT THE GAS–LIQUID INTERFACE

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In the talk a concept of nanostructuring of organic compounds at the gas-liquid interface, according to which the structural units of a floating layer can be as single molecules (Langmuir approach) and their nanoaggregates (the so-called M-nanoaggregates), will be presented [1–4]. The method developed for determining the quantitative parameters of the structure and properties of such layers [1], and applied to phthalocyanines and porphyrins [2] will be also presented. Using the developed approach, under conditions of confined spaces, nanostructures of a number of different kind of organic compounds were formed at air-water interface, in Langmuir-Schaefer (LS) films and in polymeric capsules [3,4].

The influence of nature of the compound and the formation conditions on the structure and properties of the ensembles has been established. Nanostructured layers of μ-nitrido dimer of iron octapropylporphyrazine (μ-[(OPTAP)Fe]$_2$N) highly sensitive to aromatics were formed. Conditions of formation of T-shaped structures of μ-[(OPTAP)Fe]$_2$N in LS-films were determined. The reactions of complexation of 5-(4′-N-*tert*-butyloxycarbonyl-D-leucylamidophenyl)-10,15,20-triphenylporphine ((D-LeuPh)TPP) with zinc and axial coordination of cobalt tetraphenylporphine with imidazole were carried out in the layers at air-water interface at the room temperature. LS-films consisting of Zn complex of (D-LeuPh)TPP and cobalt tetra-(p-methoxyphenyl)porphyrin nanostructures, absorbing in near IR (768, 856 nm and 695, 916 nm, respectively) were formed. The formation of nanostructures of chlorin e$_6$ (absorbing at 676 and 710 nm), *methylpheophorbide a* (absorbing at 426 and 697 nm), and tetraphenylporphine (transparent for visible light and week absorbing at 720 nm) is established. By a non-covalent self-assembly at the water-air interface, the first porphyrin supermolecules were obtained. They were formed from magnesium porphine (the ancestor of all porphyrins and the functional element of chlorophyll). It was shown that their photophysical properties fundamentally differ from properties of initial molecules. In particular, in contrast to the pink color of the monomer solution, solutions of supermolecules are transparent for visible light and absorb in the ultraviolet and near-infrared regions. Structural study of the films was carried out using synchrotron radiation. The formation and properties of described nanoparticles determined by strong exciton coupling in the ensembles [4].

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Mamardashvili N.Zh.[1], Koifman O.I.[1,2]

ION-DEPENDENT PROCESSES OF METALOPORPHYRINS COMPLEXATION WITH ORGANIC MOLECULES OF DIFFERENT NATURE

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Design of new materials with a predetermined architecture and functional properties is an important task of chemistry and material sciences. Selective chemical modification of porphyrins by fragments of other classes of compounds allows the synthesis of molecular systems with different nature and mutual arrangement of the reaction centers. The report will discuss the results of studies in the field of complexation of heterotopic organic ligands with porphyrins, in which the tetrapyrrole core along the periphery of the molecule is surrounded by carbazole branches of the first and second generation with different conformational mobility. The dependence of the coordination capacity of the modified porphyrins on the number and location of carbazole fragments, as well as the presence of alkali metal cations (Li^+, Na^+ and K^+) in the reaction system will be analyzed. The dependence of the porphyrin based receptor ability on the number and conformational mobility of the peripheral tetrapyrrole macrocycle branching is shown. The possibility of formation of intramolecular cavities and channels of various shapes in such systems, in the case of a good match of the geometrical parameters of the reagents, significantly increases the efficiency of substrate-receptor interactions occurring with their participation. Created polyfunctional porphyrin-containing systems can be used to construct supramolecular assemblies, including polymeric, of various functional purposes.

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DESIGN, SYNTHESIS AND PROPERTIES OF BIOMOLECULAR COMPLEXES OF NATURAL CHLOROPHYLL DERIVATIVES WITH IMAGING MOIETIES FOR DIAGNOSTICS AND PDT OF CANCER

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Successful development of Photodynamic Therapy (PDT) of cancer is closely related to the production of novel efficient preparations – theranostic agents – which, along with, reliable diagnostics of malignant tumors enable their further elimination to be fulfilled. One of the promising ways to design the photosensitizers (PS) of this kind is preparation of natural chlorin and bacteriochlorin conjugates with additional external moieties possessing an intense fluorescence as well as chelating patterns which cant incorporate metals with big ionic radius. making their use possible in MRI, PET and other physical methods of tumor detecting and imaging, as well as applying other destructive methods, along with PDT, by means of chemo- and radiotherapy. The possibility to introduce various types of metals into the patterns being produced provides wide prospects to apply the theranostic agents of this type in oncology.

Pheophorbide *a*, bacteriopheophorbide *a*, N-aminopurpurinimide and N-aminobacteriopurpurinimide have been used as a basis to produce the complexes being reported. Tetrazo- containing macrocycles of the cyclen type and open pyridine chelating structures have been used to incorporate metals with big ionic radius (Gd, Ga, Yb).

Perspective production ways of similar conjugates, their chelating characteristics and physicochemical properties have been examined.

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Semeikin A.S.

THE SYNTHESIS OF *MESO*-PHENYLPORPHYRINS AND MODIFICATION IN THEIR PHENYL RINGS

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The derivatives of metal complexes of porphyrins and their analogs are natural objects which provide the bonding of solar energy in plants, transfer the oxygen in the animal organism, and carry out catalysis of redox processes. The studying of the biological role of porphyrins and their practice application as catalysts and medicine needs available sources of porphyrins. From this point of view, synthetic porphyrins, which are obtained with high yields and to which *meso*-phenylporphyrins belong, have a great interest.

The methods of the synthesis of *meso*-phenylporphyrins obtained by the condensation of α-non-substituted pyrroles, dipyrrolylmethanes or biladienes with aldehydes are regarded in the report.

The general methods of modification of substitutes in phenyl rings of *meso*-phenylporphyrins with the aim of the introducing required groups and giving them demanded physical-chemical properties, are shown.

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SURFACE CHEMISTRY, OPTICAL PROPERTIES AND EXCITED STATE RELAXATION IN NANOSTRUCTURES BASED ON SEMICONDUCTOR QUANTUM DOTS AND PORPHYRINS

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At the moment, a prominent class of organic-inorganic nanostructures is related to colloidal semiconductor quantum dots (QDs) in combination with organic dye molecules, which are perspective for applications in sensorics, photovoltaics and biomedicine. The main obstacle on the path to develop efficient QD-based nanomaterials is our limited understanding of QD surfaces, their interaction with attached functionalized organic molecules, and their impact on QD excited states relaxation, including charge/energy transfer processes.

Here, we discuss surface properties, structural dynamics and excitation energy relaxation in QD-Dye nanocomposites of two types: i) nanostructures based on TOPO-capped CdSe/ZnS QDs surfacely attached by non-covalent binding interactions with tetra-*meta*-pyridyl-porphyrin in solutions at 77–295 K, and ii) nanoassemblies including Ag-In-S/ZnS core/shell QDs (AIS/ZnS) stabilized by thioglycolic acid (TGA) as native ligand, and coupled with 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyn tetraiodide (H_2P) molecules via Coulomb attraction between negatively charged terminal groups of TGA and positively charged sites of H_2P molecules.

For nanostructures "CdSe/ZnS QDs + H_2P", the attachment of H_2P molecules occurs preferentially to those QDs with low ligand coverage, and nanoastructures formation deviates strongly from Poisson statistics. The efficiency of the energy transfer QD→Porphyrin is Φ_{FRET}~10 %, while a strong Non-FRET quenching is caused by the formation of specific new Cd^{2+} trap states following depletion of several ligands by the spacious dye molecules and results in new and enhanced long-lived weakly emitted intra-gap states. In addition, in a temperature range 220–230 K for TOPO ligands the low-temperature „phase transition" of capping layer takes place manifesting itself in related changes of QD absorption and emission which become considerably pronounced upon attachment of only one H_2P molecule to the QD surface.

In the case of nanostructures including AIS/ZnS QDs (stabilized by TGA) and electrostatically coupled H_2P molecules, QD photoluminescence is completely quenched by one attached porphyrin molecule, while porphyrin fluorescence remains unquenched. Surprisingly, the interaction of AIS/ZnS QDs and H_2P molecules is followed by an additional chemical reaction between the porphyrin and Zn^{2+} ions in the vicinity of QD-TGA surface thus leading to the formation of Zn-complexes of 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyrin. The formation ZnP molecules in these nanoassemblies is confirmed by UV-vis absorption and Raman spectroscopies.

Concluding, here we show that surface-mediated processes dictate the probability of several of the most interesting and potentially useful photophysical and chemical phenomena observed not only for colloidal QDs but for porphyrin molecules also.

Financial support from BSPSR Program "Convergence 2020-3.03" (Belarus), BRFFR grant № Ф18Р-314 (Belarus-Russia) and Volkswagen project № I/79 435 (Germany) is gratefully acknowledged.

Stuzhin P.A.

PHTHALOCYANINE ANALOGUES – HETEROATOM SUBSTITUTION AND CONTRACTION OF THE MACROCYCLE

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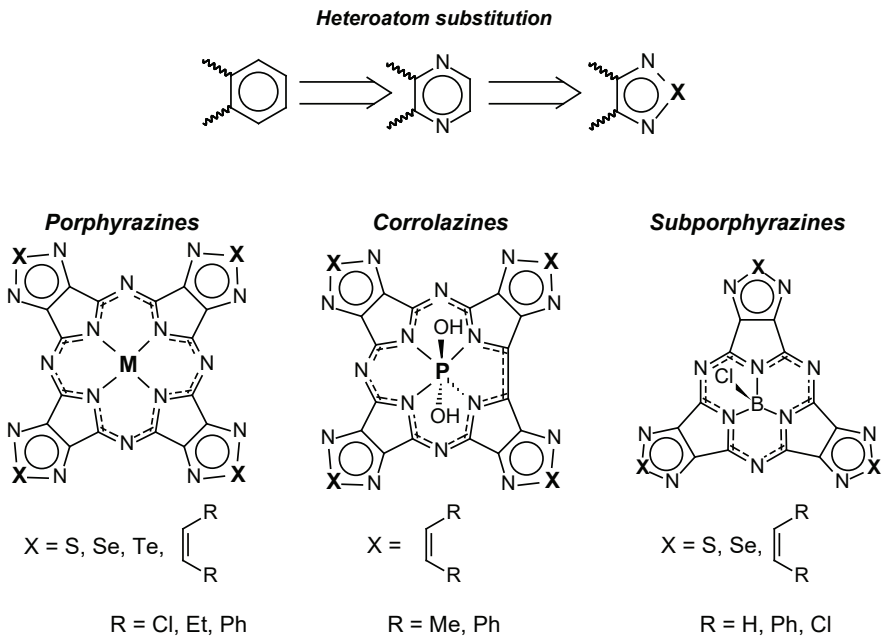
Properties of phthalocyanines and their metal complexes are usually tuned in accordance with the demands of their application in various fields by introduction of the substituents in the peripheral and/or non-peripheral positions of benzene rings. The direct heteroatom substitution in benzene rings and contraction of the macrocyclic core by exclusion of one meso-nitrogen atom or isoindole unit is a more powerful tool for modification of the electronic properties of phthalocyanines. This approach is especially useful for design of phthalocyanine analogues possessing enhanced electron-acceptor properties. The substitution of the CH groups in non-peripheral positions by electronegative nitrogen atoms followed by consecutive substitution of the peripheral CHCH fragments by a chalcogen atom (S, Se, Te) leads to especially electron-deficient phthalocyanine analogues - porphyrazines, corrolazines and subporphyrazines with fused pyrazine or 1,2,5-chalcogendiazole ring. Advances in the synthesis of these compounds, investigation of their geometrical and electronic structure will be presented and discussed.



Financial support from Russian Science Foundation (grant 17-13-01522) is gratefully acknowledged.

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NEW APPLICATION AREAS OF PHTHALOCYANINE COMPLEXES AND THEIR ANALOGUES

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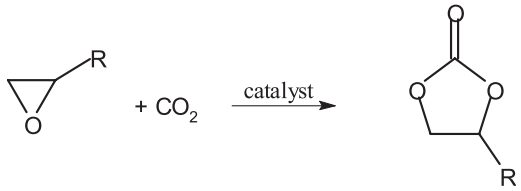
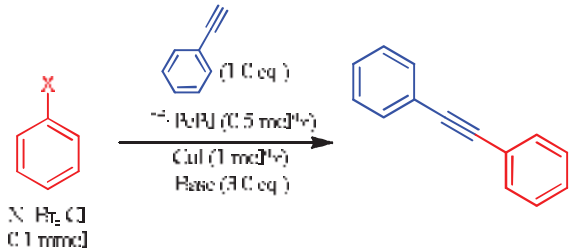
Due to its unique electronic structure phthalocyanine complexes and their analogues are used in many areas, for example, in semiconductor, electrochromic displays, non-linear optical devices, solar cells, photodynamic therapy (PDT) as photosensitizers, etc [1, 2]. Recently, they are widely used as catalysts for both homogeneous and heterogeneous processes.

The outstanding results were obtained at study of reactions of CO_2 with propylene oxide.



There were detected that reactions of CO_2 with propylene oxide results in quantitative yields of propylene carbonate due to use of phthalocyanines. These results allowed to develop and patent continuous wasteless ecologically safe technology of propylencarbonate reception.

Octaalkoxy- and octaphenoxysubstituted palladium phthalocyanines were used as a new family members of cross-coupling catalysts in the Sonogashira reaction. For the first time it was shown that terminalalkynes reacted mildly with p-substituted aryl bromides in mild conditions to give the corresponding phenylacetylenes [3].



Novel hexadecachloro-substituted phthalocyanine complexes of Ln were synthesised and comparison of its linear and nonlinear optical properties was carried out [4]. A bioelectronic tongue formed by an array of the SubPc based biosensors has been able to discriminate red wines according to their Total Polyphenol Index.

The work was supported by the Russian Science Foundation (Project 17-13-01197). Electrochemical investigations were supported by RFBR ERA (Project 18-53-76006).

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Xu Liang, Yingjie Niu, Weihua Zhu

MODULATION THE ELECTROCATALYTIC BEHAVIORS BY THE SYNTHETIC PORPHYRINOID

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Water splitting is an ideal energy storage carrier for the next generation of renewable energy systems, other molecules such as CH_4, and CO can also be used for energy storage to provide clean renewable energy. HERs, oxygen reduction/evolution reactions (ORRs/OERs), CO_2 reduction reactions (CO_2RRs) and even N_2 reductions are relevant in this context. These procedures can be readily achieved by photocatalysis, chemical catalysis and electrochemical catalysis. The low cost, environmentally friendly properties of electrocatalysis has received most attention in this context. Recently, molecular electrochemical catalysis has been demonstrated to have various advantages, including high efficiency or tuneable catalytic efficiency, and provides stable molecular catalysts. Thus, the catalytic reactions can be easily modulated by changing the molecular electronic structures by introducing various substituents and metal centres. In this presentation, the modulation of electrochemical reactions through molecular electrocatalysis by singly or doubly electrochemically reduced metallo-porphyrins, metallo-phthalocyanines and metallo-corroles, and the catalytic efficiency can be modulated by the symmetric and asymmetric introduction of various substituents. The key advantage of using macrocyclic ligands are that dianionic and/or trianionic ligands, which stabilizes the various oxidation states of first-row transition metals, thus enhancing their utility for electrocatalytic reactions.

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Zimcik P., Demuth J., Novakova V.

J-DIMERS OF AMINO-AZAPHTHALOCYANINES: CHARACTERIZATION AND IMPLICATION FOR THEIR USE IN OLIGONUCLEOTIDE LABELS

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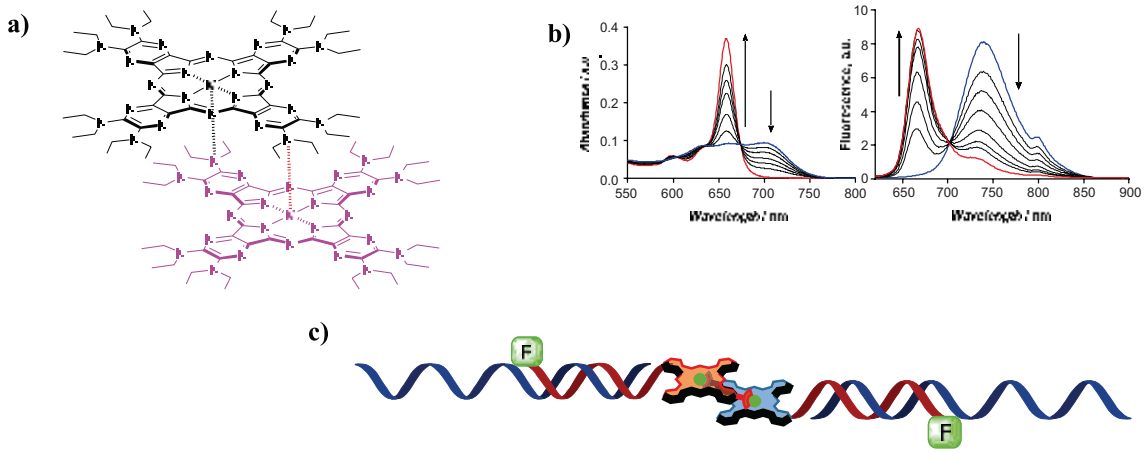
Magnesium and zinc (di)alkylamino substituted azaphthalocyanines (AzaPcs) of tetrapyrazinoporphyrazine type are able to form interesting slipped J-dimers in non-coordinating solvents.[1] The J-dimers are formed by complexation of the peripheral amino substituents with the central metal of another molecule (Figure a). The dimers are highly stable (K_a over 10^9 M^{-1}) and are well detected in solution by strongly shifted both absorption and fluorescence emission spectra (Figure b). Addition of coordinating solvent (e.g. pyridine) breaks down the dimers and separates the molecules in solution.

The (di)alkylamino AzaPcs, irrespective of central metal, are only weakly fluorescent due to extensive intramolecular charge transfer that deactivates the excites states. For this reason, they are advantageously investigated as dark quenchers in DNA hybridization probes for monitoring rt-PCR.[2] Recent results indicated that even upon binding to oligodeoxynucleotide probe, the AzaPcs form strong J-dimers in buffer and that these dimers are not separated even after hybridization with complementary antisense oligodeoxynucleotide (Figure c). The separation may be again achieved only by coordinating solvents. The consequences of the J-dimer formation for rt-PCR or potential development of biomolecular logic gates based on two different principles (hydridization and complexation) will be discussed.



Acknowledgement. *The work was supported by Czech Science Foundation (17-19094S).*

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NOVEL USE OF CHLOROFILLIPT, CHLOROPHYLONG AND FOOD ADDITIVE E 141 AS A PHOTOACTIVE AGENT

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The long-established drug "Chlorophyllipt" is used in the treatment of infectious diseases [1]. The objective of our study was to study the biological and photophysical properties of the drug "Chlorophyllipt" as a new promising agent for photodynamic therapy of tumors. Comparison preparations were selected "Chlorophyllong" and food supplement E 141, which are also derived from chlorophylls and have similar properties. All drugs showed dark toxicity on the breast carcinoma cells MCF-7 culture at 48 h incubation with cells and the maximum concentration of the active substance 4.82–$6.87 \cdot 10^{-4}$ M.

To solubilize the oil preparation "Chlorophyllipt", oil-in-water microemulsions were prepared with an oil: phosphatidylcholine molar ratio of 1:1; 1:3 and 1:7, which were characterized spectrophotometrically and using dynamic and electrophoretic light scattering methods. The most stable was an emulsion with a molar ratio of 1:1 (Z-potential = –59.8 ± 0.2); average particle size was ~ 500 nm.

The photodynamic activity of the preparations was assessed by the change in the absorption spectra of hemoglobin during deoxygenation [2], thus, the rate of deoxygenation of hemoglobin is directly proportional to the rate of generation of singlet oxygen. To record the absorption and fluorescence spectra of the samples under study, a LESA-01-BIOSPEC fiber-optic spectrometer was used. To excite the PS, a semiconductor laser source with a wavelength of 660 nm was used, the power density in the measurements was 200 mW / cm^2. Solutions of the studied drugs were prepared in the blood plasma of cattle, and then erythrocyte mass was added, the percentage of plasma in the test sample was 60 %, erythrocyte mass – 40 %. Irradiation was carried out for three minutes. It was shown that an alcoholic solution of chlorophyll ("Chlorophyllong") has the highest photodynamic activity among the studied samples. At the same concentration (4.82 μM), the rate of hemoglobin deoxygenation in the study of the "Chlorophyllong" preparation was 0.011 [1/s], "Chlorophyllipt" – 0.005 [1/s] and for E 141 0.0005 [1/s], respectively.

This work was financially supported by the Program of Fundamental Scientific Studies of the State Academies of Sciences for 2013–2020.

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Bazanov M.I., Kokorin M.S., Berezina N.M., Semeikin A.S.

ELECTROCHEMICAL PROPERTIES OF NITRO-DERIVATIVES OF PORPHYRIN IN ALKALINE SOLUTION

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Currently, the study of physico-chemical and catalytic properties of macroheterocyclic compounds of porphyrin series is of great scientific and practical interest. Among them, a special place can take nitrosubstituted porphyrins. A distinctive feature of the compounds studied is that of the nitro group are located in the peripheral substituents, and directly in the porphyrin macrocycle.

The regions of redox potentials associated with the electroreduction of the π-electron system of the macrocycle and the nitro groups are determined for nitrosubstituted porphyrins in the argon atmosphere.

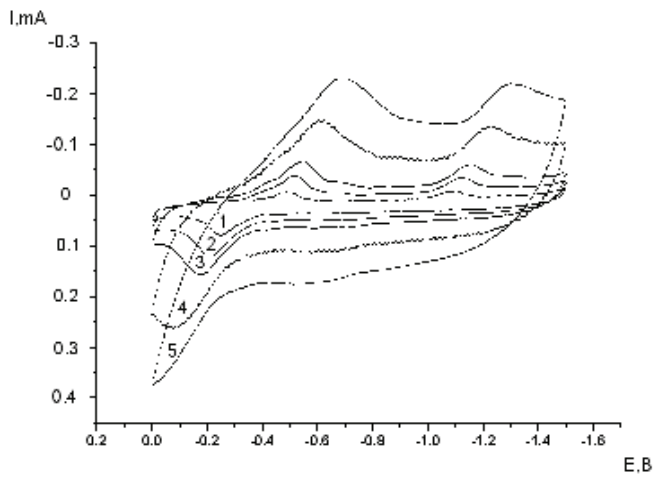

Fig. *The influence of scanning rate on the I,E-curves with the introduction of argon electrolyte for electrode with 10,15(20)-dinitro-5-phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin. V, mV/s: 1 – 5; 2 – 10; 3 – 20; 4 – 50; 5 – 100*

As can be seen from *I,E*-curves, a number of cathode and anode maxima are observed, the position of which depends on the scanning speed (V). The position of the cathode maxima is shifted to the region of negative potential values with an increase in V, and the anode ones to the region of positive ones. The value of the redox potential (the sum of the cathodic and anodic peaks) are slightly. Additional introduction of O_2 into the electrolyte leads to an additional maximum in the potential region (-0.1÷-0.4 V), which is associated with the process of electroreduction of molecular oxygen. Subsequent processing of the experimental data allowed us to calculate the effective number of electrons for this processes of nitro derivatives of porphyrins and molecular oxygen. The authors suggest the relationship between the chemical structure of the studied compounds and their electrocatalytic activity.

Work is performed in Research Institutes of MHCC.

Berezin M.B., Antina E.V.

FLUOROPHORES BASED ON DIPYRROLYLMETENES COORDINATION COMPOUNDS: SYNTHESIS AND PROPERTIES

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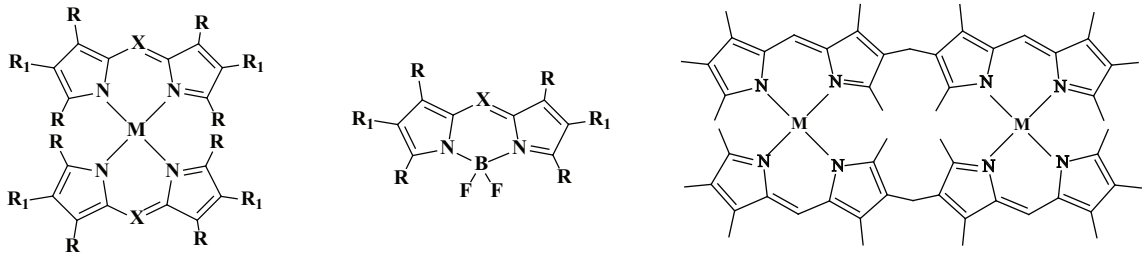
One of the priorities of modern chemistry is to obtain new materials, in particular, luminophore, suitable for use in industry, laser technology, biochemistry, molecular biology. Among the known variety of phosphors, dyes based on coordination compounds of a number of transition metals and boron with dipyrromethenes are of particular interest. The advantages of these phosphors are the high sensitivity of the quantum yield of fluorescence, absorption and emission wavelengths to structural-solvation effects, which allows their characteristics to be used for specific practical tasks.

Solutions of *d*-metals dipyrromethenates [ML_2] intensively absorb light in the visible spectral region, some of them, in particular Zn-complexes, are fluorophores. This contributed to the search for new phosphors based on coordination compounds of dipyrromethenes and their analogues, bis (dipyrrometenes), and the study of their properties.



X=CH, R=CH_3, R_1=H, Me, Et, Pr, Bu, Hc, Hp, Bz;
X=CH, R=H, R_1=Ph;
X=N, R=Ph, R_1=H, Cl, Br, I

A block of coordination compounds of dipyrromethenates and bis (dipyrromethenates) with *d*-metals was synthesized, and their key physicochemical properties, including spectral-luminescent characteristics, were determined. On their example, it was established that the nature and amount of substituents in pyrrole fragments and the structure of the meso-spacer of dipyrrolylmethylene ligands allow changing the position of the band maxima in the absorption and emission spectra, as well as other properties of the complexes formed by them.

The family of dyes based on coordination compounds of boron(III) with dipyrrolylmethenes is characterized by intense absorption and fluorescence in the visible and near-IR spectral regions. The high molar absorption coefficient ≈ 10^5 $M^{-1}\cdot cm^{-1}$ and the fluorescence quantum yield, which depends little on the properties of the environment, determined the use of these compounds in science, technology and medicine.

The report summarizes the results of a study of the dependence of the spectral-luminescent properties of these compounds, their resistance to thermal decomposition and photo-oxidation on the structure of the molecule.

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SOLVATION INTERACTIONS, PHOTO- AND TERMAL STABILITY OF TETRAPYRIDYLPORPHYRIN DERIVATIVES

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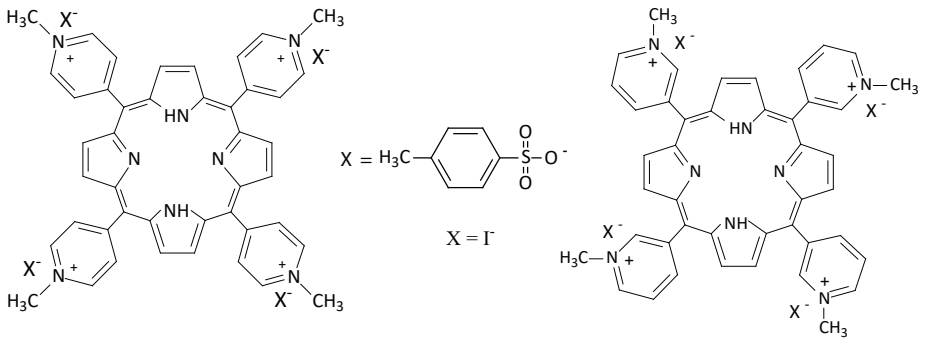
Watersoluble porphyrins, tetrapiridylporphyrins in particular, represent a special group of compounds which properties use in electrochemical, chemical and photochemical reactions, electronics, medicine are of great interest. Therefore, potentially active porphyrin compounds require comprehensive study.



The enthalpy changes of *meso*-tetrakis(1'-methyl-pyrid-4- and 3-yl)porphyrin tetratosylates dissolution in water, alcohol and phosphate buffer (pH = 6.86) were determined by the calorimetric method at 298.15 K. The effects of peripheral substituent on enthalpy of solvation have been studied by calorimetry and UV-visible spectroscopy. Porphyrin ligand is a strong electrolyte with an extreme dissociation degree, determined only by electrostatic interaction of four ions and large porphyrin cation [1]. The $\Delta_{sol.}H^m$ of tetrapyridylporphins was determined by the nature of the anionic component of the molecule in water and alcohol. Tthe porphyrin-tosylates were solvated several times better than iodide analogs. The isomerism of functional substituents which affects the strength of the molecular crystal lattice of porphyrin has a significant effect on the thermochemical characteristics of dissolution.

The stability to photooxidative destruction of porphyrinic salt derivatives has been also measured in aqueous solutions. The results indicated that *N*-methyl-pyridyl porphyrins were stable and slowly degrade under the influence of UV light in aqueous solutions. The effect of the porphyrin anion nature on the photooxidative degradation rate is likely to be apparent in the different polarizing effects of compact iodine anions and large *p*-toluenesulfonic acid anions on the porphyrin tetracation, the porphyrin stabilized by the four I^--anions being more stable than the Ts^- stabilized analog.

The nature of the process of thermo-oxidative destruction depends on the nature of porphyrin anion. The thermal stability of the studied compounds in the argon is higher in all cases than in the atmosphere of air oxygen [1]. *N*-substituted pyridylporphyrins having as molecule counterion as tosylate ions were more stable compounds in the argon and oxygen.

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Burmistrov V.A., Aleksandriiskii V.V., Novikov I.V., Koifman O.I.

CHIRAL MACROCYCLIC INDUCERS OF SPIRAL LIQUID-CRYSTALLINE PHASES

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Progress in the design and operation of spiral liquid-crystalline phases is necessary to create efficient electro-optical compositions for display devices and highly selective chiral stationary phases for chromatography. The report is devoted to solution the actual fundamental scientific problem of establishing the regularities of chiral induction in hybrid materials based on nematic liquid crystals and optically active macroheterocycles resulting in the formation of spirally twisted functionalized mesophases.

Camphor substituted hepiporphyrazines and porphyrins with optically active substituents were used as chiral dopants.

The data of polarization thermomicroscopy, phase transition temperatures, helix pitch and twisting power values are discussed. The anomalous behavior of the dielectric and rheological properties of chiral liquid crystals is established, which is associated with the competing action of the chiral dopant on the one hand and the orienting action of the magnetic field and the liquid crystal flow, on the other.

Analysis of the chiral transport from an optically active macrocycles to a nematic liquid crystals was performed by quantum chemistry and two-dimensional NMR. The most effective induction of the spiral mesophase was shown to be observed when a combination of two mechanisms of chirality transfer is performed – axial coordination and the inclusion of nematic liquid crystal.

Given study was supported by the Russian Foundation for Basic Research (Grant N 18-03-00498).

Danilova E.A.[1], **Butina Yu.V.**[2]

MACROHETEROCYCLIC COMPOUNDS ON BASED DIAMINOAZOLES CONTAINED NITROGEN AND SULFUR ATOMS. SINTHESIS. STRUCTURE. PROPERTIES.

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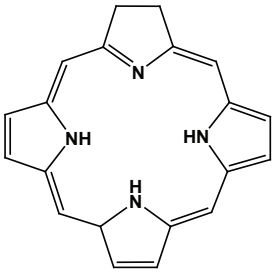
The development of methods for synthesis of hydrogenated porphyrin derivatives such us chlorins and bacteriochlorins presents particular interest to researcheres. These compounds absorb light in the long-wave-length region of the spectrum due to a change in symmetry after reduction of one or two double bonds with retention of aromaticity. Sensitizers for photodynamic therapy of oncological diseases, namely, Fotoditazin, Radahlorin, and Photolon, being water-soluble chlorin e_6 salts, are allowed for use in the Russian Federation. The complexity of the synthesis of such compounds is the process of porphyrin reduction, after which a mixture of chlorins (**1**) and bacteriochlorins (**2**) is formed.



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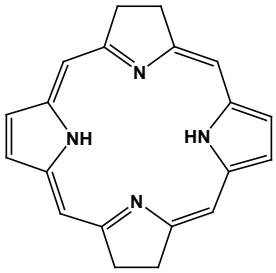

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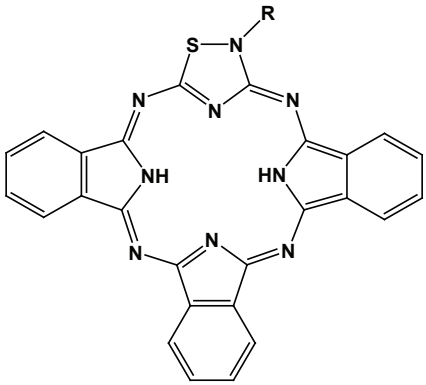

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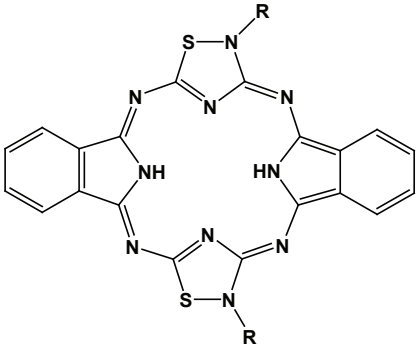

4

From this point of view, macroheterocyclic compounds of ABAB- (**3**) and ABBB-types (**4**) are interesting, where A is a fragment of 2N-substituted 5-amino-3-imino-1,2,4-thiadiazoline, B is a residue of 1,3-diiminoisoindoline. The work presents data on the methods of synthesis of such compounds, the proof of the structure, and properties.

The financial support was got from Russian Scientific Fund (agreement 14-23-00204P). The work was carried out using the resources of the Center for the collective use of scientific equipment "ISUCT".

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2-NAPHTHYL- AND 2-NAPHTHOXY-SUBSTITUTED 2,3-NAPHTHALOCYANINES: SYNTHESIS AND ELECTROCHEMICAL PROPERTIES

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Thanks to high solubility in organic solvents and presence of intensive absorption in the near IR region, 2,3-naphthalocyanines can be used as photoactive materials in printing electronics. Introduction of bulky aryl and aryloxy groups in 2,3-naphthalocyanine macrocycle leads to increase in solubility of target complexes and bathochromic shift of its absorption maxima in the near IR region comparing to alkyl-substituted analogues.

6,7-Dibromo-2,3-dicyanonaphthalene is useful initial compound for introduction of functional groups. Using Suzuki cross-coupling and nucleophilic substitution reactions novel 2-naphthyl- and 2-naphthoxy-substituted 2,3-naphthalocyanines were obtained. In order to assign the signals in NMR spectra two-dimensional NMR spectroscopy techniques were applied: ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC. Zinc and magnesium 2,3-naphthalocyaninates were obtained in a boiling isoamyl alcohol using template approach on the basis of corresponding substituted 2,3-dicyanonaphthalenes. Target complexes were identified using mass-spectrometry, IR and NMR spectroscopy. In order to assign the proton signals ^{1}H-^{1}H NOESY NMR spectra were measured.

In comparison with phenyl- and phenoxy-substituted 2,3-naphthalocyanine complexes, bathochromic shift of *Q* band up to 800 nm was observed for naphthyl- and naphthoxy-substituted compounds. The shift of *Q* band to the near IR region is observed in a row of substituents at 6,7-positions of naphthalene ring: phenoxy >2-naphthoxy > phenyl >2-naphthyl.

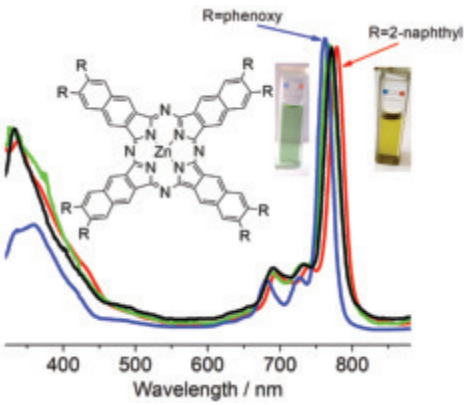

Fig. *UV-Vis spectra of phenoxy- (blue line), 2-naphthoxy- (green line), phenyl- (black line) and 2-naphthyl-substituted (red line) zinc 2,3-naphthalocyaninates in THF*

Electrochemical and spectroelectrochemical properties of target naphthalocyanine complexes were investigated. Reversible and contrast change in color of naphthalocyanine solutions was detected under oxidation-reduction processes.

We thank the Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grant MK-3115.2018.3). Electrochemical investigations were supported by RFBR (Grant 18-53-76006 ERA).

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TETRAPYRROLE-CAPPED CLATHROCHELATES: SYNTHESIS, SPATIAL AND ELECTRONIC STRUCTURES

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Macrobicyclic cage complexes with encapsulated metal ions (clathrochelates) are representatives of a class of coordination compounds with unusual chemical, physical and spectral properties [1].

Di- and tritopic metalloporphyrinato-capped [2] as well as ditopic metallophthalocyaninato-capped [3] macrobicyclic iron (II) dioximates have been prepared using a two-step synthetic procedure *via* transmetallation reaction of their labile triethylantimony-capped precursors.

Using the same synthetic approach the polunuclear pseudomacrobicyclic tris-pyridineoximates of iron and nickel(II) based on metal(IV) phthalocyaninates [4] and porphyrinates have been obtained.

Also, we were able to elaborate a new efficient synthetic pathway to the preparation of the metallophthalocyaninato-capped polunuclear pseudomacrobicyclic iron and nickel(II) tris-pyridineoximates. This synthetic approach is based on a one-pot template condensation of 2-substituted pyridine- [5], pyrazole- and -imidazole oximes with zirconium and hafnium(IV) phthalocyaninate on the corresponding metal ion(II) as a matrix.

New polynuclear hybrid complexes were characterized by UV-Vis, MALDI-TOF MS, IR and polynuclear 1D and 2D NMR spectra as well as using single crystal X-ray diffraction. Redox properties of new hybrid compounds were studied by cyclic and differential pulse voltammetry methods.

This work was supported by the Russian Science Foundation (project 16-13-10475), the Russian Foundation for Basic Research (grants №19-03-00357 and №18-29-23007) and EU Research and Innovation Staff Exchange (RISE) (H2020-MSCA-RISE-2017, Project 778245 "CLATHROPROBES")

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THE INFLUENCE OF ALKYL SUBSTITUENTS ON THE EFFICIENCY OF PORPHYRINE DYES IN DSSC

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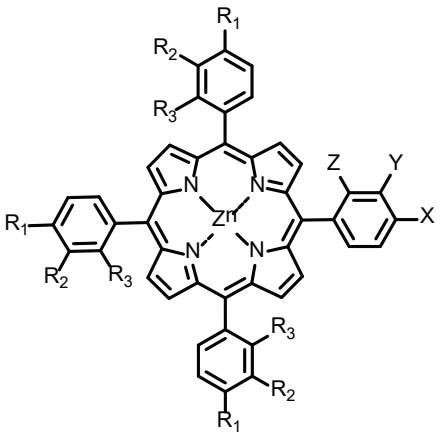
The central element of dye-sensitized solar cells (DSSC) is the dye, on which the overall efficiency of such devices largely depends. Among the dyes for DSSC, zinc complexes of porphyrins, possessing high thermal and photostability, and strong absorption in the visible region of the spectrum, are widely used. A convenient chemical modification of the dye is the introduction of alkyl groups that interfere with the aggregation of the sensitizer and minimize unwanted recombination of charges on the photo-anode surface. The literature contains a number of data on the effect of the length of alkyl substituents and their location in the molecule [1–3]. However, there remains a need for a more detailed study of the effect of such substituents for each specific dye.



$-OC_6 = -O(CH_2)_5CH_3$
$-OC_{12} = -O(CH_2)_{11}CH_3$

№	R^1	R^2	R^3	X	Y	Z
1	$-OC_6$	-H	-H	-COOH	-H	-H
2	$-OC_6$	-H	-H	$-OC_6$	-H	-H
3	$-OC_{12}$	-H	-H	-COOH	-H	-H
4	$-OC_{12}$	-H	-H	$-OC_{12}$	-H	-H
5	-H	-H	$-OC_6$	-COOH	-H	-H
6	-H	-H	$-OC_6$	-H	-H	$-OC_6$
7	$-OC_6$	$-OC_6$	-H	-COOH	-H	-H
8	$-OC_6$	$-OC_6$	-H	$-OC_6$	$-OC_6$	-H
9	$-OC_6$	-H	$-OC_6$	-COOH	-H	-H
10	$-OC_6$	-H	$-OC_6$	$-OC_6$	-H	$-OC_6$
11	$-OC_6$	-H	-H	$-NPh_2$	-H	-H
12	$-OC_{12}$	-H	-H	$-NPh_2$	-H	-H

The work is devoted to the study of the influence of the length, position, and number of alkyl chains in meso-tetraarylporphyrins with or without a carboxyl anchor group. In the second case, an axial ligand, isonicotinic acid, was used to bind the sensitizer with a photoanode. Such an approach makes it possible to use simple symmetric structures as dyes or to introduce additional donor substituents, such as triarylamines. All compounds were synthesized by the condensation of pyrrole and substituted benzaldehyde according to Lindsay method with yields of 35–40 % for symmetrical and 10–13 % for asymmetric structures. Measurement of photoelectrochemical parameters of DSSC with obtained dyes was carried out on test cells with an area of 1 cm^2.

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SUPRAMOLECULAR REGULATION OF PHOTOPHYSICAL PROPERTIES AND PHOTOCHEMICAL ACTIVITY OF TETRAPYRROLIC COMPOUNDS

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Development of the novel supramolecular approaches towards the control upon photophysical properties and photochemical / photodynamic activity of tetrapyrrolic photosensitizers will significantly expand their application area. In this report we consider the possibility to change their properties at the supramolecular level without using any covalent modification methods due to the controlled changing of their aggregation state by means of varying the local parameters of the photosensitizers in hybrid supramolecular systems [1–3].

Hybrid systems based on a number of tetrapyrrolic compounds (phthalocyanines, chlorins, porphyrins) and nanodispersed carriers selectively stabilizing certain forms of the photosensitizers (monomers, J- or H-aggregates) were synthesized using non-covalent self-assembly methods. The carriers included silica nanoparticles (n-SiO_2), montmorillonite (MM) and copolymer of lactic and glycolic acids (PLGA), as well as micellar solutions of different surfactants (SDS, CTAB, TX-100) and polyelectrolyte complexes (PECs). The systems obtained were characterized by absorption abd fluorescence spectroscopy, optical and electron microscopy and dynamic light scattering. The relationship between the local parameters of the microenvironment within hybrid supramolecular systems and the photophysical properties of tetrapyrrolic compounds was established. The above parameters were also found to determine the predominant type of their photochemical activity: photosensitization by means of the triplet-triplet energy transfer, photocatalytic activity due to the electron transfer, or fluorescence. The applicability of the supramolecular approach in the development of the effective heterogeneous photocatalysts and the design of the controlled nanocontainers for targeted drug delivery (in particular, for the novel photosensitizers for photodynamic therapy) has been shown.

This work was financially supported by the Russian Foundation for Basic Research (Project 18-03-00539).

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CRYSTAL STRUCTURES, OPTICAL AND MAGNETIC PROPERTIES OF RADICAL ANION SALTS OF PHTHALOCYANINES AND PORPHYRINS

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Phthalocyanines (MPc) and porphyrins (P) are perspective components for preparation of conducting an magnetic compounds. Such compounds are generally prepared by oxidation of MPcs. Essentially smaller attention is payed to reduced MPcs due to thier high air sensetivity.

New method for the reduction of phthalocyanines and porphyrins is developed. We obtained series of crystalline salts of phthalocyanine radical anions $\{M(Pc^{\bullet 3-})\}^{\bullet -}$, where M = Cu^{II}, Ni^{II}, H_2, Sn^{II}, Pb^{II}, $Ti^{IV}O$, $V^{IV}O$ and $Sn^{IV}Cl_2$.[1] Radical anions of MPcs have spin state of $S = 1/2$ but salts with paramagnetic M = Cu^{II}, $V^{IV}O$ metals have two $S = 1/2$ spins. Depending on the axial ligands these salts can have isolated (without axial ligands), dimeric (one axial ligand) or layered (two axial substituents) packing of the macrocycles. Magnetic properties of salts with the $[\{M^{IV}O(Pc^{\bullet 3-})\}^{\bullet -}]_2$ dimers are defined by the counter cations size (Fig. 1a) [1]. Increase in the counter cations size results in the shift of the macrocycles in the dimers and decreases magnetic coupling between macrocycles from very strong ($J/k_B = -256$ K) to nearly the absence of such coupling. Transition from one- to two-dimensional layers increases magnetic coupling between spins in the $[Sn^{IV}Cl_2(Pc^{\bullet 3-})]^{\bullet -}$ salts.

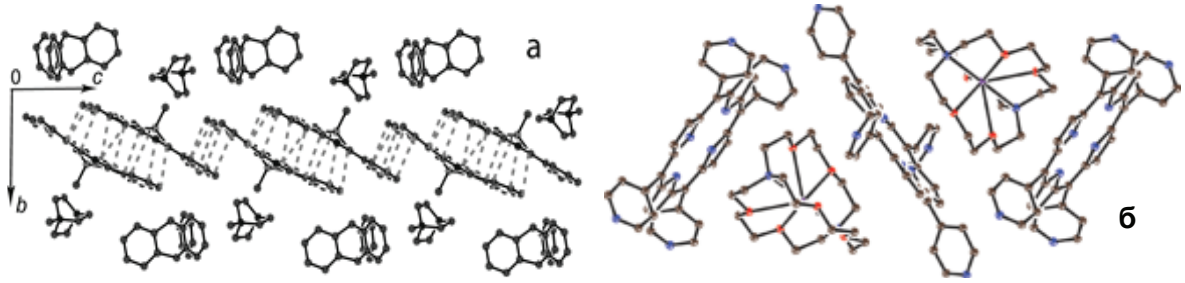

Figure 1. *(a) View along the layers composed of the $[\{Ti^{IV}O(Pc^{\bullet 3-})\}^{\bullet -}]_2$ dimers in salt $(MDABCO^+)\{Ti^{IV}O(Pc^{\bullet 3-})\}^{\bullet -}$(TPC) [1]; (b) packing of metal-free tetra(4-pyridyl)porphyrin$^{\bullet -}$ radical anions in the salt with cryptand[2.2.2](K^+) cations [2]*

Radical anion salt of metal free tetra(4-pyridyl)porphyrin with the cryptand[2.2.2](K^+) cations was obtained for the first time (Fig. 1b) [2]. Analogous salts were also obtained with the porphyrins containing phenyl and pentafluorophenyl substituents, that allow to study the effect of substituents on molecular structure, optical and magnetic properties of porphyrin radical anions.

This work is supported by Russian Science Foundation, project № 17-13-01215.

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Kudayarova T.V., Mochalina K.E., Piteva Yu.A., Danilova E.A.

SYNTHESIS OF GUANAZOLE DERIVATIVES, ALLOWING EXPANDING THE POSSIBILITY OF THEIR PRACTICAL APPLICATION

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Analysis of literature data shows that guanazole contains several reaction centers in its structure, which can be used to introduce additional groups. It open up the prospect of bioavailability, selectivity of accumulation, and effectiveness of use.

In addition, guanazole, as a ligand, binds to inorganic or organic anions, forming a variety of structure complexes, which leads to interesting properties - ligands in organometallic complexes, optical brighteners, intermediates for plasticizers, corrosion inhibitors, herbicides, catalysts.

Complex compounds of many transition elements, including gallium or manganese, can possess a wide range of useful properties. However the chemistry of complex compounds with heterocyclic products has not yet been sufficiently studied.

At present, there wasn't information in the literature about the synthesis, characterization and testing of the biological activity of guanazole complexes with gallium (III) and manganese (II).

This work discusses the approach to the synthesis and the studying of structure of possible complex compounds based on guanazole with gallium (III) and manganese (II) ions, which are formed by the interaction of the salts of the corresponding metals and guanazole in various media.

The structure of the synthesized compounds was established of mass spectrometry, electronic, vibrational, ^{1}H NMR spectroscopy, elemental and X-ray structural analysis data. The further use of the synthesized compounds in antibacterial PDT is discussed.

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INFLUENCE OF THE NATURE OF X-BRIDGED ATOM (O, N, C) ON THE PROPTIES OF M-X DIMERS WIH IRON PORPHYRAZINES

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μ-X-bridged diiron phthalocyanine complexes are effective catalysts for oxidation of organic compounds, in particular methane and benzene. It's well known, that these compounds demonstrated quite different physico-chemical and catalytic properties, in particular, spectral, stability and activities in catalysis. For understanding of these differences, we investigated of all compounds using DFT calculations and modern instrumental methods. Figure 1 demonstrated how nature of bridged atom influence on their structures.

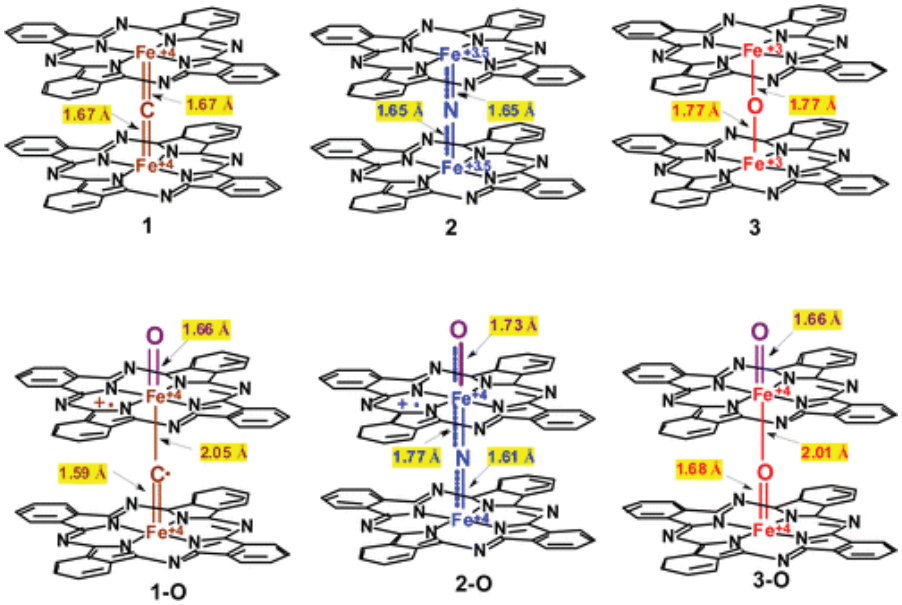

Figure 1. *Schematic representation of the DFT structures of the complexes 1–3and their hypothethical oxo species 1-O–3-O with indication of the most importance bond lengths. The structural features of 1–3 determined by EXAFS measurements and DFT calculations are identical [1].*

The μ-bridged diiron phthalocyanine complexes [PcFeXFePc] (X = C, N, O) was studied by core hole spectroscopies at the Fe K edge, including EXAFS, XES, and resonant XANES. Spectroscopy-calibrated DFT calculations provide a coherent description of the molecular geometry and electronic structure. Theory calculations extrapolated to the high-valent putative oxo complexes of three diiron species allow explaining of the outstanding catalytic activity of the μ-nitrido complex as compared to its μ-oxo and μ-carbido counterparts.

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PECULIARITIES OF PROTONATION AND SELF-ASSEMBLY OF METHYLATED N-CONFUSED TETRASULFOPHENYLPORPHYRIN

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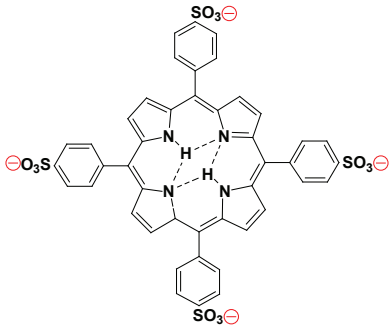
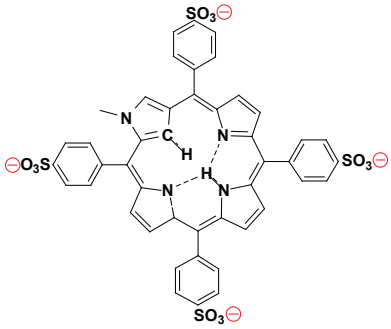
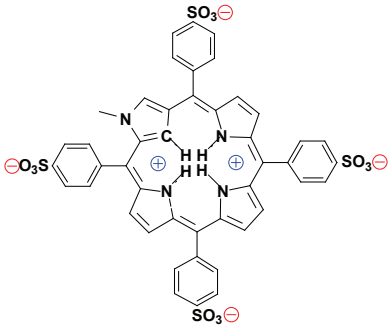
Efficient approach to effective therapy of tumors and other diseases can prove to be self-assembly of porphyrin fragments into nanotubes. As building blocks, water-soluble derivatives of 5,10,15,20-tetraphenylporphine, are widely used, thanks to the successful combination of availability and good solubility of such compounds in water. Promising derivative of **H_2P(**$PhSO_3H)_4$ is water-soluble porphyrinoid with inverted pyrrole ring 2-N-methyl-5,10,15,20-tetrakis-(4′-sulfophenyl) -2-aza-21-carbaporphyrin **HMeIP(**$PhSO_3H)_4$.



H_2P $(PhSO_3^-)_4$



HMIP$(PhSO_3^-)_4$



H_3MIP^{2+} $(PhSO_3^-)_4$

Previously it was shown that zwitterions **H_3MeIP^{++}**$(PhSO_3^-)_4$ of such porphyrin are able to form supramolecular J-aggregates [1]. The inspired peculiarity of obtained J-aggregates is their stability in neutral aqueous solutions, whereas $TPPS_4$ J-aggregates are stable only at low pH values. Equilibria of methylated N-confused platform of 2-N-methyl-5,10,15,20-tetrakis-(4′sulforhenyl)-2-aza-21-carbaporphyrin tetraanion **HMeIP(**$PhSO_3^-)_4$ platform diprotonation by perchloric acid in water, H- and J-aggregates self-assembly were investigated using synchronous UV-Vis-fluorescence-pH titration and DFT/B3LYP/6-31++G(d,p) calculations. This new compound differs from the initial **H_2P**$(PhSO_3^-)_4$ by symmetry and platform planarity breaking, which affect on the properties. Protonated natural polysaccharide chitosan was used as inducer and chiral scaffold of CW-H- and tubular CW-J-aggregates (porphyrin nanotubes) self-assembly. Chiral H- and J-aggregates of water-soluble methylated N-confused porphyrin were obtained at the first time [2].

Work, concerning synthesis of investigated compounds and synchronous UV-Vis/Fluorescence/pH titration experiment was supported by Russian Science Foundation (Project № 18-73-00234). Work, concerning quantum chemistry calculations and CD investigations was supported by RFBR according to the research project № 18-53-00035 Bel_a.

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Lebedeva N.Sh., Yurina E.S., Gubarev Y.A.

INFLUENCE OF THE BINDING BY ALBUMIN OF MACROHETEROCYCLIC COMPOUNDS ON THE AGGREGATE STATE OF PROTEIN IN THE SOLUTION

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Scientific interest in the problems of protein aggregation is increasing every year. This is due to the practical significance of this biochemical phenomenon, which leads to the growth of various diseases (Alzheimer's disease, Parkinson's disease, Huntington's disease, prion encephalopathy, amyotrophic lateral sclerosis, cystic fibrosis). Aggregation of proteins, which are part of pharmacological drugs, is an undesirable phenomenon, which reduces the shelf life and effectiveness of the drug. On the other hand, globular protein aggregates are of particular interest for use in food products due to their properties, such as gel formation, thickening properties, stabilization of emulsions and foams, film formation, and encapsulation of various substrates.

In dilute solutions under physiological conditions, the forces of attraction arising between protein globules in the native state are not strong enough to overcome repulsive forces, and therefore the molecules exist either as separate objects or as small aggregates. To a large extent this phenomenon is facilitated by the fact that most of the residues of hydrophobic amino acids are located inside the globular proteins, while the surface of the protein globules have the same charge that prevents aggregation.

The report discusses the effect of low molecular weight compounds, including macroheterocyclic compounds, which, when bound to a protein, cause exposure of hydrophobic residues to a solution, "unfold" a protein and cause its subsequent aggregation. The effect on protein aggregation of water-soluble porphyrins, phthalocyanines, hydrophobic porphyrins and tetraanthraquinone porphyrazines, phthalocyanines is considered. It has been established that the influence of the nature of a macroheterocycle, its affinity for a protein, caused by binding to a protein, changes in the secondary structure of a protein ultimately determines not only the aggregation mechanism of protein globules, but also the size of the aggregates.

The work was supported by Russian Foundation for Basic Research, grant № 19-03-00468.

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CONJUGATES OF PORPHYRINS WICH BIOMOLECULES

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More than 300 000 publications for topic search "porphyrin" was refined in Web of Science data base from year 1950 up to date. Of these, over the past five years (2015–2019), more than 35000 publications as near 26000 articles, 1800 reviews and other documents was published. The great majority of these works are research in medical fields such as biochemistry and molecular biology, pharmacology and pharmacy, hematology, cardiology, immunology and other. The potential medical materials on the base of porphyrin-core are supramolecular systems constructed from porphyrin and fragments of biomolecules.

In this work we shown our synthetic strategies for preparation conjugates porphyrins with biomolecules such as amino acids, mono- and polysaccharides (cyclodextrines among them).

Both synthetic approaches pyrrole-aldehyde condensation and modification of active centrums on the porphyrin periphery was utilized for preparation of the porphyrin-glycosyl and porphyrin-cyclodextrin conjugates. The latter compounds are represented by 2 types of conjugates: systems of covalent and non-covalent binding

Porphyrin-amino acid conjugates were synthesized via modification procedures by 2 strategies: acylation of *meso*-aminophenylporphyrins with amino acids or its Boc-protected derivatives and acylation of amino acids with meso-carboxyphenylporphyrins.

Spectral and photo physical properties new conjugates porphyrins with biomolecules was studied and discussed.

The work was supported by State task for research of Ministry of Education and Science of Russian Federation, project № 4.1929.2017/4.6

Mamardashvili G.M.

MOLECULAR FLUORESCENT ROTORS BASED ON SN(IV)-PORPHYRINS

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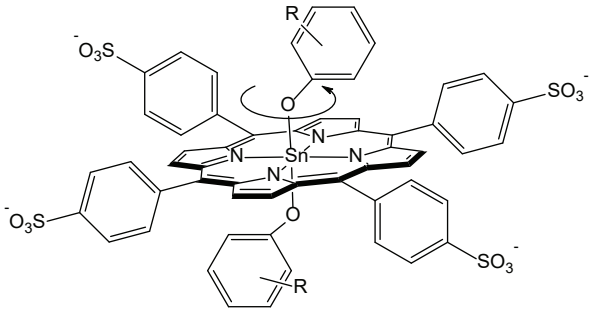
Molecular rotors are compounds whose molecules consist of two or more fragments that can rotate relative to each other. Intramolecular rotation in them is carried out under external influence (light, fluid flow, etc.). Among the variety of molecular rotors there is a group of compounds that have fluorescent properties and their quantum fluorescence yield significantly depends on the viscosity of the medium. This dependence is used to change the local viscosity in chemical and biological systems, in particular in the cells of living organisms.

The Sn-porphyrins derivatives are interesting class of molecular rotors. The introduction of axial ligands (various phenolic derivatives) into the Sn porphyrin molecule results in the quenching of porphyrin fluorescence as a result of electron phototransfer from the phenolate to the porphyrin fragment. The quenching efficiency depends on the conformational dynamics in the ligand, and as a result of this, on the viscosity of the medium.

The aim of this research is design and production of new types of fluorescent molecular rotors suitable for visualization in various biological systems and environments. Photosensitizers, the emission efficiency of which is highly dependent on viscosity, make it possible to monitor the photodynamic processes in real time, because it is known that the intracellular medium properties (including viscosity) change significantly during the photoinduced cell death. Furthermore, the information about the structure of supramolecular complexes obtained during this study will be useful for designing more effective and suitable photosensitizing agents.



$Sn(IV)P(L)_2$

Supramolecular triads consisting of hydrophilic Sn(IV)-tetra(4-sulfophenyl)-porphyrin and two axial guests such as 4-cresol, 3-hydroxypyridine, propylphenol, antioxidants (methoxydol and ionol), tyrosine, and 2-(2-hydroxyphenyl)benzoxazole were synthesized. The structures of synthesized complexes were identified by experimental spectroscopic and quantum-chemical simulation methods, and their fluorescent properties were studied in various viscosity media (mixed phosphate buffer-glycerin solvents of different composition). The effect of axial ligand structure on the fluorescent properties of these triads (due to the hydrogen bonding or π-π stacking between the components of «host-guest» systems) is discussed. The potential use of synthesized complexes as environmental probes of local viscosity is proposed.

This research was funded by the Russian Foundation for Basic Research (project № 18-03-00048-a).

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INTRAMOLECULAR AND INTERMOLECULAR INTERACTION EFFECTS IN THE CHEMISTRY OF DIPYRRINS WITH P-ELEMENTS

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The field of molecular sensory can be attributed to the currently developing branches of chemical science. Among all sensors that differ in the nature of the analytical signal, the class of fluorescent sensors is distinguished as the most promising in terms of the capabilities and mechanisms for obtaining a detectable signal, sensitivity and selectivity of sensors. Compared with classical physical methods of analysis, these fluorescent molecular sensors have a number of indisputable advantages: high accuracy, selectivity, high speed of analysis, the ability to perform measurements *in vivo*, without compromising the integrity and viability of samples. Among all the fluorescent sensors, fluorescent dyes based on dipyrrins are separately distinguished. This class of compounds has the necessary combination of physicochemical properties, namely, high values of quantum yields, high photostability, narrow absorption and fluorescence spectra peaks, low toxicity and ease of modification of dipyrrin core, causing wide possibilities for practical use of this group of compounds. It is worth highlighting the simplicity and possibilities of synthetic and postsynthetic modification of the dipyrrin core, which provide fine tuning of the compounds to solve specific applied problems as laser dyes, singlet oxygen photosensitizers, components of photovoltaic systems, fluorescent molecular sensors and markers. A decisive factor in the practical applicability of compounds will be the possibility of implementing various mechanisms of the spectral response to changes in the molecular environment parameters of compounds. In particular, the compounds considered in the report implement the mechanisms of intramolecular energy transfer, rotation of substituents relatively to each other, aggregation, and Förster resonance energy transfer. The spectral-luminescent characteristics of a number of dipyrrin coordination compounds obtained under conditions of varying the nature of the solvate environment, temperature, and viscosity of the system would be discussed. Borfluoride and oxophosphoryl complexes of dipyrrins are shown to be fluorescent molecular rotors that are not inferior to the best commercial samples in efficiency, exhibit a spectral response to a change in the polarity of the environment, and their equilibrium monomer-aggregates shift.

The reported study was funded by the grant from the President of the Russian Federation for state support of scientific research of young Russian scientists MK-1098.2019; RFBR, projects No. 18-43-370035 and 18-33-20218.

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STUDY OF THE PHOTODYNAMIC PROPERTIES OF COMPOUNDS CREATED ON THE BASIS OF PORPHIRASINE FOR THE DIAGNOSTICS AND THERAPY OF ONCOLOGICAL DISEASES

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Photodynamic therapy (PDT) of malignant neoplasms is a modern, non-invasive therapeutic method used to destroy tumor cells and tissues. Creating new promising photosensitizers (PS) and studying their photodynamic properties is an important problem. In this regard, the aim of the work was to study the photophysical and photochemical properties of new compounds from the class of 1,4-diazepinoporphyrazines as potential PS.

In vitro studies on mammalian cell culture and mouse brain homogenates were performed using an AL-HT-Elomed laser facility. The duration of irradiation is 30 minutes, at a wavelength of 670 nm and a power of 1.5 watts.

The photodynamic effect of aqueous solutions of 1,4-diazepinoporphyrazines was assessed by cytotoxic effects on cell culture of human cervical adenocarcinoma M-HeLa cells using the MTT test, as well as an increase of the intracellular content of reactive oxygen species and the ability to photoinduce lipid peroxidation (LPO) according to TBA-test.

As a result of the work, it was established that the studied diazepinoporphyrazines were able to intensify the processes of lipid peroxidation and also revealed the dose-dependent manner of the cytotoxic effect of the studied compounds when irradiated with visible light at the maximum absorption. The absence of a cytotoxic effect of the diazopinoporphyrazines in the studied concentrations without photoirradiation was shown. It has been established that the cytotoxic effect of drugs is accompanied by an increase of the intracellular concentration of reactive oxygen species.

Thus, the studied compounds can be recommended for further research as promising photosensitizers for photodynamic therapy.

The work was financially supported by the RSF (Grant 17-73-10413).

Osipova G.V., Petrov O.A.

KINETIC STABILITY OF B, B-ANNELATED PORPHYRAZINES IN PROTON-ACCEPTOR ENVIRONMENTS

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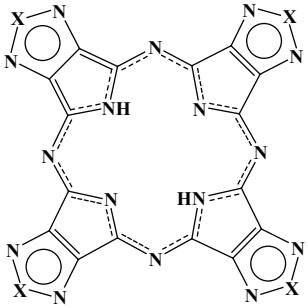
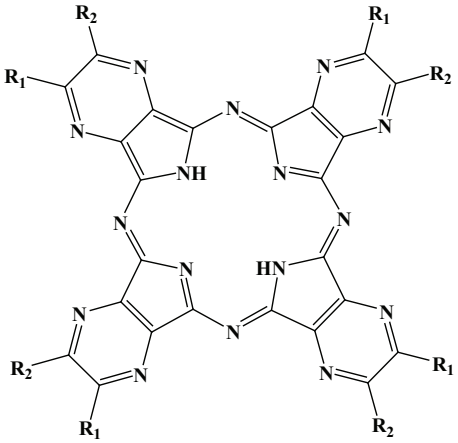
The condition of β, β - annelatedporphyrazines in chlorobenzene, dimethylsulfoxide (DMSO), and the system "nitrogen-containing base – DMSO" was investigated.



$H_2Pa(XN_2)_4$
X = S, Se



$H_2Pa(R_1R_2Pyz)_4$

R_1= Bu^t; R_2 = H - $H_2Pa(Bu^tPyz)_4$

R_1= R_2 = Et - $H_2Pa(Et_2Pyz)_4$

R_1= R_2 =  - $H_2Pa(Ph_2Pyz)_4$

It is shown that the studied porphyrazinesin the environmentof an inert low-polar solvent (chloroform) contain a non-cleaved Q-band corresponding to the D_{2h} symmetry of the π-chromophore of the molecule.When chloroform is replaced by DMSO, the symmetry of the molecule changes from D_{2h} to D_{4h}, which indicates the acid-base interaction between the intracyclic protons of the NH-groups of the porphyrazine macrocycle and the DMSO molecules, leading to the formation of proton transfer complexes.

It was found that complexes with proton transfer of porphyrazines with DMSO have a sufficiently high kinetic stability, and their formation proceeds at speeds that do not allow measuring them by ordinary spectrophotometric methods.

Further studies showed that the addition of sufficiently weak nitrogen-containing bases (pyridine, 2-methylpyridine) to DMSO does not destabilize proton transfer complexes. On the contrary, the addition of stronger bases (morpholine, piperidine, *n*-butylamine, *t*-butylamine) contribute to the destruction of complexes with proton transfer, which is accompanied by the of the π-chromophore system of the macrocycle.

On the basis of the obtained kinetic data, a possible scheme for the decompositionof the porphyrazine macrocycle is proposed.

It is shown that the speed and activation parameters of destruction depend on the acidic properties of the porphyrazine molecule, as well as the strength and steric capabilities of nitrogen-containing bases.

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THIN-FILM MORPHOLOGY AND CHARGE TRANSPORT PROPERTIES OF HEXACHOLRO-SUBSTITUTED SUBPHTHALOCYANINE DERIVATIVES

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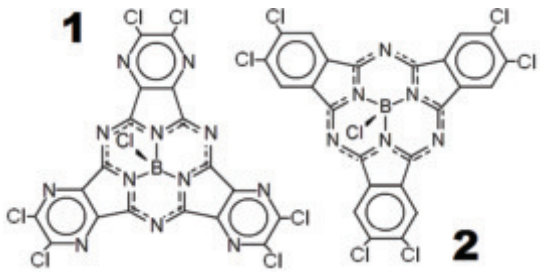
Subphthalocyanines (SubPcs) represent the most intensively studied class of macroheterocyclic compounds in organic photovoltaics today [1]. The ability of most SubPcs to sublime in vacuum without decomposition is complemented by the increased solubility compared to their conventional four-leaf phthalocyanine analogs, thus offering ample opportunities for integration into thin-film devices [2]. Recently, we synthesized a new sub-class of thermally stable SubPcs bearing thiadiazolo- or pyrazino- fragments with potentially interesting photoelectrical properties in the solid state [3]. Further progress could be associated with the introduction of halogen atoms on the periphery, which increases the electron-accepting properties of a molecule. However, the right balance between the parameters of individual molecules and charge transport characteristics of the bulk phase should be maintained to successfully meet the requirements of practical application.



In this work, we report on the optical and electrical properties of the vacuum-deposited films of the compound **1** in comparison with its closest congener, compound **2**, a well-known acceptor for the heterojunction-based solar cells [1,2]. Then, the archetypal photovoltaic devices with the planar molecular and hybrid heterojunctions employing **1** and **2** as acceptor (*n*-type) components were fabricated. The output parameters of these devices were estimated from the current-voltage characteristics under 1sun illumination. The contribution of the solid-state effects to the photoconversion efficiency is discussed.

This work is supported by RSF project # 17-13-01522.

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NEW MODIFIED CHLORIN DERIVATIVE AS AN ANTITUMOR PHOTOSENSITIZER: OVERCOMING ANTIOXIDANT DEFENSE IN OVARIAN CARCINOMA CELLS SENSITIVE AND RESISTANT TO CISPLATIN

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Chemical modifications of tetrapyrrole containing compounds are carried out to optimize their photosensitization properties. Conjugation of boron clusters at the periphery of the porphyrin macrocycle may enhance the ability to trigger cell photodamage. This effect is associated with an increased affinity of the amide of boronated chlorin to the plasma membrane [1]. To further modify the scaffold by adding 44 ^{10}B atoms and to optimize the amphiphilicity, a water soluble tetrasodium salt of 5,10,15,20-tetrakis [4-(1-carba-*closo*-dodecaboran-1-yl)tetrafluorophenyl]-17,18-dihydroporphyrin (fluorinated carboranylchlorin, FCB) was synthesized. We found a 4-fold decrease in the expression of the NADH oxidase *NOX5* gene, a 3-fold increase of glutathione peroxidase (*GPx1*) and a tendency of elevation of superoxide dismutase (*SOD*1-3) genes expression in the cisplatin resistant SKOV-3/CDDP subline compared to parental SKOV-3 cells. Thus, emergence of resistance of ovarian carcinoma cells to cisplatin was accompanied by a dysregulation of redox balance genes. We used photoactivation of FCB to kill cisplatin resistant cells. FCB caused a negligible dark cytotoxicity (IC_{50}> 50 μM) after 72 h of cell exposure. The maximum intracellular FBC accumulation in each cell line was achieved within 36–48 h. A monochromatic light illumination (30 J/cm^2) of SKOV-3 and SKOV-3/CDDP cells loaded with 5 μM FBC resulted in a rapid (within 5–15 min) death accompanied by dramatic changes of morphology and incorporation of propidium iodide, a marker of cell necrosis. Thus, the mechanisms of antioxidant defense in cisplatin resistant cells did not prevent their lethal damage upon FCB photoactivation. Water solubility, low dark toxicity and an irreparable photodamage of tumor cells (both sensitive and resistant to cisplatin) allows to consider FCB as a promising antitumor drug candidate, in particular, in situations when conventional chemotherapy is inefficient.

The publication was prepared with the support of the «RUDN University Program 5-100».

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SIMPLE SYNTHESIS OF 1-ALKOXY-2-IODINE-ETHYL DERIVATIVES OF CHLOROPHYLL *A*

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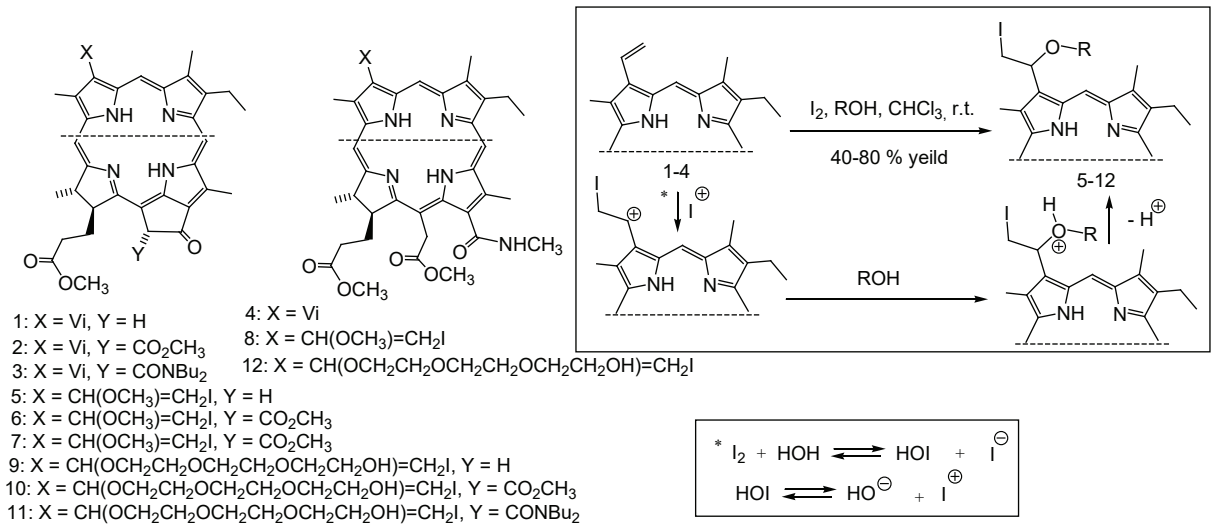
One of the possible ways to improve photosensitizers (PS) for photodynamic therapy (PDT) of oncological diseases is to modify the peripheral substituents of the porphyrin macrocycle to obtain PS with a higher quantum yield of singlet oxygen. It is known that porphyrin compounds with halogen atoms on the periphery of the macrocycle have better spectral characteristics compared to similar macrocycles that do not contain halogen. The presence of a halogen atom in a molecule causes an increase in the quantum yield of singlet oxygen [1] and an increase in the lifetime of the triplet state [2]. In this regard, the synthesis of chlorophyll *a* derivatives with halogen atoms on the periphery of the macrocycle is of considerable interest. This report presents a simple synthesis of 1-alkoxy-2-iodine-ethyl chlorophyll *a* derivatives, consisting in the action of an excess of iodine and alcohol (Scheme 1).



Scheme 1

This work performed using equipment of the CCU «Chemistry» at the Institute of Chemistry of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar)

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Rumyantsev E.V.[1,2], Marfin Yu.S.[1], Kochergin B.A.[1], Usoltsev S.D.[1], Merkushev D.A.[2], Solomonov A.V.[3]

CHEMISTRY OF BILIRUBIN AND ITS ANALOGUES: LAST RESULTS OF OUR LABORATORY

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The latest data obtained in the authors' laboratory, which establish the fundamental laws of the mutual influence of structural and physicochemical factors in the chemistry of bilirubin and its analogues, are presented. Di- and tetrapyrrole compounds, being precursors of synthesis and decomposition products of natural porphyrins, are a special class of heterocyclic compounds. Their π-systems experience instantaneous polarization as a result of chemical modification and solvation effects. Thus, interesting and sometimes unique opportunities are created for the use of compounds and materials based on them in chemistry, biomedicine and technology. The results are discussed, which allow to consider bordipyrrins as sensors of biovisualization of the mechanism of platelet apoptosis in the process of blood coagulation. Currently, a collaboration of the Ivanovo State University of Chemistry and Technology and the Ivanovo State Medical Academy has been established to conduct joint research in this area. The next direction is the study of the possibilities of creating sensory molecules based on boardipyrrins and bis(dipyrrinates) of zinc for non-invasive diagnostics of various physiological and pathological processes. A unified strategy is being developed to create methods for the targeted synthesis, production, physicochemical and clinical studies of bordipyrrins with reactive groups that can provide effective and selective interactions with the functional groups of steroid hormones. The report will also consider other research areas developed by the authors.

The presented results were obtained as a result of the work performed under the RFBR grants (grants No. 18-43-370035 and 18-33-20218).

Salnikov D.S., Makarov S.V.

INTERACTION OF COBALAMINS WITH SULFUR-CONTAINING REDUCTANTS IN THE PRESENCE OF DIOXYGEN AND HYDROGEN PEROXIDE

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Vitamin B_{12} (cobalamins, Cbls) is a group of cobalt-containing biologically active compounds containing a corrin macrocycle. One of the most important causes of loss of biological activity of cobalamins in food is the formation of stable yellow corrinoids (SYCs, Fig. 1). They are formed in the simultaneous presence of oxidizing (dioxygen, hydrogen peroxide) and reducing agents (including sulfur-containing reductants, for example, cysteine, which is an important component of food) in solution.

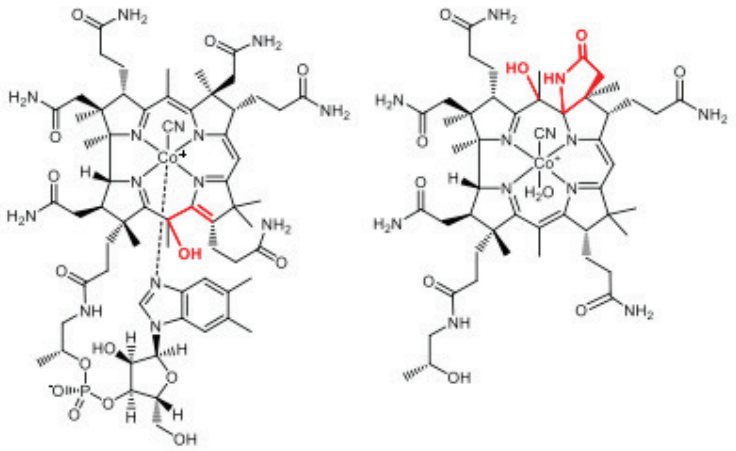

Fig. 1. *Structures of stable yellow corrinoids*

In this report we discuss the influence of reductants (sulfite, sodium hydroxymethanesulfinate), the oxidants (dioxygen, hydrogen peroxide), a value of pH, the structure of cobalamin and other factors on the products composition and kinetics of reactions in the system cobalamin – reductant – oxidant.

Sheinin V.B.[1], **Koifman O.I.**[2]

EXTRAORDINARY ACID-BASE IONIZATION OF THE PORPHYRIN PLATFORM

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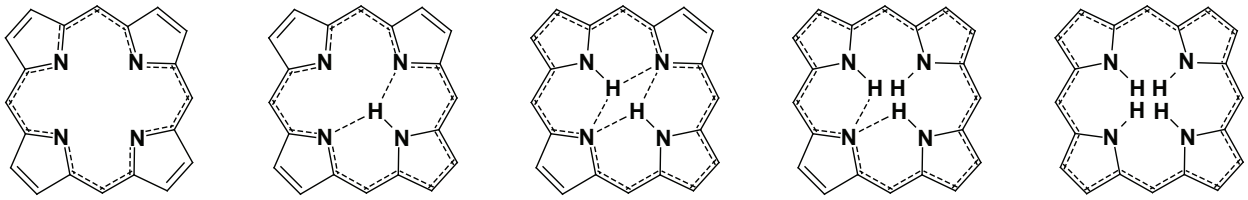
Porphyrin platform **H_2P** is formed by pyrrole rings which are donors of intramolecular hydrogen bond (IMHB) and pyrrolenine rings which are acceptors of IMHB. Cyclization of linear tetrapyrrole into porphyrin macroheterocycle lead to intramolecular tightness, results in all intracyclic atoms approach each other over the overlap distances of their van der Waals radii. Intramolecular tightness causes opposing forces of hydrogen repulsion HH on one hand and hydrogen bonding HN on the other. Macrocyclic effect causes intracyclic H-complex formation As a result of hydrogen atoms chelation, four bifurcated IMHB are formed, which compensate van der Waals repulsion and, together with the aromatic system, keep the pyrrole and pyrrolenine rings of the porphyrin platform in a coplanar state. Total energy of four bifurcated IMHB of unsubstituted porphin platform is only 12.8 kcal/mol, but they form strong framework of four six-membered and one four-membered cycles and have an advantage over intermolecular hydrogen bonds.

Bifurcated IMHB block the **HP^-**, **H_2P** and **H_3P^+** reaction centers from intermolecular interactions with solvents, cations, anions and play an important role in protolytic equilibria involving **H_2P**.



P^{2-} ***receptor*** **HP^-** **H_2P** **H_3P^+** **H_4P^{2+}** ***receptor***

Due to the molecular structure peculiarities, **P^{2-}** dianions and **H_4P^{2+}** dications have properties of ionic and molecular receptor-chromophores, which act as basic platforms in the recognition and ionic self-assembly processes of various supramolecular systems, including discrete highly ordered nanoparticles, such as, for example, single-walled and multi-walled porphyrin nanotubes [1,2].

Acknowledgement: *The reported study was funded by RFBR according to the research projects № 18-03-01104 and № 18-53-00035 Bel_a*

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Pursey J.,[a] Radecki J.,[c] Radecka H.,[c] Khelevina O.G.[b]

DNA BASED MULTI-PORPHYRIN SYSTEMS: FROM LIGHT PIPES TO MEMBRANE ANCHORS

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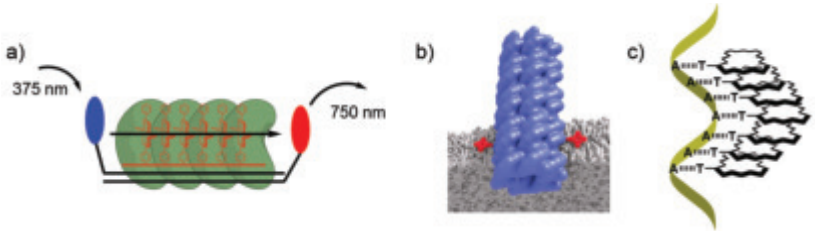
DNA has become very attractive as scaffold for functional molecules on the nanometre scale. The sequence specific insertion of modified nucleotides using automated DNA synthesis allows for the creation of designer molecules with a wide range of potential applications. We have established a general synthetic route to porphyrin-nucleosides and their subsequent site-specific incorporation into oligonucleotides to create multi-porphyrin arrays.[1] The spectroscopic data and structure calculations indicate the formation of a stable helical array in the porphyrin-DNA, but also reveals intermolecular interactions giving discrete assemblies. The π-stack of the porphyrins leads to strong electronic interaction between the chromophores.

The porphyrin modified DNA is now being used in several applications, spanning optics, electronics, medicinal chemistry and sensors. We will present our latest research in these fields with several selected examples (see Figure):



a) Currently, we are creating a new multi-porphyrin based light pipe which is bio-templated using protein-DNA interactions (RecA), yielding an efficient energy transfer system over a distance of >15 nm.

b) In addition to their photophysical properties, porphyrins are very hydrophobic; we made use of this property to anchor DNA stably into lipid bilayers. In this way, we could create a nano-pore consisting of six DNA helix bundles, where the central cavity of around 2 nm diameter leads to an ionic current.[2] Going small, a DNA duplex with six porphyrins inserted equally well into the membrane, and ionic currents can be observed due to leakage of ions along the DNA. This gives rise to the smallest possible DNA based nano pore.[3]

c) The electrochemical properties of the porphyrins are perfect to create genosensors to detect complementary DNA strands of biological and medicinal relevance. We have made both single and multiplex sensors, including microfluidic devices, exploring different designs in the sensor strands.[4–5] DNA sequences related to H5N1 avian flu virus and to bladder cancer can be detected down to the atto-molar concentration, which approaches single molecule detection. This includes detection of single nucleotide polymorphism in the target strand. Additionally, self-assembled porphyrazine systems can be used in sizing forensic short tandem repeat sequences by simple fluorescence readout.[6]

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Tarakanov P.A.[1,2], **Simakov A.O.**[1], **Kozlov A.V.**[2], **Goryachev N.S.**[2,3], **Mischenko D.V.**[2,4], **Balakina A.A.**[2,4], **Bondarenko S.D.**[2,3], **Sergeeva I.A.**[3], **Fedorova K.V.**[3], **Krot A.R.**[3], **Tarakanova E.N.**[1], **Pushkarev V.E.**[1]

1,4-DIAZEPINOPORPHYRAZINES – ON THE WAY TO MEDICINE

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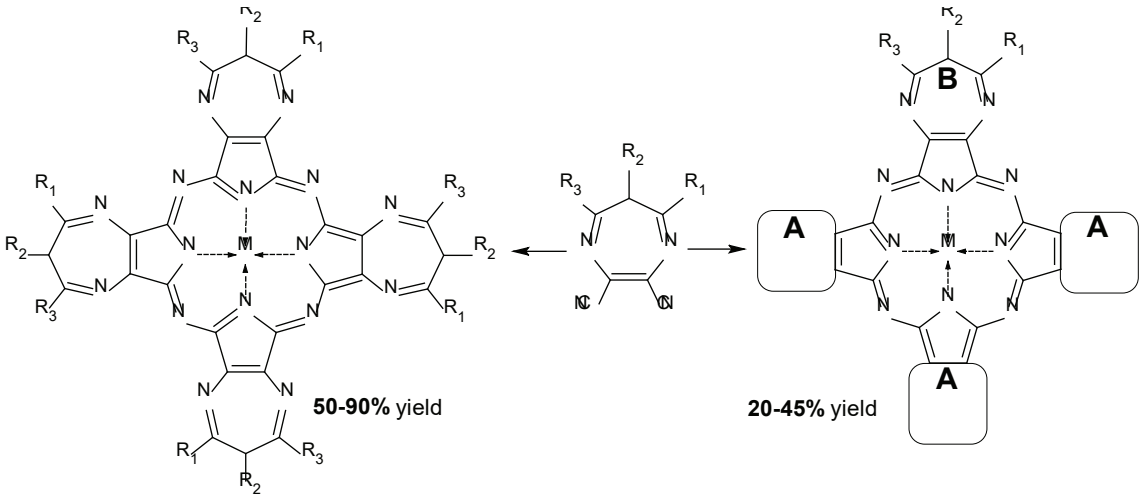
For the first time, 1,4-diazepinoporphyrazines have been reported 20 years ago. However, significant progress in understanding structure–property relationships for these compounds, as well as the first X-ray structural data [1], was obtained only during the last 5 years. This opened opportunities for developing new materials based on the 1,4-diazepinoporphyrazines for medicine applications.

Optimization of the molecules for medical applications requires the presence of changeable substituents in their structure. The aim of this work was to develop synthetic methods for 5,6,7-substituted 1,4-diazepine-2,3-dicarbonitriles and 1,4-diazepinoporphyrazines based on them.



The developed techniques give the high symmetry B_4 type 1,4-diazepinoporphyrazines and low symmetry A_3B type 1,4-diazepinoporphyrazines with yields of 50–90 % and 20–45 %, respectively. Physicochemical studies of the obtained compounds have shown that low symmetry A_3B type 5,6,7–substituted-1,4-diazepinoporphyrazines are promising as photosensitizers for photodynamic therapy.

This work was supported by the RSF (Grant 17-73-10413).

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Tikhomirova T.V., **Nalimova K.A., Aleksandrova E.A., Erzunov D.A., Vashurin A.S.**

RARE-EARTH METAL COMPLEXES OF ARYLOXY-SUBSTITUTED PHTHALOCYANINES

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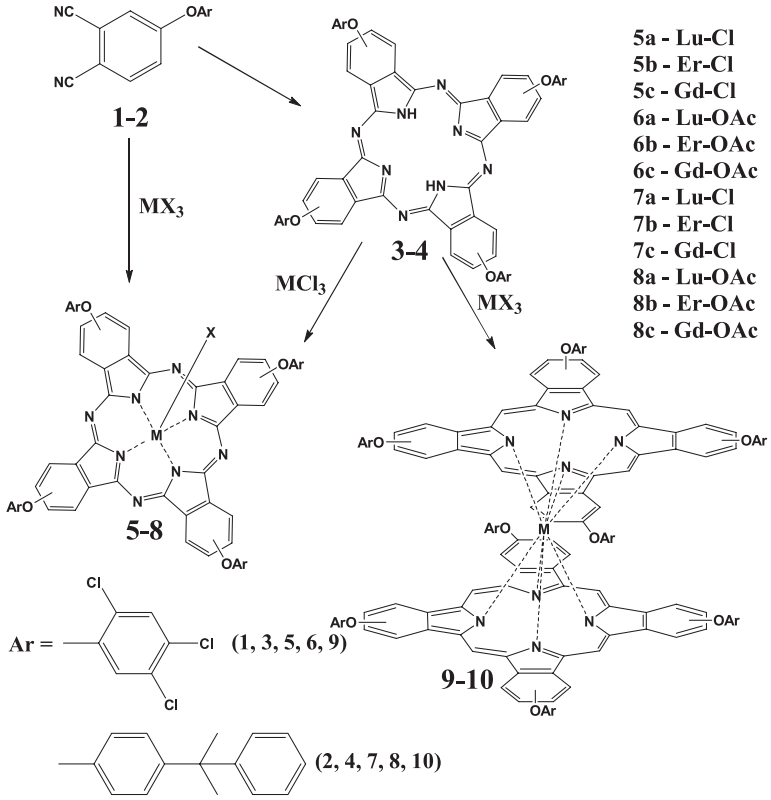
Present report presents data on the synthesis and study of some physicochemical properties of various structures based on tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]- and tetra-4-[(2,4,5-trichlorophenoxy]-phthalocyanines metal complexes with erbium, lutetium and gadolinium.



The synthesis of lanthanides metal complexes was carried out either by template condensation of the corresponding phthalonitriles (**1**, **2**) with metal salt and DBU in a boiling solvent or by metalation of free ligands (**3**, **4**) with metal salt in a boiling solvent. The structure of all the compounds obtained was confirmed by MALDI-TOF mass spectrometry, IR, NMR and absorption spectroscopy.

It is shown the nature of the aryloxy substituent affects not only the composition of the resulting reaction mass, but also the conditions of the synthesis.

The spectroscopic properties of the phthalocyanines synthesized in organic solvents are studied.

The work was supported by the Russian Science Foundation (project No. 17-73-20017).

Znoiko S.A., Petlina A.I., Tikhomirova T.V., Vashurin A.S., Shaposhnikov G.P.

SPECTRAL-LUMINISENT PROPERTIES OF OCTA-SUBSTITUTED PHTHALOCYANINWS AND ITS METAL COMPLEXES

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Phthalocyanine derivatives exhibit unique properties suggesting the enormous potential of its usage as nanomaterials. The presence of an aluminum or lanthanide atom in the macrocyclic nucleus is known to lead to an additional shift of the Q absorption band to the region of large wavelengths and gives phthalocyanine derivatives pronounced luminescent properties.

Substituted phthalocyanines, combining substituents of different nature in the benzene rings, occupy a special place among the compounds of the phthalocyanine series. For example, metal complexes of 1,8,15,22-tetra (phenylsulfonyl) -3,10,17,24-tetra (tert-butyl) phthalocyanines with manganese, zinc or aluminum are proposed as contrast agents for magnetic resonance diagnostics and immunoliposomal forms of photosensitizers. At the same time, information on the effect of mixed-substituted phthalocyanines structure on its spectral-luminescent properties is extremely limited.

Therefore, the purpose of this work was to further modify the phthalocyanine molecule by introducing additional electron-donating or electron-withdrawing fragments to the periphery and varying the nature of the complexing metal (by introducing zinc, aluminum or some lanthanide atoms) in the coordination center of the compounds modified in this way and determining the influence of the chemical structure of phthalocyanines, containing from 4 to 8 fragments of arylsulfonyl, aryloxy, and also nitro groups on their physicochemical and, in particular, luminescent properties.

These compounds were synthesized by the nitrile method on the basis of previously obtained 4,5-substituted phthalonitriles, which simultaneously contain arylsulfonyl / aryloxy and nitro or benzotriazolyl fragments. Water-soluble derivatives are obtained by sulfochlorination followed by hydrolysis of octa-substituted phthalocyanines and their metal complexes with zinc and aluminum.

The spectral-luminescent properties of phthalocyanines synthesized in organic solvents are studied.

This work was supported by the Russian Science Foundation, the project 17-73-20017.

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ФОТОДИНАМИЧЕСКАЯ ТЕРАПИЯ КАК РЕЗУЛЬТАТ ДОСТИЖЕНИЙ СОВРЕМЕННОЙ ХИМИИ ПОРФИРИНОВ

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Фотодинамическая терапия (ФДТ) – эффективный, безоперационный, органосохраняющий, щадящий и безопасный метод лечения рака различных локализаций, а также целого ряда неопухолевых заболеваний. Метод ФДТ за счет однократности лечебной процедуры, проводимой при большинстве локализаций рака в амбулаторных условиях, позволяет значительно сократить сроки лечения по сравнению с наиболее распространенными хирургическим, лучевым и лекарственным методами терапии рака, уменьшить количество осложнений, восстановить трудоспособность в соответствующих возрастных группах или сократить сроки нетрудоспособности больных. В 2002 г. ФДТ впервые включена в «стандарты лечения злокачественных опухолей», а с 2013 г. ФДТ официально рассматривается в качестве одного из альтернативных методов лечения большинства локализаций злокачественных новообразований.

ФДТ интенсивно развивается во всем мире, в том числе в России, где методом ФДТ уже успешно пролечены десятки тысяч больных раком различных локализаций и стадий процесса. В 1992 г. мы впервые в клинической практике применили для ФДТ отечественный фотосенсибилизатор из группы производных гематопорфирина Фотогем. Следующим этапом в развитии ФДТ в России стал синтез и, начиная с 1994 г., клиническое применение фотосенсибилизатора второго поколения Фотосенса – сульфированного фталоцианина алюминия с большей длиной волны возбуждающего света, что позволяло успешно применять ФДТ при более распространенных опухолях. Важным этапом развития ФДТ в нашей стране явилась разработка в институте биомедицинской химии им. В.Н.Ореховича под руководством профессора Г.В.Пономарева и передача нам в ГНЦ лазерной медицины для клинических испытаний в 1998 г. нового фотосенсибилизатора, производного хлорина е6 – Фотодитазина. Фотодитазин, благодаря своим преимуществам по физико-химическим свойствам перед фотосенсибилизаторами – предшественниками, уже с первых лет применения в клинике стал «рабочей лошадкой» ФДТ на территории всей Российской Федерации, от Пскова и Сан-Петербурга до Владивостока, Камчатки и Сахалина. Мы имеем возможность представить карту Российской Федерации, где наши ученики и последователи успешно применяют Фотодитазин для ФДТ рака и других, неопухолевых заболеваний. Это прежде всего ФДТ длительно не заживающих гнойных ран и трофических язв сосудистой этиологии, в том числе с антибиотикорезистентной флорой, это широкое применение ФДТ с мазевыми и гелевыми композициями Фотодитазина и других хлориновых производных в стоматологии, дерматологии, гинекологии.

В настоящее время ФДТ успешно применяется для лечения наиболее распространенного по частоте во всем мире рака кожи, который и в России, начиная с 2007 года, является наиболее частым онкологическим заболеванием. При этом, при ФДТ резорбируются в 95 % случаев очаги первичного рака кожи и даже рецидивы после традиционных методов лечения. Особо важным достижением является возможность применения ФДТ при периокулярной и других «неудобных», критических локализациях рака. Необходимо отметить, что ФДТ значительно расширила возможности современной онкологии в лечении не только начальных стадий рака внутренних органов, но успешно применяется при далеко зашедших опухолевых процессах, когда традиционные методы лечения, хирургическая операция и лучевая терапия, не выполнимы или применялись и оказались не эффективными. Это прежде всего эндоскопическая паллиативная ФДТ, рассчитанная на реканализацию и ликвидацию тягостных симптомов обтурации внутренних органов опухолью: при опухолевом сужении пищевода с нарушением глотания и проходимости пищи, при дыхательной недостаточности вследствие поражения раком трахеи и главных бронхов, при механической желтухе вследствие закупорки большого дуоденального сосочка и внепеченочных желчных протоков. Применение ФДТ у этой тяжелой категории больных, ранее, до ФДТ, мало доступных для специального лечения, позволяет улучшить качество и продолжительность жизни пациентов. Благодаря однократности лечебной процедуры ФДТ и возможности у большинства больных применять ее в амбулаторных условиях, ФДТ дает большой социальный и экономический эффект.

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PHENYL-SUBSTITUTED TERBIUM(III) SINGLE- AND MULTIPLE-DECKER PHTHALOCYANINATES: SYNTHESIS AND STUDY OF PHYSICOCHEMICAL PROPERTIES

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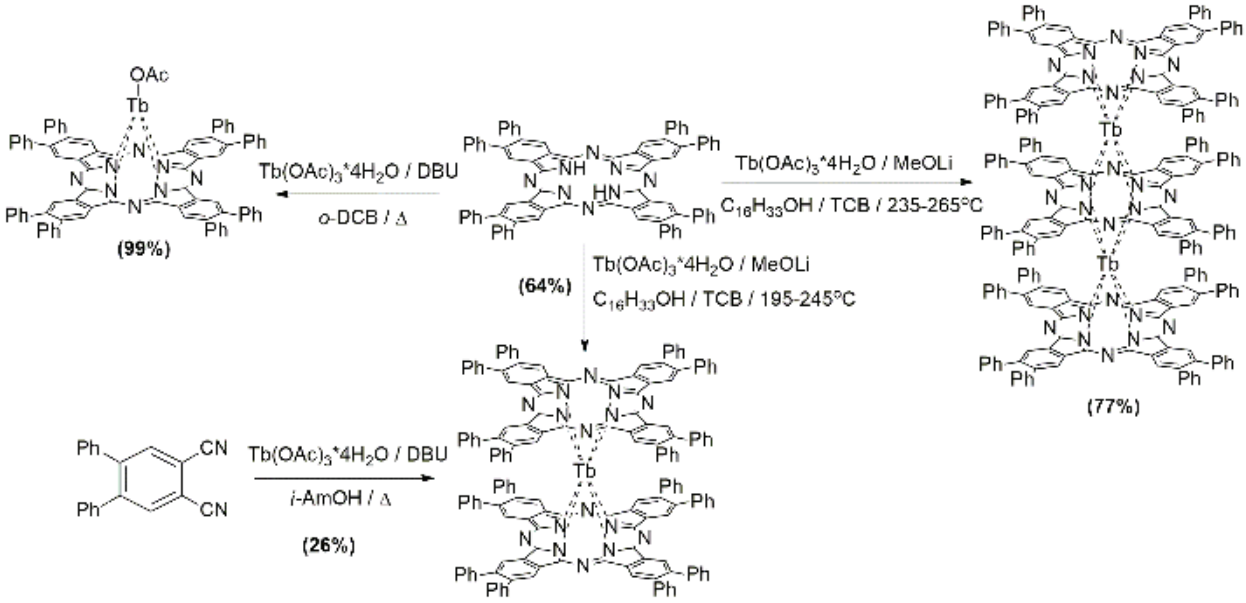
Complexes of rare earth elements with phthalocyanine ligands are of increasing research interest due to their unique physio-chemical properties and wide range of applications. Change of central metal ion and introduction of peripherical substituents leads to significant changes in properties of corresponding complexes, making these compounds promising in organic field effect transistors, IR-lables and optical filters. Employment of paramagnetic lanthanide ions, especially terbium(III), in multiple-decker phthalocyaninates allows the formation of single molecule magnets. In current study selective synthesis of novel single and multiple-decker terbium(III) phthalocyaninates, bearing peripheral phenyl groups, was accomplished in high yields. Two main approaches to the synthesis of target terbium(III) phthalocyaninates were used. Template synthesis based on 4,5-diphenylphthalonitrile and multi-step approach through the formation of phthalocyanine ligand.



It was found that in template synthesis of terbium(III) monophthalocyaninates, despite the presence of steric hindrances, the double-decker complex is formed predominantly. It results from Tb^{3+} large ionic radius. Direct synthesis of terbium(III) bisphthalocyaninate and trisphthalocyaninate was carried out starting from phthalocyanine ligand. Noteworthy that for selective synthesis of triple-decker complex was carried out at higher temperature, comparing with one for bisphthalocyanine complex.

Absorption in the near IR region was measured for bisphthalocyanine complex: red valence band (921 nm) and inter valence band (1433 nm). The conductivity of bisphthalovyaninate was also measured ($\sigma = 5\times10^{-10}$ Sm/cm). For the triple-decker complex, the formation of ring-shaped self-assembly was found using AFM technique. The "rings" consisted of small grains. The ring diameter was about 400 nm and each grain average diameter was 40 nm.

We are grateful for financial support from grant MK-3115.2018.3.

Ivanov D.A.[1], **Sheinin V.B.**[1], **Aleksandriiskii V.V.**[2], **Koifman O.I.**[1,2]

WATER-SOLUBLE AZO-BISPORPHYRIN BASED ON 5-(4`-AMINOPHENYL)-10,15,20-TRIS(4`-SULFOPHENYL)PORPHINE AND H-ACID

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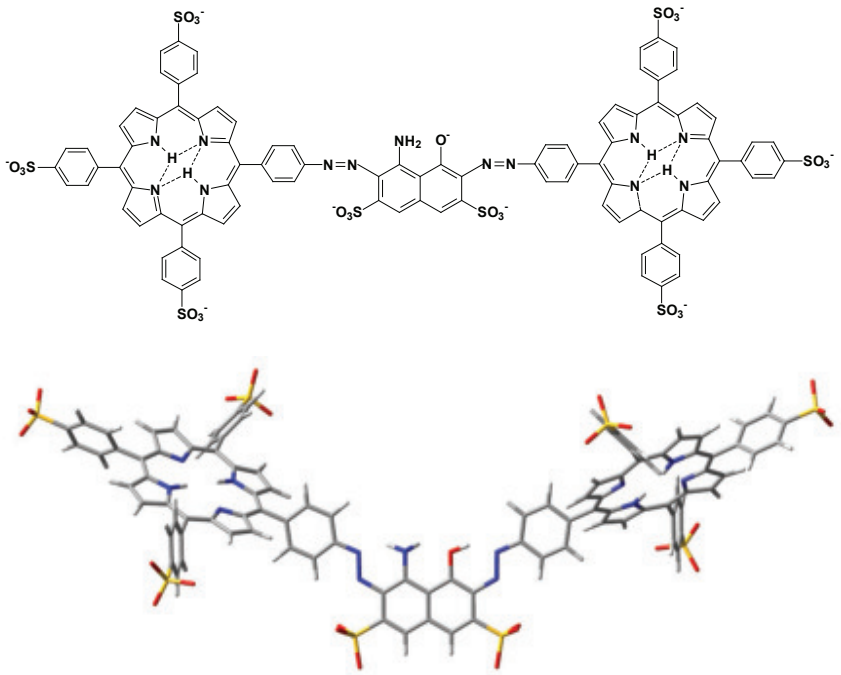
Directly linked bisporphyrins or linked by various spacers shows interesting absorption and emission properties based on strong electronic interactions between poprhyrin platforms which can be used as systems for energy and electron transfer. Such dimers are used in various fields of photophysics and are promising compounds for the formation of new functional and hybrid materials [1–2]. Formation of water-soluble derivatives significantly develops the field bis-porphyrins and derivatives of supramolecular systems practical application. In this work show synthesis of new water-soluble free-base azobisporphyrin based on 5-(4`-aminophenyl)-10,15,20-tris(4`-sulfophenyl)porphine and H-acid as spacer.



This work was supported by RFBR (grant № 18-33-01025 mol_a).

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Ivanov E.N., Islyakin M.K.

HEMIHEXAPHYRAZINES WITH BULKY (2,6-DIISOPROPYL) PHENOXYGROUPS. SYNTHESIS AND PHOTOPHYSICAL PROPERTIES

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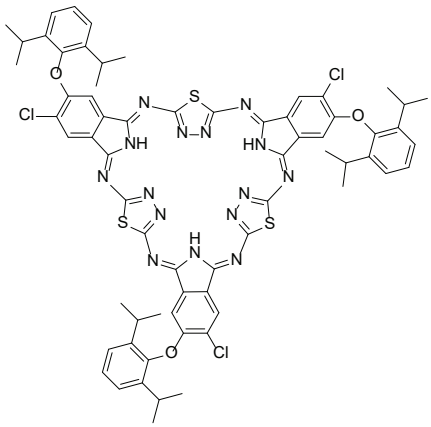
Since the beginning of this millennium considerable efforts have been devoted to the synthesis, structure elucidation and study of the properties of expanded macroheterocyclic compounds (Mc's). Among them, hemihexaphyrazines (HHph) containing six consecutively interlinked 1,3,4-thiadiazole subunits (A) and isoindole (B) moieties bridged by nitrogen atoms induce a particular interest. Indeed, various substituted macroheterocyclic compounds of this type were synthesized and their structures were elucidated by gas electron diffraction (GED) [1] and single crystal X-ray diffraction [2] methods. It was established that HHph have on the base of their structure a nonaromatic macrocyclic backbone containing 27 carbon and nitrogen atoms which form an expanded coordination cavity able to hold 3 atoms of d-elements.

In this work we report on the synthesis of novel representatives of HHph: tri- (I) and hexa(II) (2,6-di-iso-propylphenoxy)substituted macroheterocyclic compounds ABABAB-type derivatives and their complexes with Co and Ni.



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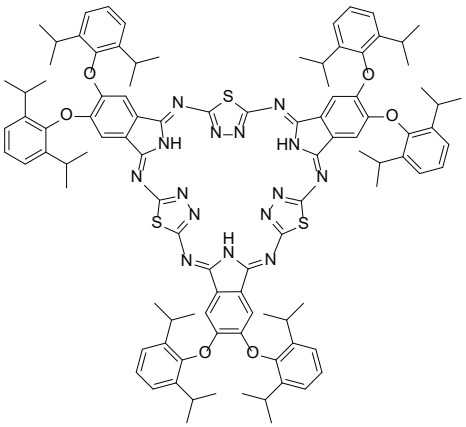

II

These compounds were characterized by ^{1}H NMR, IR, UV-vis spectroscopy, MALDI TOF spectrometry and elemental analysis.

With their π-conjugated planar organic structure, thiadiazoloporphyrinoids interact strongly with light and demonstrate huge Stock's shifts.

Acknowledgements. *This work was financially supported by Russian Science Foundation (project № 18-03-00888).*

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T-SHAPED STRUCTURE OF M-NITRIDO DIMER OF IRON OCTAPROPYLPORPHYRAZINE IN LANGMUIR-SCHAEFER FILMS

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Nitrogen-bridged diiron porphyrin complexes are effective catalysts for oxidation of organic compounds, in particular methane and benzene. Formation of thin-film catalysts based on these compounds is a promising task. It is known that the structure of an ensemble is determined both by the structure of the compound [1] and the conditions of the formation of the ensemble [2]. The objective of this work is to obtain and to investigate the structure of the Langmuir-Schaefer (LS) films of μ-nitrido dimer of iron octapropylporphyrazine (μ-[(OPTAP)Fe]$_2$N).

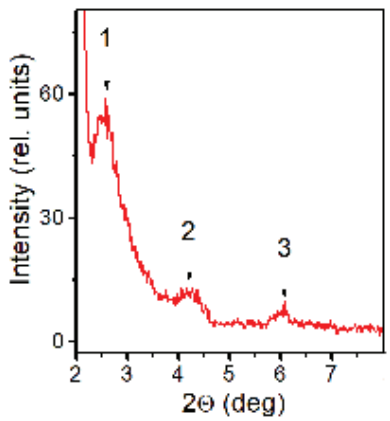

Fig. 1. *Diffraction pattern of the LS-film of μ-[(OPTAP)Fe]$_2$N.*

The floating layers were formed with the use of the NT-MDT Langmuir trough (Zelenograd, Russia) from a solution of μ-[(OPTAP)Fe]$_2$N in a toluene (C = 10^{-4} M), at a compression rate of 2.3 $cm^2 \cdot min^{-1}$. The structure of the floating layers was analyzed within the framework of an original model and method for quantitative analysis of compression isotherms of nanostructured M-monolayers [3, 4]. LS-films of μ-[(OPTAP)Fe]$_2$N were formed by transferring the layer onto silicon plates at diverse initial surface coverage degrees (from c_{edge} = 21 % to 78 %). The number K of touchdowns of the layer by the substrate was 30. The states of floating layers at the transfer points (π_{tr} = 13–14 mN/m) were monolayers and polylayers. XRD patterns were collected on a Bruker D8 Advance diffractometer operating at 40 kV, and 40 mA with Cu K_α radiation. Measurements were performed in θ–2θ geometry, in the 2θ range from 2° to 8° in steps of 0.02° and different counting time per step.

The data indicate that in LS-films, as well as on the water surface, the two type of structural unit can be formed: the face-to-face stacks and T-shaped (1, d=35 Å, Fig. 1). In the films T-shaped structures arranged perpendicular to the substrate. Face-to-face stacks are both parallel to the substrate (2, d = 0.8 Å, Fig. 1), and perpendicular to it (3, d = 14.7 Å, Fig. 1).

The work is performed in the framework of tasks of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018/4.6).

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TARGETED SYNTHESIS OF NEW TYPES OF PHTHALOCYANINES AND PROSPECTS FOR THEIR APPLICATION

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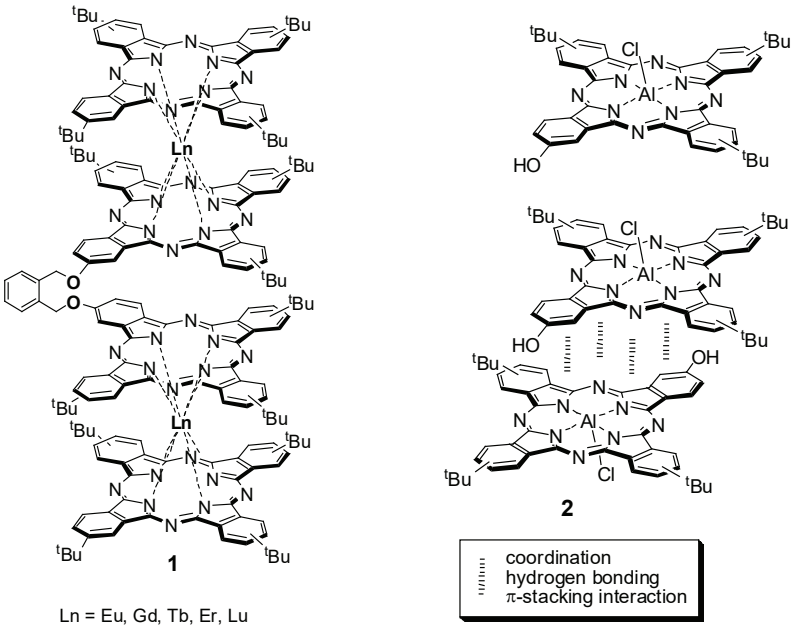
Today phthalocyanines are applied in many areas, including electrochromic components in information display media and molecular magnets, as well as photosensitizers in photodynamic therapy (PDT). Dimeric and sandwich-type phthalocyanine complexes have special prospects for use in these areas.



In the current study, compounds of both types have been synthesized with high yields, namely, sandwich-*clamshell* quadruple-deckers **1** containing an intramolecular flexible spacer group and dimeric aluminum complex **2**. The composition and structure of the obtained compounds were studied using physicochemical methods: ^{1}H NMR, UV-Vis-NIR spectroscopy, MALDI-TOF mass spectrometry and thermogravimetry (TG). The TG data showed stability of the synthesized complexes up to 350 °C. A study of the spectral properties of **1** showed the presence of an intense absorption in the NIR region. It was established that the nature and position of the absorption bands of **1** is determined by the lanthanide nature. Thus, with an increase in the ionic radius, a bathochromic shift of the main bands is observed both in the visible and NIR region from 1260 to 1620 nm for Ln = Lu and Eu, respectively. The EPR data (g = 2.0046) in combination with the UV-Vis-NIR indicate the existence of compounds **1** in the form of free radicals. Electrochemical study conducted in the range from –2.5 to 1.3 V shows that compounds **1** can be used in electronic memory devices, while the Tb(III) derivative possesses intrinsic magnetic properties. Studies have been started for the application of compound **2** as the part of a biosensor for antibiotics.

We are grateful to the Russian Scientific Fund (Grant 17-13-01197) for main support of this research.

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ARYL-SUBSTITUTED TETRAPYRAZINOPORPHYRAZINE COMPLEXES OF RARE-EARTH ELEMENTS: SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES

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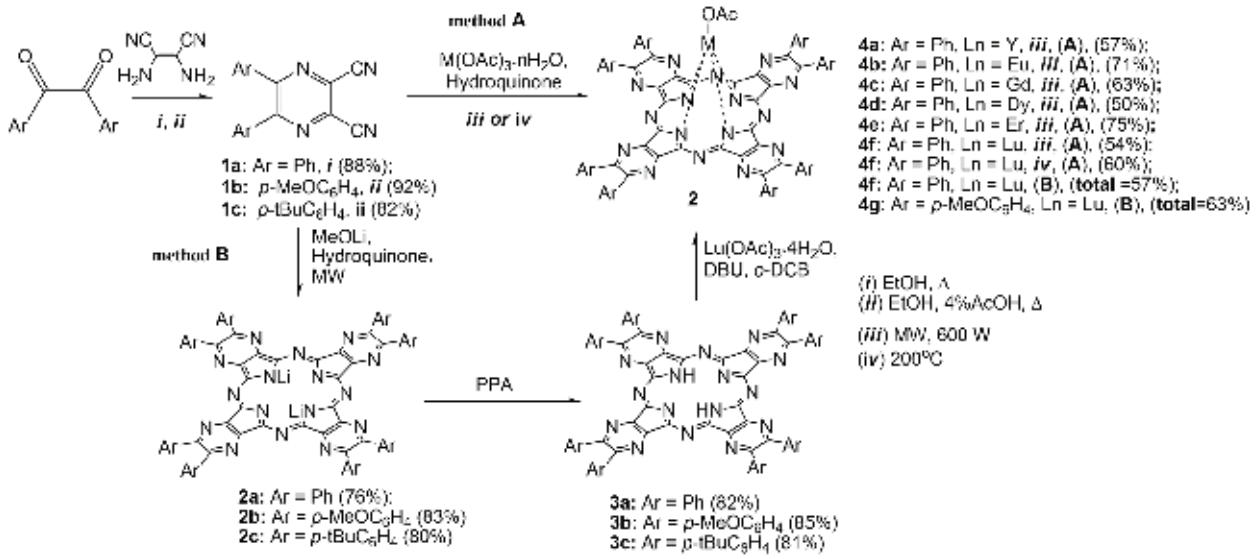
Thanks to the combination of electron-deficient pyrazine moieties and the electron-rich porphyrazine core, tetrapyrazinoporphyrazines can possess nonlinear optical response and *n*-type conductivity. Thus, these macroheterocycles are promising for obtaining on their basis materials for nonlinear optics and microelectronics, for instance, organic field-effect transistors and photovoltaics.

Present study focuses on the development of synthetic approaches to novel substituted tetrapyrazinoporphyrazine complexes of rare-earth elements (REE), bearing *tert*-butyl-, *p*-methoxy-phenyl and phenyl groups. The employment of tervalent rare-earth elements as central ions and the presence of additional mobile axial ligand increase solubility of target complexes in contrast to porphyrazine complexes with M(II) central ion. Presence of axial ligand makes these compounds promising precursors for creating hybrid materials on their basis.



Preparation of target compounds was carried out by the template method (method A), as well as through the tetrapyrazinoporphyrazine ligand (method B). Initial nitriles **1a-c** were obtained starting from corresponding 1,2-diketones using condensation with DAMN. Template synthesis was carried out under thermal and microwave effects, while the yields of the target compounds are comparable.

A monomeric erbium tetrapyrazinoporphyrazine complex film was obtained in the polymer matrix. Its conductivity (in the temperature range 170–300 K) and the energy spectrum were determined. The position of the energy levels are determined: LUMO, Fermi level, and a number of intermediate levels. This information is important for the design of efficient photolayers for organic solar cells based on new tetrapyrazinoporphyrazines, acting as *n*-type semiconductors.

We thank grant MK-3115.2018.3 and grant RFBR 18-33-00519. Electrochemical investigations were supported by RFBR (Grant 18-53-76006 ERA).

Kostrova E.A., Malyasova A.S., Tikhomirova T.V., Khelevina O.G.

STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF PHTHALODNITRILES CONTAINING HYDROXYL GROUP

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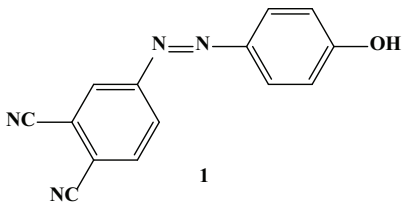
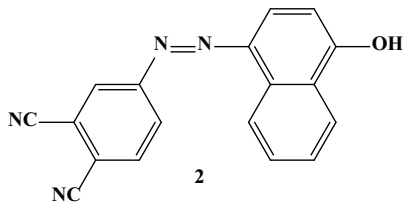
4-[(E)-(4'-hydroxyphenyl)diazenyl]phthalonitrile **1** and 4-[(Z)-(2-hydroxy-1-naphthyl)diazenyl]-phthalonitrile **2** were obtained according to the procedures [1, 2]. The compounds obtained were characterized by UV-spectroscopy, infrared spectroscopy, ^{1}H NMR spectroscopy, as well as mass spectrometry and elemental analysis data.





When an alcoholic Bu_4NOH solution is added to a solution of phthalodinitriles in dichloromethane, a decrease in the intensity of the absorption band corresponding to the neutral form of phthalodinitrile is observed. Further, an increase in the new absorption band is observed, shifted by 150–200 nm more bathochromic. These spectral changes can be explained by the deprotonation of hydroxyl groups.

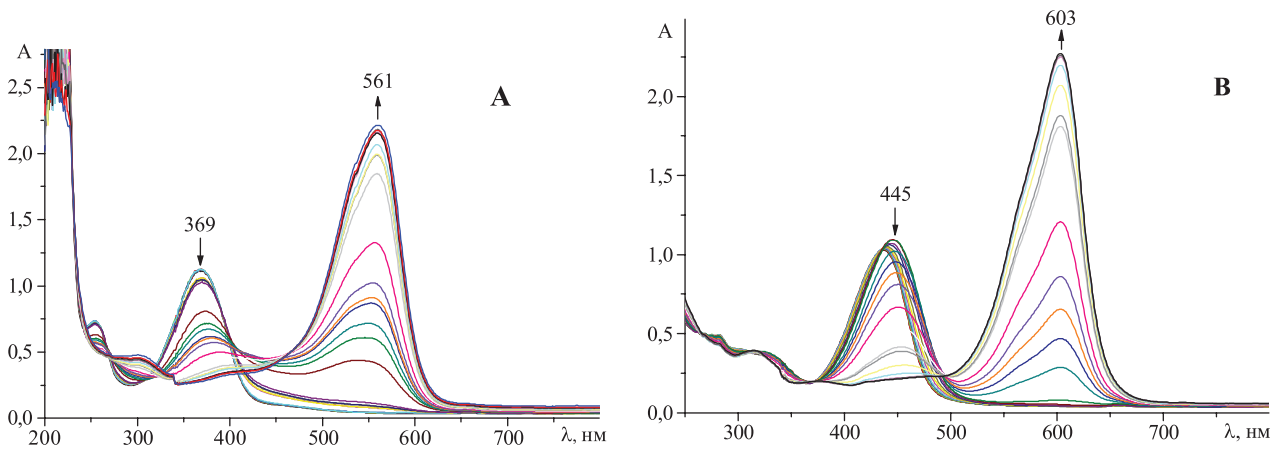


Fig. 1. *Change UV-vis spectra of phthalodinitrile* **1** *(***A***) and phthalodinitrile* **2** *(***B***) during acid–base titration in* $CH_2Cl_2 - Bu_4NOH_{(alc.)}$

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COMPLEXES OF PORPHYRINS WITH HUMAN SERUM ALBUMIN: STRUCTURAL INSIGHTS REVEALED BY EPR SPECTROSCOPY

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Many photosensitizers promising for photodynamic therapy are lipophilic substances with low solubility in water. Therefore, the effective delivery of such photosensitizers requires the use of special transport systems. Human serum albumin (HSA) is a natural transport protein with multiple ligand binding sites, making it a promising carrier for the delivery of lipophilic drugs. HSA is able to bind with some photosensitizers with high efficiency and to accumulate in malignant and inflamed tissues. Photophysical properties of photosensitizers bound to HSA depend on its localization at the protein. In order to create new efficient agents for photodynamic treatment it is necessary to investigate the structure of such complexes.

In this paper, we for the first time applied various methods of electron paramagnetic resonance (EPR) spectroscopy to study complexes of human serum albumin (HSA) with porphyrin derivatives. As a result, we obtained the distribution functions for the distances between the photoexcited triplet of photosensitizers and the nitroxyl radical selectively introduced at HSA. This allowed us to establish binding sites on HSA for various porphyrins. We estimated also the accessibility of the photosensitizer triplet to solvent molecules in complex with protein. In addition, the effect of binding to HSA on the singlet oxygen generation efficiency and on the distribution of the electron spin density in the porphyrin triplet molecules was evaluated.

For example, it was shown that tetra (hydroxyphenyl) porphyrin forms a complex with HSA in two binding sites located in domains IIa and IIIa. In these sites, porphyrin has practically no access to solvent molecules, but demonstrates effective production of singlet oxygen. In contrast to this, EPR methods have showed binding of cationic porphyrin (5,10,15,20-tetrakis (4-N-methylpyridyl porphyrin) mainly in one site in domain 1B of HSA, in which porphyrin is highly accessible to solvent molecules. The significant decrease in the efficiency of singlet oxygen generation is observed for this porphyrin in complex with HSA, despite the fact that according to EPR data the formation of a complex does not affect the quantum yield of the triplet state and the structure of porphyrin.

The work was supported by the RSF № 18-73-00292.

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THERMOSTABILITY AND QUANTUM-CHEMICAL ANALYSIS OF THE STRUCTURE OF CATIONIC SALTS OF PORPHYRINOIDS

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Porphyrins and their analogues – porphyrinoids (H_nPn) can be considered as promising materials for catalysis, medicine and other fields. Here we have studied the thermal stability and NH-acidity of mono- and doubly-protonated forms of the series of macrohererocycles (MHC) including *meso*-tetraphenylporphyrin (H_2{*ms*-Ph}$_4$P **I**), its confused (**IV**) and N-substituted analogues (H{N-Me}{*ms*-Ph}$_4$P **II**), as well as corrole (H_3{*ms*-Ph}$_3$Cor **III**) with acetic and trifluoroacetic (TFA) acids.

Samples of solid mono- and dicationic salts of H_nPn **I-IV** were obtained by evaporation of saturated solutions of MHC in acetic and trifluoroacetic acids and studied in inert atmosphere using derivatograph STA 449 F3 JUPITER (298–1223 K). Geometry optimization of cationic forms of H_nPn was made using DFT method, B3LYP hybrid functional and CC-pVDZ basis set. The interaction energies (E_{int}) of acid-base centers in H_n-Pn·nHX associate, the values of charge transfer (q_{st}) between them and the stabilization energies of non-bonding orbitals (E_{st}) were calculated by means NBO analysis.

Unlikely H_nPns porphyrin **I** forms a symmetric N,N'-dicationic salt. The asymmetry of H_nPn protonated forms caused by different location or steric shielding (H{N-Me}{*ms*-Ph}$_4$P [1]) of their acid-basic centers. H_3{*ms*-Ph}$_3$Cor forms a stable N-monocation, but further protonation takes place at the *meso*-carbon atom in the solution of strong acids only [2]. Compound **IV** may exists in two tautomeric forms with a different location of basic centers [3].

Usually the thermogram of cationic salts of comp. **I-IV** is presented by three stages of destruction: splitting off the water and acid, and macrocycle thermal decomposition. Water is removed from the sample at a temperature of 63–88 °C and evaporation enthalpy (ΔH_{vap}) of 3–9 kJ/mol per one molecule, depending on the structure of MHC and the nature of acid. The evaporation of acid molecules from the cationic salts of macrocycles takes place in the temperature range of 128–185 °C and correlates to the basicity of MHC according to the NBO-analysis data. The destruction of the macrocycles occurs at higher temperatures in the range of 310–470 °C corresponding to a free porphyrin bases thermal decomposition.

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OCTASULFOPHENYLSULFANYLPHTHALOCYANINES: SYNTHESIS, AGGREGATION BEHAVIOR AND ANTIMICROBIAL PROPERTIES

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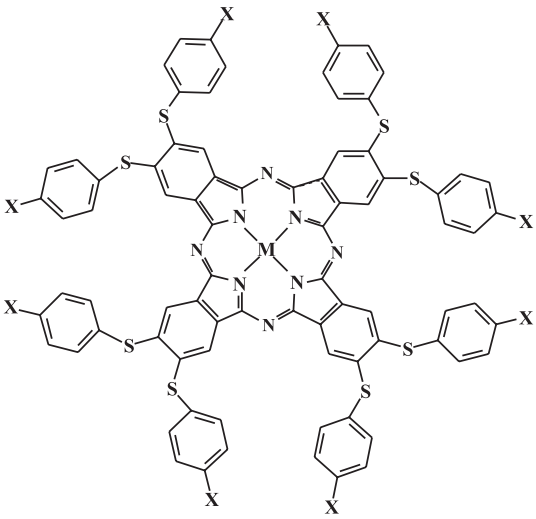

(1) M = 2H*, X = SO_3NH_4;
(2) M = Al(Cl), X = $SO_3N\ H_4$.

Phthalocyanines with sulfanylphenyl fragments can be considered as 2nd generation photosensitizers (PS) for killing bacterial infections and fungal diseases [1]. In the present work ammonium salts of octa-4,5-(4-sulfophenylsulfanyl) phthalocyanine ligand and its (Cl)Al-complex (comp. **1**, **2**) were studied. PS*s* has been identified via UV-Vis-, ^{1}H NMR- and MS-spectra [2].

An intensive bathochromic $Q_{x(0-0)}$-band (lg ε = 4.4–4.9 depending on the solvent) between 700 and 725 nm within the therapeutic window is typical for this type of compounds. Absorption in this region close to the IR-wavelengths favors to the penetration of the light through the living tissues and to higher efficacy of photodynamic therapy (PDT).

Comp. **1**–**2** are found to have a strong (but different) tendency to the aggregation in both aqueous and ethanolic solutions. Known that aggregation strongly decreases generation of singlet oxygen by PS and inhibits PDT effect. The dynamic light scattering (DLS) at PS concentration of about 10^{-4} mol/kg in water demonstrates the formation of large aggregates with one (PS **1**, 540 nm) or two (PS **2**, 15 and 400 nm) hydrodynamic diameters. Even at $m_{PS} = 7.3\cdot10^{-6}$ mol/kg in aqueous solutions of DMF according to the UV-Vis-spectra the molecular form of PS is maintained only up to 40 % of water for PS **1** and up to 90 % for PS **2**. The later observation means that extraligand prevents to the π-π-interaction between macrocycles and aggregates formation in the case of Al-complex **2**.

Surfactant micelles are considered as an effective means for PS disaggregation and delivery [3,4]. Spectrophotometric titration of PSs aqueous solutions with a non-ionic surfactant Tween 80 shows the strong interaction between solutes which is much more pronounced for less aggregated comp. **2** (K_b value is 10.99±0.98 *vs* 6.68 ± 0.20 for PS **1**).

The antimicrobial activity of anionic PS was studied on museum strains of bacteria and fungi. Phthalocyanines **1**–**2** have demonstrated an antibacterial photodynamic effect on *Staphylococcus Aureus* ($m_{PS} = 5\cdot10^{-4}$ mol/kg, 0.5 % Tween 80). An addition of EDTA (0.05 %) to improve the cell permeability even at PS concentration of $5\cdot10^{-5}$ mol/kg causes a similar effect for more resistant gram-negative *E. Coli*. Details are presented in a talk.

This work was partially supported by the Russian Scientific Foundation (Grant 15-13-00096).

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Morshnev Ph.K.[1], **Shukhto O.V.**[1], **Krest'yaninov M.A.**[2], **Kustov A.V.**[2], **Likhonina A.E.**[1], **Berezin D.B.**[1]

N-CONFUSED *MESO*-TETRAKIS(*4*-SULFONATOPHENYL) PORPHYRIN: POTENTIAL SENSITIZER FOR ANTIMICROBIAL PHOTODYNAMIC THERAPY

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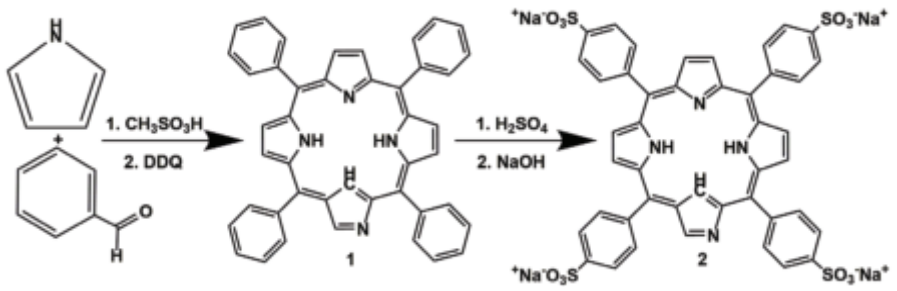
Increasing polyresistance of pathogenic microorganisms began to threaten the health and lives of people. Therefore, antimicrobial photodynamic therapy (PDT) is becoming a promising method of treatment for many diseases. The current trend of PDT is thesearch of new effective photosensitizers (PS).The aim of our work was to synthesize potential PS, 2-aza,21-carba-tetra-*meso*-(*p*-sulfophenyl)porphyrin **2**[1], from hydrophobic inverted porphyrin**1** and to study properties that allow to evaluate the possibility of using this macroheterocycle (MHC) as a drug in antimicrobial PDT.



Efficient PS should have the following characteristics: a Q-band with a high extinction coefficient in the red part of the spectrum, a high quantum yieldof PS-generated singlet oxygen, which strongly depends on the balance of hydrophilic and lipophilic properties of MHC, the degree of its aggregation in water and surfactant solutions as well ason photosensitivity of PS.

According to the spectrophotometric titration datathe sulfonic derivative of inverted porphyrin**2** in aqueous solutions and mixtures of EtOH– H_2O with a water content above 61 % ($m_{PS} = 7.3\cdot10^{-6}$mol/kg) found to besubjected to association.Using the method of dynamic light scattering (DLS) it was shown that compound**2** to remain in an associated form in both aqueous and ethanolic solutions at PS concentration of 10^{-4}mol/kg.The association of PS is known to decrease an efficacy of PDT dramatically. To solve this problem, a biocompatible non-ionic surfactant Twin 80 was used, the PS-Twin 80 interaction constants for both, hydrophilic (**2**) and hydrophobic (**1**) MHC were calculated.

Microbiological testing ofcompound**2**inan aqueous solution of Twin 80on museum strains of pathogenic bacteria and fungi showed PS nottopossessdark cytotoxicity and to exhibit antimicrobial activity against Gram-positive bacteria *Staphylococcus Aureus* by means of PDT (reduction in CFU from 10^7 to 15 units at the irradiation dose 40 J/cm^{2}and m_{PS} = 0.5mM).

This work was partially supported by the Russian Scientific Foundation (Grant 15-13-00096).

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SYNTHESIS OF NATURAL BACTERIOCHLORIN DERIVATIVE WITH GLYOXALASE I INHIBITOR

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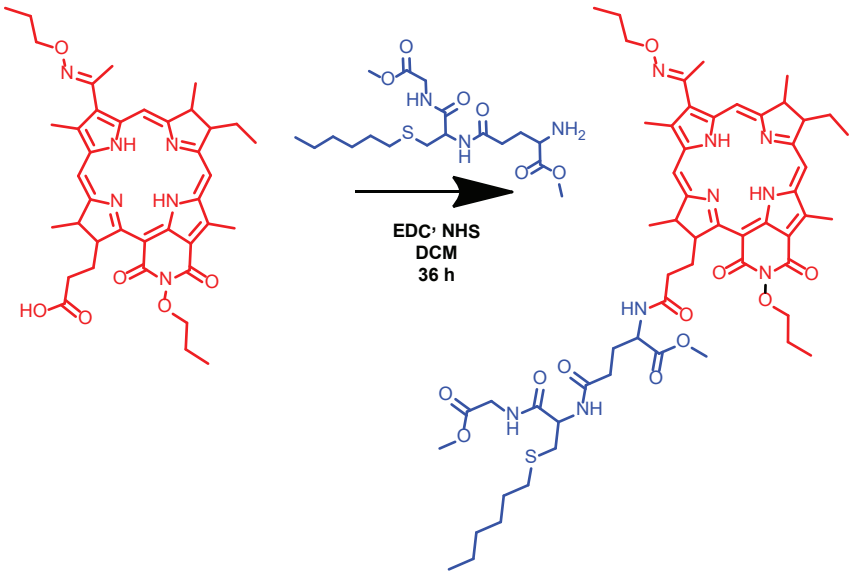
The glutathione-dependent glyoxalase system is a potential aim for targeted chemotherapeutic effect on tumor cells. Glyoxalase I (GloI) is the limiting enzyme of this system. Inhibition of GloI leads to system deactivation and accumulation of cytotoxic methylglyoxal in cells. This fact gives an ability to consider drugs affecting this enzyme as potential antitumor agents. One of the best-known inhibitors of glyoxalase I is S-hexylglutathione.

The purpose of this work was to create a bifunctional compound based on a bacteriochlorophyll *a* derivative with S-hexylglutathione, which would have the properties of an IR photosensitizer and a chemotherapeutic agent with a targeted effect on tumor cells detoxifying system.

O-propyloxime-N-propoxy-bacteriopurpurinimide (DPBP) was chosen as a photosensitizer, which has an absorption maximum near 800 nm. Earlier, we obtained a number of derivatives of DPBP with sulfur-containing amino acids, and showed their ability to interact with the antioxidant system. [1]

Eventually, we synthesized S-hexylglutathione dimethyl ester, which was conjugated to DPBP. Dimethyl derivative was used because of better permeability across the membrane.



The addition of the cytotoxic fragment did not affect the spectral properties of DPBP, which makes the obtained compound an interesting object for further *in vitro* and *in vivo* studies.

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Ostroverkhov P.V.[1], Vedenyapina D.G.[1] Semkina A.S.[2,4], Plotnikova E.A.[3], Naumenko V.A.[4], Melnikov P.A.[2], Vodopyanov S.S.[3], Mironov A.F.[1], Majouga A.G.[5], Chekhonin V.P.[2], Abakumov M.A.[2,4], Grin M.A.[1]

MONITORING OF THE ACCUMULATION OF PHOTOSENSITIZERS BY MRI

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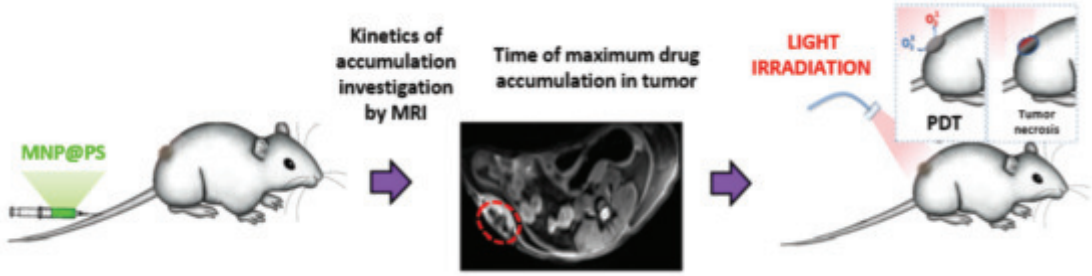
Earlier nanostructured photosensitizers (PS) based on bacteriochlorophyll *a* derivatives and magnetic nanoparticles (MNPs), coated with human serum albumin (HSA), were obtained. Their physicochemical properties, including spectral properties, size, shape, and elemental composition, were investigated. During in vitro biological tests accumulation in tumour cells and photoinduced cytotoxicity of MNP @ PS were shown. [1].

In this work, a comprehensive study of the biological properties and effectiveness of previously obtained structures was carried out *in vivo*. To study the biodistribution and kinetics of the accumulation of MNP@ PS in tumours of different genesis, we used the methods of local electron spectroscopy, optical imaging IVIS and magnetic resonance imaging. It was demonstrated that all three methods give similar results for the biodistribution of the drug, as well as the time of maximum accumulation of the drug in the tumour and it was 1 hour after intravenous administration.

The study of photodynamic efficiency in vivo confirmed the data of the kinetics of drug accumulation in the tumour: the most effective inhibition of tumour growth was observed during irradiation within 1 hour after the injection of MNP@ PS.

Thus, it became possible to track the accumulation of PS in the tumour using MRI without resorting to optical methods that have several limitations.



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Pogorilyy V.A., Noev A.N., Evdokimova E.V., Goncharova A.S., Tihonov S.I., Grin M.A.

PERIPHERAL MODIFICATION OF NATURAL BACTERIOCHLORINES MACROCYCLE BY SULFUR-CONTAINING AGENTS

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Numerous sulfur-containing compound including amino acids are used in development of pharmaceutical substances in medicinal chemistry. Attachment sulfur-containing fragments to chlorine and bacteriochlorine macrocycle can change the pharmacokinetics, biodistribution in organ and tissues, can increase photodynamic efficiency of PS due to interaction with antioxidant system. The structure of bacteriochlorine macrocycle opens up the opportunities for modification of periphery including propionic residue at the 17 position and exocycle-E.

The treatment of bacteriopurpurin (BP) with a sulfur-containing compound lead to introduction tiol-fragment to molecule with obtaining of sulfoxides, sulfones and also alkylation of the sulfur atom in order to obtain a new sulfur-containing derivatives of BP with given properties.

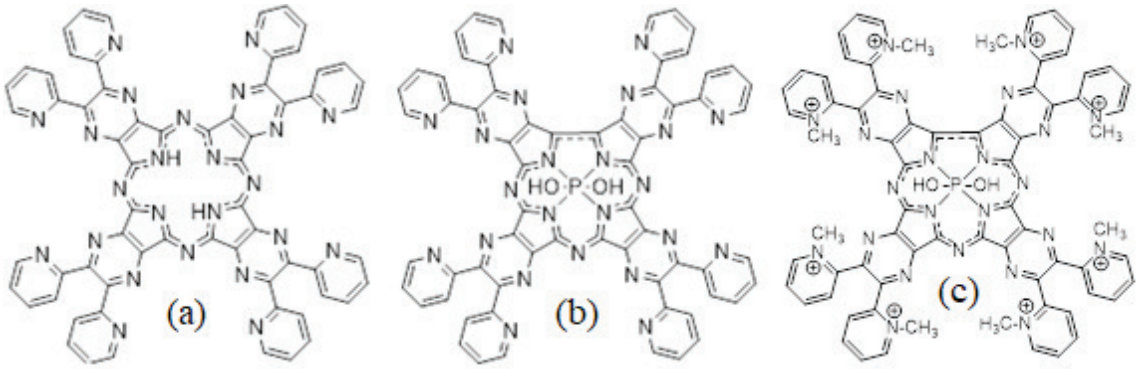
During the work the 17 position of macrocycle was modified by sulfur-containing amino acids. Received derivatives in experiments in vitro and in vivo showed greater activity then leader compound O-propiloxime-N-propoxibacteriopurpurinimid.

Popov A.A., **Sal'nikov D.S., Donzello M.P., Ivanova S.S., Stuzhin P.A.**

SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE PHOSPHORUS(V) TETRAPYRAZINOCORROLAZINE BEARING EIGHT N-METHYLATED 2-PYRIDYL GROUPS

Ivanovo State University of Chemistry and Technology
Dipartimento di Chimica, Università di Roma "La Sapienza", Italy

Tetrapyrazineporphyrazines (TPyzPz) and their complexes are actively studied as efficient photosensibilizers for PDT. For 2-pyridyl substituted macrocycle [$Py_8TPyzPzH_2$] (a), its metal complexes hydrophylic N-methylated derivatives and multimetallic complexes for bimodal cancer therapy were obtained by Ercolani and others [1].



Previously it was shown for phenyl and alkyl substituted porphyrazines, that heating of [$R_8TPyzPzH_2$] (R = Ph, Me. Et) with PBr_3 leads to contaction of the macrocycle and formation of corresponding P(V) corrolazines [($R_8TPyzCz$)$P(OH)_2$] [2]. In a similar way we have obtained 2-pyridyl substituted complex [($Py_8TPyzCz$) $P(OH)_2$] (b) by reaction between [$Py_8TPyzPzH_2$] and PBr_3 in pyridine. It was proved by ^{31}P NMR that P is in sp^3d^2-hybrid state and has two axial -OH groups exhibiting acidic properties. It is unsoluble in most organic solvents except pyridine, DMSO, DMF. However it is soluble in acid or alkaline water solutions of acids due to protonation of pyridyl groups or acid ionization of phosphonate moiety $P(OH)_2$. Water soluble octacationic form with N-methylated pyridine [$(PyCH_3)^+_8TPyzCz$)]$P(OH)_2$ (c) was also obtained. Dependence of the electronic absorption and emission spectra from the pH of aqueous solutions have been studied and two ionization constants pKa_1 = 3.57 and pKa_2= 8.29 were determined for [$(PyCH_3)^+_8TPyzCz$)]$P(OH)_2$]. Octaquaternized corrolazine is non-aggregated in water solution and exhibit high singlet oxygen quantum yield $\Phi(^1O_2)$ = 0.56.

The work was supported by Russian Science Foundation (Grant 17-13-015220).

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Skvortsov I.A.[1], **Novakova V.**[2], **Zimcik P.**[2], **Stuzhin P.A.**[1]

SYNTHESIS AND PHOTOPHYSICAL FEATURES OF SUBAZAPHTHALOCYANINES

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Subphthalocyanines (subPcs) are lower homologes of phthalocyanines with three isoindole units and a boron atom in the center. Their conical shape and possibility to atach an axial substituent are useful to prevent aggregation, which made subPcs interesting fluorophores for biological studies.[1] Azasubstitution in benzene rings of subPcs, forming thus subpyrazinoporphyrazines (subPyzPzs), should affect their photophysical properties, similarly as observed at phthalocyanines and their aza-analogues tetrapyrazinoporphyrazines.[2]

Herein, we present synthesis and study of a series of hexaphenyl and unsubstituted subPcs and subPyzPzs (Fig. 1). For axial modifications, Cl-, phenol (A), dimethyl-*p*-aminophenol (B) or hydroquinone (C) were chosen to study the possibility of photo-induced electron transfer (PET) from an axial ligand to macrocyclic core. PET is responsible for quenching of excited states keeping compound in inactive form, while blocking of PET lead to switching on intense fluorescence. Synthesis of target the compounds was done as a one-pot cyclotrimerization by heating coresponding dinitrile with boron trichloride followed by an addition of appropriate axial ligand.

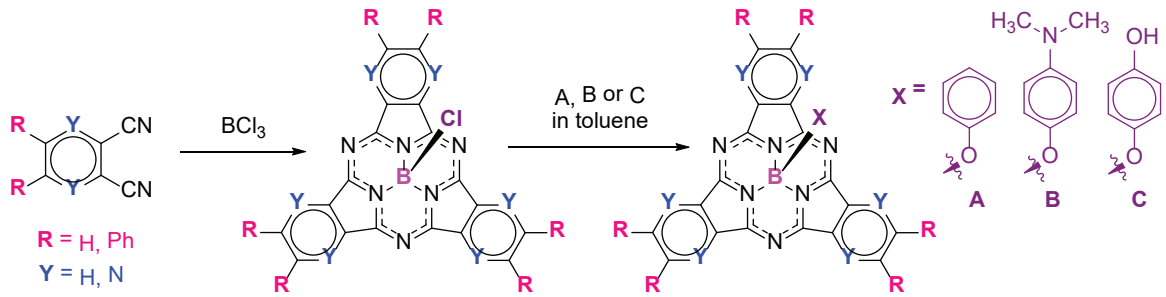

Fig. 1.

All compounds were studied from spectral and photophysical point of view. Quantum yields of fluorescence and singlet oxygen production were determined both in neutral medium (DMF, DCM) and after addition of acid or base. Subsequent effect on switching the photophysical properties on and off will be discussed.

Acknowledgement. *This work was supported by Russian Science Foundation (grant № 17-13-01522) – synthesis; Russian Federation Presidential internship for study abroad in 2018-19 (order № 410) – axial modification and photophysical measurements.*

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NANOSTRUCTURED LANGMUIR-SCHAEFER FILMS OF METAL-FREE TETRAPHENYLPORPHINE

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The objective of this work is to study the possibility and conditions for the formation of nanoaggregates of metal-free tetraphenylporphine (H_2TPP) at the air-water interface and in the films on quartz plates formed by Langmuir-Schaefer (LS) technique. The floating layers were formed on the Langmuir trough "KSV-NIMA" from the solution of the compound in dichloromethane ($C = 3.3 \cdot 10^{-5}$ M, compression rate is 2.2 $cm^2 \cdot min^{-1}$). The structure of the floating layers was analyzed within the framework of an original model and method for quantitative analysis of compression isotherms of nanostructured M-monolayers [1,2].

It is shown that tetraphenylporphine at the air-water interface, at the range of initial surface coverage degree c_{face} from 5 to 15 % and low surface pressures (up to 0.5 mN/m) forms stable monolayers. Molecules of H_2TPP in nanoaggregates are parallel to the water surface. The surface area per molecule in a nanoaggregate (A_{mol}) is in the range of 13–9 nm^2, the number of molecules in an aggregate (n) is 32–92. M-nanoaggregates are characterized by a large size (the diameter of the aggregates is 25–32 nm) and the relatively low density (0.12–0.18). For comparison, the diameter and density for the previously studied derivatives of macroheterocyclic compounds are 10–13 nm and 0.8, respectively [3,4]. The density of the layer at initial points of the stable state, according to the surface coverage degree by M-aggregates (c_{aggr}), is 93 %, instead of 75–87 % for azaporphyrins. Compressibility of the monolayer is 280–160 m/N.

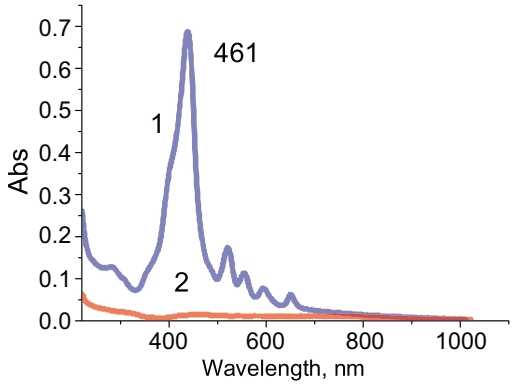

Fig. 1. *UV-Vis spectra of the LS-films of H_2TPP: (1) initial, (2) ten days aging*

The spectra of Langmuir-Schaefer films obtained from nanostructured polylayers of H_2TPP are characterized by strong red shift of the Soret band (17 nm), and red shift of the Q bands (4–6 nm) with respect to the spectrum of the solution (Sore – 434 nm, main Q – 515 nm). It was shown that in ten days the film quasi not absorbs in visible region (very week absorption at 460 and in the region of 700–800 nm, Fig. 1).

The work is performed in the framework of the State task of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018/4.6).

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NOVEL USE OF CHLOROFILLIPT, CHLOROPHYLONG AND FOOD ADDITIVE E 141 AS A PHOTOACTIVE AGENT

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The long-established drug "Chlorophyllipt" used in the treatment of infectious diseases was proposed by our team to study its biological and photophysical properties as a new promising photoactive agent. Comparison preparations were selected «Chlorophyllong» and food supplement E 141, which are also obtained on the basis of chlorophylls and have similar properties. All preparations showed dark toxicity on the MCF-7 breast carcinoma cell culture with a maximum active substance concentration of $4.82–6.87\times10^{-4}$M.

To solubilize the oil preparation "Chlorofillipt" micellar solutions of oil: phosphatidylcholine (PC) were prepared in a molar ratio of 1:1; 1:3; 1:7, which were characterized spectrophotometrically and using the method of laser light scattering, calculated their z-potential. The solution with the molar ratio 1: 1 turned out to be the most stable; the particle size was about 500 nm.

The photodynamic activity of the preparations was assessed by the change in the absorption spectra of hemoglobin during deoxygenation [1], thus, the rate of deoxygenation of hemoglobin is directly proportional to the rate of generation of singlet oxygen. To record the absorption and fluorescence spectra of the samples under study, a LESA-01-BIOSPEC fiber-optic spectrometer was used. To excite the PS, a semiconductor laser source with a wavelength of 660 nm was used, the power density in the measurements was 200 mW/cm^2. Solutions of the studied drugs were prepared in the blood plasma of cattle, and then erythrocyte mass was added, the percentage of plasma in the test sample was 60 %, erythrocyte mass – 40 %. Irradiation was carried out for three minutes. It was shown that an alcoholic solution of chlorophyll ("Chlorophyllong") has the highest photodynamic activity among the studied samples. At the same concentration (4.82 μM), the rate of hemoglobin deoxygenation in the study of the "Chlorophyllong" preparation was 0.011 [1 / s], "Chlorophyllipt" – 0.005 [1/s] and for E 141 0.0005 [1/s], respectively.

This work was financially supported by the Program of Fundamental Scientific Studies of the State Academies of Sciences for 2013–2020.

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Alpatova V.M.[1,2], **Ol'shevskaya V.A.**[1], **Kononova E.G.**[1], **Bragina N.A.**[2], **Konovalova N.V.**[2]

CARBORANE CONJUGATES OF PORHYRINS BASED ON *MESO*-AMINOPHENYLPORPHYRIN AND MERCAPTO-CARBORANES

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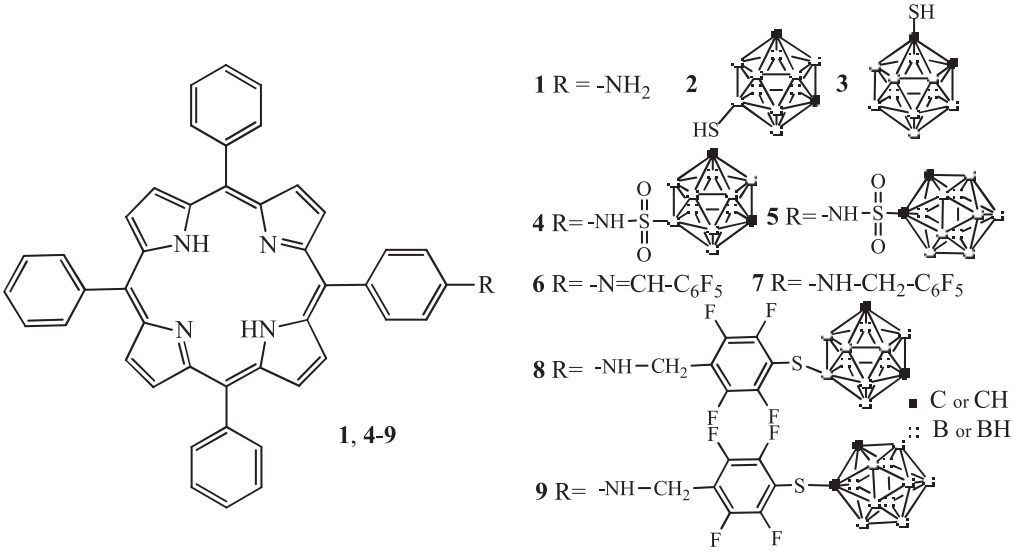
Porphyrins and chlorins play an important role as photosensitizers in antitumor photodynamic therapy (PDT). Due to their low or null dark toxicity and the ability to generate oxidative burst in the cells upon activation with light make these compounds exceptionally suitable for the design of therapeutic photosensitizers. The functionalization of the porphyrin/chlorin macrocycles with boron polyhedra makes it possible to selectively destroy malignant tumors using PDT and boron neutron capture (BNCT) therapy. A new carboranylporphyrins bearing sulfonamide or tetrafluorophenyl groups were synthesized starting from 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (**1**) and 9-mercapto-*m*-carborane (**2**) or 1-mercapto-*o*-carborane (**3**).

A series of novel carboranyl-substituted sulfonamide porphyrins **4**, **5** were synthesized in good overall yields by the reaction of amino group of porphyrin **1** with carboranylsulfonyl chlorides prepared *in situ* by oxidative chlorination of mercapto groups in carboranes **2** and **3** with trichloroisocyanuric acid (TCCA) in $MeCN–H_2O$ system.

Pentafluorophenyl-substituted porphyrin prepared by condensation of amino group of porphyrin **1** with 2,3,4,5,6-pentafluorobenzaldehyde resulted in Shiff bass **6** which was reduced into corresponding secondary amine **7** with $NaBH_4$. Nucleophilic substitution of the *para*-fluorine atom in prepared pentafluorophenyl-substituted amino porphyrin **7** with carborane **2, 3** proceeded readily providing fluorinated carboranyl porphyrins **8**, **9** in good yields.



The structure of all compounds obtained was confirmed by means of different spectroscopic techniques such as UV-Vis, IR, ^1H, ^{11}B, ^{19}F NMR and mass spectra.

Andreeva V.D.[1,2], **Shkirdova A.O.**[1,2], **Zamilatskov I.A.**[2], **Tyurin V.S.**[2], **Lonina N.N.**[1], **Ponomarev G.V.**[3]

SYNTHESIS OF HYDRAZONES AND AZINES OF NI(II) AND PD(II) COMPLEXES OF BALKYLPORPHYRINES

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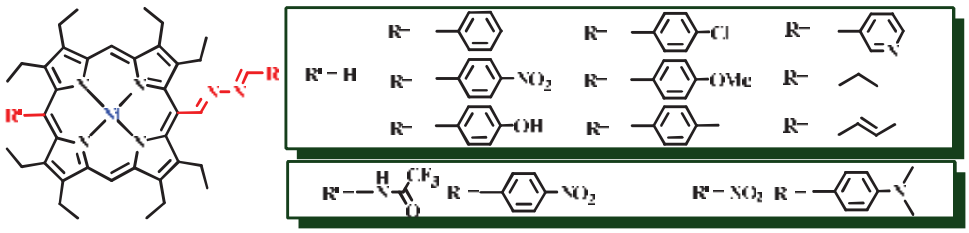
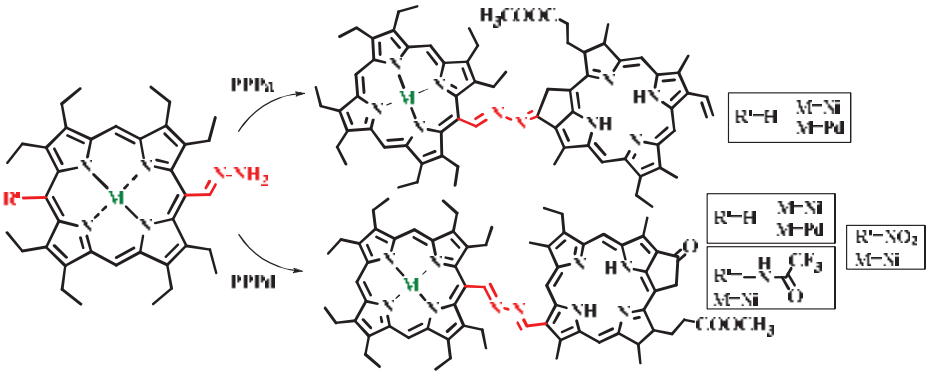
It's known that azines are widely used as dyes, sensitizers, luminescent liquid crystal materials, optoelectronic materials in nonlinear optics and components of organic field-effect transistors (OFET) due to its optical and electronic properties. These compounds are also potential antiviral and anticancer agents.

A new approach to functionalize Pd(II) and Ni(II) complexes of β-tetraalkyl porphyrins based on the azine formation from the corresponding carbonyl derivatives was developed and a new class of the compounds namely porphyrin azines was obtained.

Starting object for preparation of azines was chosen to be tetrapyrrolic compound - β-octaethylporphyrin (OEP). Palladium and nickel complexes of OEP were subjected to the Vilsmeier-Haack reaction, during which the Vilsmeier's reagent electrophilically substituted proton at a *meso*-position of the tetrapyrrolic macrocycle. Then, the hydrazine hydrate was added to the intermediate *meso*-iminium salt, leading to the formation of an unsubstituted *meso*-hydrazone. The obtained hydrazones were then introduced into a reaction with various aldehydes (aromatic, aliphatic, α,β-unsaturated) resulting in the formation of a number of porphyrin azines where the azine bridge linked OEP metal complexes with other functional fragments.



Dyads of metal complexes of OEP with pyropheophorbides-*a* and -*d* linked by the azine bridge were also obtained.



With the aim to study the mutual effect of both donor and acceptor substituents at *meso*-positions of OEP on its optical properties, we obtained a number of new porphyrin azines, which were so called "push-pulls".

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NOVEL CHLORIN E_6 DERIVATIVES WITH BULKY SUBSTITUENTS IN THE 13-AMIDE GROUP

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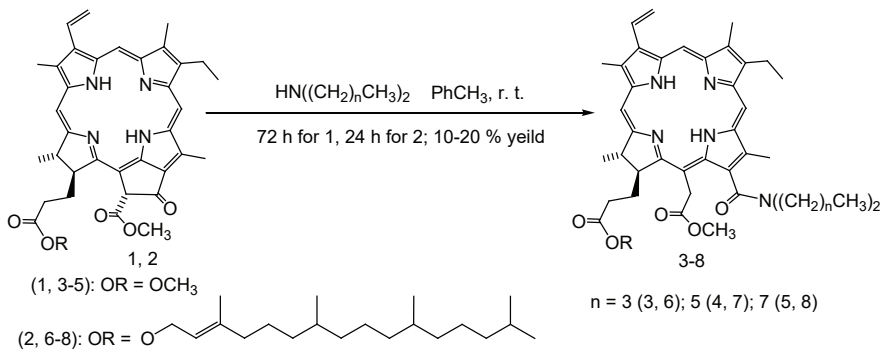
The reactions of exocycle of methylpheophorbide *a* **1** and its analogs can be used for synthesize of new macrocyclic compounds. It is known that under the action of amines on **1**, the excocycle can be opened to form the corresponding 13-amide chlorin e_6 derivatives or amidation of the esocycle esocycle while preserving the latter and it depends on the structure of the amine and the reaction conditions [1 and references there]. Opening exocycle to date has only been achieved under the action of primary and secondary aliphatic amines of relatively simple structure, and the corresponding dialkylamines 13-amide derivatives were obtained under the action of dimethyl-, diethyl- and dipropylamine. The data available in the literature allow us to conclude that the most favorable conditions for the formation of the hydrogen bond of an amine molecule with the esocycle group of the exocycle, contributing to exocycle opening, are low temperature and a large excess of amine. Based on these considerations, we studied the interaction of large (500 or more times) molar excesses of dibutyl-dihexyl- and diocthylamines with **1** and pheophytin *a* **2** and the corresponding 13-amide derivatives of chlorin e_6 were synthesized with average yield (Scheme 1).



Scheme 1

The study is supported by Program of UD RAS, project No 18-3-3-27. This work performed using equipment of the CCU «Chemistry» at the Institute of Chemistry of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar)

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THE INTERACTION PHEOPHYTIN *A* WITH ETHANOLAMINE

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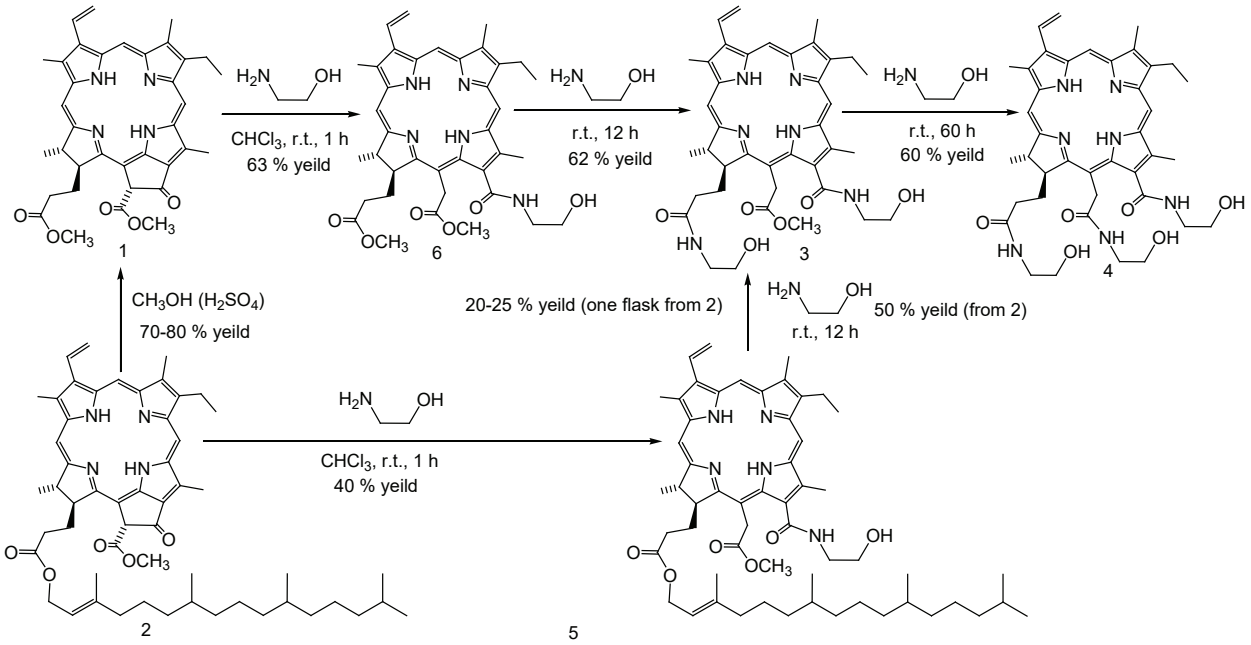
At present methylpheophorbide *a* **1** is the most accessible chlorophyll *a* derivative, in most cases it is this compound that is used as a starting material in the synthesis of various chlorins. Pheophytin *a* **2** may enter into similar reactions. It is known that under the action of ethanolamine on **1** hydrophilic chlorin e_6 derivatives can be obtained with two **3** and three **4** hydroxyl groups (Scheme 1) [1], the total yield of **3** (3 stages from 1) is about 30 %. In the present work, the interaction of **2** with ethanolamine was studied with the aim of obtaining compounds **3** and **4**, bypassing the preparation of **1**. It was shown that the entire sequence of transformations can be carried out for **2** under the same conditions as for **1**. The relatively low yield of **3** from **2** due, apparently, to a lower yield of 5 compared to 6 at the stage of exocycle opening but it is largely offset by a reduction in synthesis of one stage and the possibility of carrying out the process without using methanol. Thus, pheophytin *a* **2** is an acceptable alternative to **1** when preparing hydrophilic chlorin e_6 derivatives **3** and **4**.



Scheme 1

The study is supported by Program of UD RAS, project No 18-3-3-27. This work performed using equipment of the CCU «Chemistry» at the Institute of Chemistry of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar)

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Belykh D.V.,[1] Kozlov A.S.,[2] Pylina Y.I.,[3] Khudyaeva I.S.,[1] Benditkis A.S.,[2] Krasnovsky A.A.[2]

COPPER COMPLEXES OF CHLORIN DERIVATIVES OF CHLOROPHYLL *A* AS POTENTIAL PHOTOSENSITIZERS FOR MEDICAL PURPOSES

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Absorption spectra, fluorescence, singlet oxygen photosensitization and photoinduced cytotoxic activity in the HeLa cells line were investigated for copper complexes of chlorins (methylpyropheophorbide *a* and exocycle-free 13-amide derivatives of chlorin e_6 dimethyl ether) (Fig. 1) obtained by chemical modification of chlorophyll *a*.

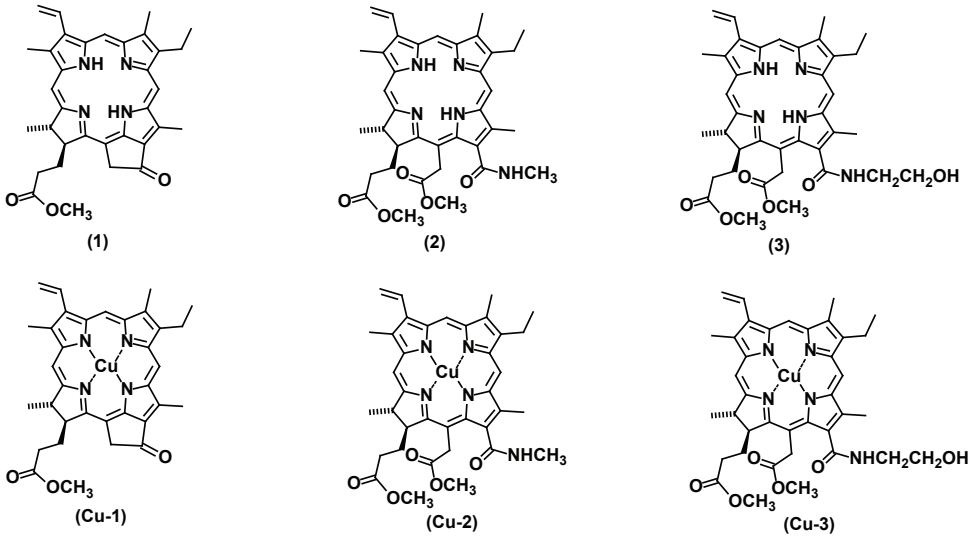

Fig. 1. *Chemical structures of the investigated compounds: (1) methykpheophorbide a; (2, 3) – exocycle-free 13-amide derivatives of chlorin e_6 dimethyl ether; (Cu-1), (Cu-2) u (Cu-3) – copper complexes of these compounds*

The results are compared with the properties of metal-free analogs. It is shown that both copper complexes and metal free chlorins generate singlet oxygen under photoexcitation in solutions and show distinct phototoxicity in living cells. The photosensitizing effect of copper complexes is 4–13 times smaller, but remains rather high. According to the biological experiments, the activity of copper complexes is sufficient for photodynamic killing of HeLa cells. At the same time, the dark toxicity of copper complexes is lower than that of metal free chlorins. These data allow us to consider copper complexes of chlorins as a new class of photosensitizers, potentially suitable for the use in PDT.

The work was performed in accordance with the State Tasks of the Institute of Chemistry, Komi Scientific Center, Ural Branch of the Russian Academy of Sciences (Syktyvkar) and FIC Biotechnology, Russian Academy of Sciences (Moscow), with partial financial support from the Russian Foundation for Basic Research (project No. 19-04-00331).

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Berezin D.B.[1], **Kustov A.V.**[1,2], **Krest'yaninov M.A.**[2], **Shukhto O.V.**[1], **Belykh D.V.**[3], **Startseva O.M.**[3], **Kukushkina N.V.**[1], **Makarov V.V.**[1]

QUANTITATIVE EVALUATION OF THE INTERACTION OF HYDROPHILIC DERIVATIVES OF CHLORIN E_6 WITH NON-IONIC SURFACTANT TWEEN 80

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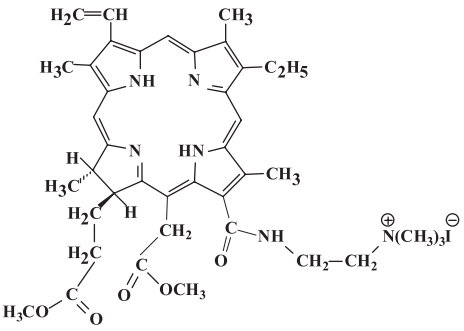
We have studied the behavior of perspective photosensitizers (PS) for photodynamic therapy (PDT) based on chlorin e_6 containing cationic trialkylammonium (I) or diethylene glycol (II) hydrophilic groups in water, aqueous solutions of ethanol and biocompatible non-ionic surfactant Tween 80 (Polysorbate 80), which forms spherical micelles with an aggregation number of 60 in highly dilute aqueous solutions.



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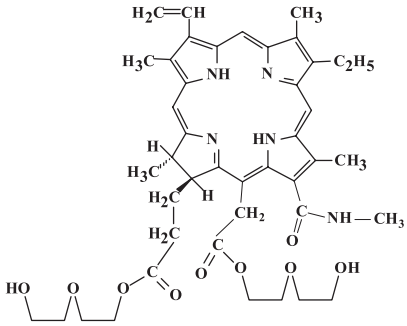

II

Monocationic chlorin PS I is a hydrophilic compound with a rather low distribution coefficient [1]. During spectrophotometric titration of ethanol solution of I and II, the H-association of PSs is observed at 60 and 80 wt.% H_2O, respectively. The formation of H-associated dimers is confirmed by a decrease in the intensity of the long-wavelength Q_x-band in the UV-VIS spectra of I and II, as well as by an efficient fluorescence quenching of PSs in water compared to the ethanol solution, where chlorins exist in molecular form [2].

During the titration of aqueous solutions of PSs I and II with the Tween 80 an absorption (A) in Q_x-band was increased and reached the value of the non-aggregated form of chlorin observed in ethanol [2]. Change of A is associated with a disaggregation of PS and its interaction with components of Tween 80 micelle. We proposed a model to estimate the interaction constant K_b and the number of PS-interacting surfactant molecules n [3]:

$$\lg[(A-A_0)/(A_{max}-A_0)]/(1-(A-A_0)/(A_{max}-A_0)) = \lg K_b + n\cdot\lg[C_T^m - n\,(C_{PS}(A-A_0)/(A_{max}-A_0))] \quad (1)$$

One of the ways to determine the location of the PS introduced into the surfactant micelle is to analyze the dynamics of its fluorescence in the presence of a quencher (KI). It was found that PS molecules are not deeply included into the structure of micelles. Chlorin I with a polar positively charged group tends to be located in superficial layers of the surfactant micelle.

This work was supported by the Russian Scientific Foundation (Grant 15-13-00096).

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Berezina G.R., Medvedeva M.A.

SYNTHESIS OF ASYMMETRIC MACROCYCLIC COMPOUNDS WITH FRAGMENTS OF CYCLOPENTA[CD]PHENALENE

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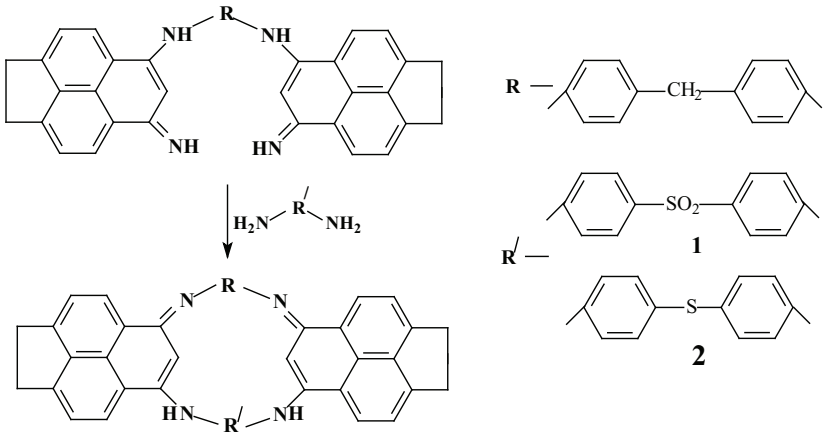
Chemistry of macroheterocyclic compounds is rapidly developing, actively accumulating the successes of synthetic organic chemistry, as well as methods of physical and chemical research.

This work is a continuation in the field of synthesis and research of macroheterocyclic compounds. The report discusses experimental data on the synthesis and spectral properties of macrocyclic compounds with cyclopent[cd]fragments of phenalene and biphenyl.

The interaction of [bis-(N-4,4′-2,7,7a,9a-tetrahydro-7-imino-1*H*-cyclopenta[cd]phenalene-5-il]biphenyl-methyl with diaminodiphenylsulfone and diaminodiphenylsulfide synthesized macrocycles of asymmetric structure, which are soluble in water and can be used in various fields of science and technology.



The synthesized compounds are powdery substances with different shades of brown, having decomposition temperatures and soluble in water, ethanol, DMF and conc. sulfuric acid. The structure is proved by spectral methods, the composition - by data of elemental analysis. Purified by column chromatography on aluminum oxide. In a solution of concentrated sulfuric acid compounds fluoresce green.

Berezina G.R., Medvedeva M.N.

THE SOLUBILITY OF THE UNSYMMETRICAL MACROCYCLIC COMPOUNDS WITH FRAGMENTS OF PHENYLINDANE AND THIADIAZOLES

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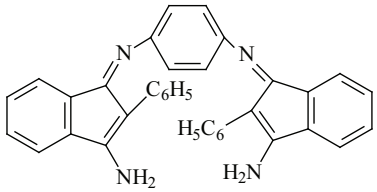
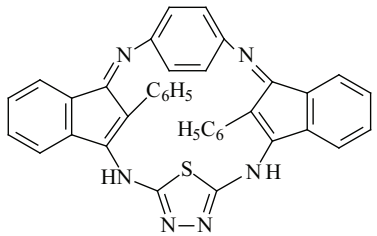
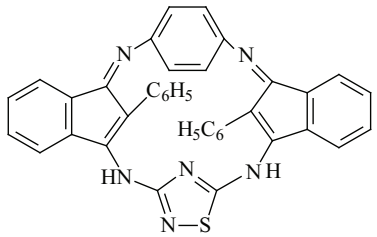
The equilibrium solubility ($\Delta G = 0$) of the synthesized compounds in ethanol and DMF at 298–318 K was determined by isothermal saturation (table). These polar solvents were chosen due to the fact that they have different structure and donor-acceptor properties. The solubility of the synthesized compounds was measured on a thermostatically controlled device for shaking the ampoules.

Connection structure	Organic solvent	lg ε	λ, nm	S·10³, mol/ l		
				298 K	308 K	318 K
 1	DMF Ethanol	3.94 3.69	455 461	20.40 2.76	125.01 6.38	225 9.7
 2	DMF Ethanol	4.08 3.50	460 466	2.71 1.74	49.29 14.35	92 27.25
 3	DMF Ethanol	4.15 4.06	450 456	5.33 1.50	45.85 2.57	83.15 3.62

The process of dissolution of the synthesized macrocyclic compounds has a positive temperature dependence. The solubility of macrocycles in DMF is 10^{-3} mol/l, which is an order of magnitude lower compared to an open compound. The increase in solubility (2 < 3 < 1) in a DMF solvent with a pronounced proton – acceptor function (DN ≈ 26) is due to a change in the protonization of NH-bonds due to the electronic effects of the d-conjugation chain. The most favorable conditions for solvation in an open joint. When considering the nature of changes in the solubility of the synthesized macrocyclic compounds, it can be concluded that despite the available centers of specific solvation, they appear to be sterically shielded from the interaction with the DMF molecule.

Bondareva E.A., **Suvorov N.V., Mironov A.F., Grin M.A.**

SYNTHESIS OF PSMA-TARGETED 13[1]- AND 15[2]-SUBSTITUTED CHLORIN E_6 DERIVITIES AND THEIR BIOLOGICAL PROPERTIES

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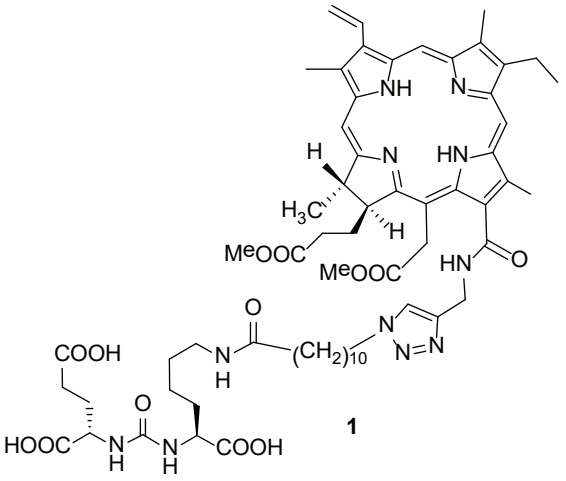
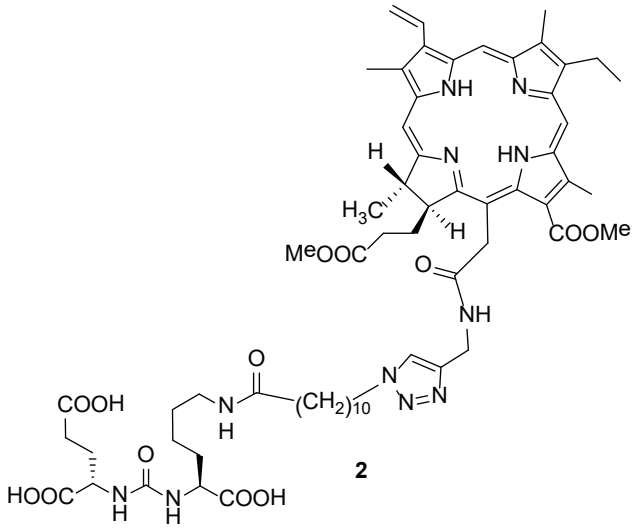
Photodynamic therapy is an effective anticancer procedure based on the administration of a photosensitizer (PS) into the body, its accumulation in a tumor with the subsequent exposure to a light wave, which leads to the generation of reactive oxygen species and the destruction of the neoplasm. At the same time, one of the disadvantages of cancer PDT is the insufficient selectivity of PS accumulation in tumor tissues, leading to diminished effectiveness of the method. A possible solution to this problem is the addition of small target molecules, such as a ligand to a prostate-specific membrane antigen (PSMA), to the PS. Overexpression of PSMA receptors is observed in prostate cancer cells, and its level correlates with the stage of the disease. This work is devoted to the synthesis of targeted photosensitizers based on chlorin e_6, containing PSMA ligand in 13[1]- and 15[2]-positions, as well as the study of their biological properties.

Conjugates of natural chlorins with the PSMA ligand were obtained by the reaction of a Cu-catalyzed azide-alkyne cycloaddition. This approach allowed to introduce of a spacer group into the molecule, which distributes the photoactive and vector elements in space, and to achieve high yields of the final products. Zinc complexes of dimethyl ether 13[1]-(propargylamido)chlorin e_6 and dimethyl ether 15[2]-(propargylamido)chlorin e_6 were obtained as alkyne components. The azide component was obtained by acylation of the terminal amino group of the PSMA ligand.





The phototoxicity of conjugates **1** and **2** was evaluated on prostate cancer cell lines 22Rv1 (PSMA +) and PC-3 (PSMA-). Radachlorin was used as a reference PS. The IC_{50} value of compound **1** for 22Rv1 cells was 1.2 ± 0.1 μM at 6 hours of incubation and exceeded the photoactivity obtained on PC-3 cells by 7 times. Radachlorin was less effective for 22Rv1 cells (IC50 = 3.0 ± 0.2 μM) compared to conjugate **1**. The values of IC_{50} for PS **2** were about the same for both cell lines.

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Chizhova N.V., Ivanova Yu.B., Mamardashvili N.Zh.

SYNTHESIS, ACID-BASE AND COORDINATION PROPERTIES OF UNSUMMETRIC SUBSTITUTED NITRO- AND BROMO-TETRAPHENYLPORPHYRINS

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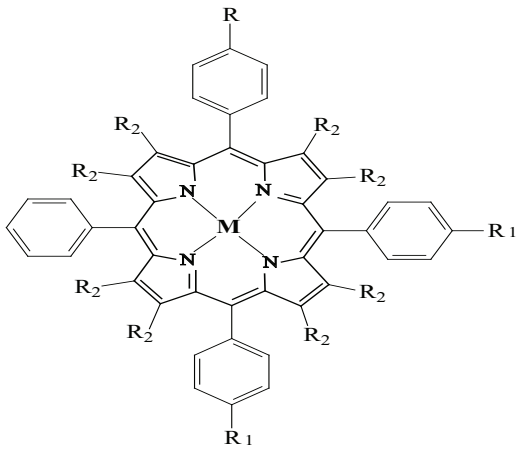
In order to obtain polyporphyrin supramolecular complexes on the basis selectively modified cobalt porphyrins in present work, the bromination reactions of Co(II)-5-(4-nirophenyl)-10,15,20-triphenylporphyrin (**1**) and Co(II)-5,10,15-tri-(4-nitrophrnyl)-20-phenylporphyrin (**2**) with N-bromosuccinimide (NBS) in a mixture of chloroform-dimethylformamide (DMF) are investigated.



R=NO_2, R_1=R_2=H, M=Co(II) (**1**),
R=R_1=NO_2, R_2=H, M=Co(II) (**2**),
R=NO_2, R_1=H, R_2=Br, M=Co(II) (**3**),
R=R_1=NO_2, R_2=Br, M=Co(II) (**4**),
R=NO_2, R_1=H, R_2=Br, M=2H (**5**),
R=R_1=NO_2, R_2=Br, M=2H (**6**).

It is shown that bromination of the compound **1** by excess of NBS in $CHCl_3$-DMF at room temperature within 2 h leads to the formation of a mixture of Co(II)- and Co(III)-octabromosubstituted porphy-rins. Chromatographic purification of the cobalt-porphyrins on basic alumina results in the formation of Co(II)-2,3,7,8,12,13,17,18- octabromo-5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**3**). Similarly, Co(II)-2,3,7,8,12,13,17,18- octabromo-5,10,15-tri-(4-nitrophenyl)-20-phenylporphyrin (**4**) is formed by interaction of the compound **2** with excess NBS in boiling $CHCl_3$-DMF mixture. When the compounds **3**–**4** were treated with a chloric and sulfuric acids mixture (4:3), 2,3,7,8,12,13,17,18-octabromo-5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**5**) and 2,3,7,8,12,13,17,18-octabromo-5,10,15-tri-(4-nitrophenyl)-20-phenylporphyrin (**6**) were obtained. The synthesized compounds were identified by UV-Vis, ^{1}H NMR spectroscopy and mass-spectrometry.

Acid-base properties of porphyrins **5**–**6** were studied by the method of spectrophotometric titration in acetonitrile. Acidity and basicity constants of the synthesized porphyrins were determined and the concentration intervals for their ionized forms existence were established.

Possibility of formation of linear polyporphyrin complexes based on cobalt complexes of synthesized asymmetrically substituted macrocycles and two-center organic ligands of different nature were investigated by methods of ^{1}H NMR spectroscopy and mass-spectrometry.

This research was funded by the Russian Scientific Foundation (project № 19-73-20079) and performed with the use of equipment of the Shared Facility Centre, "the Upper Volga Regional Centre of Physicochemical Studies".

Dmitrieva O.A.,[1] Ivanova Y.B.,[1] Puhovskaya S.G.,[2] Semejkin A.S.,[2] Mamardashvili N. Zh.[1]

THE EFFECT OF PHENYL SUBSTITUTION ON THE PD-OCTAETHYLPORPHYRIN DERIVADIVES FLUORESCENT PROPERTIES IN ACETONITRILE

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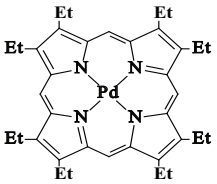
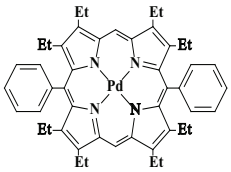
Fluorescence properties, quantum yields, excited state lifetimes and Stokes shifts of palladium complexes of the octaethylporphyrin (Pd(II)-OEP), 5,10- biphenyl octaethylporphyrin (Pd(II)-5,10-BPHOEP) and 5,15-biphenyl octaethylporphyrin (Pd(II)-5,15-BPHOEP) in acetonitrile at 295K were studied.



Pd(II) – OEP



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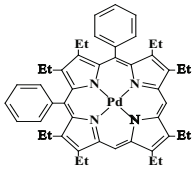

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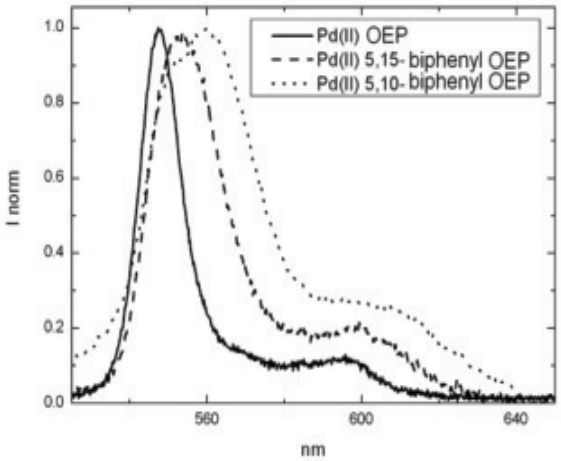

Fig. *Fluorescence spectra of palladium of palladium octaethylporphyrin complexes (cporph.~1.01·10^{-6}mol/l) in acetonitrile at 295 K, λ_{ex} =509 nm*

It was determined that introduction of the phenyl fragments into the 5.15-positions of the tetrapyrrolic macrocycle does not change the fluorescent properties of its complex. At the same time, asymmetric 5.10-biphenyl substitution of the octaethylporphyrin decrease the ligand quantum yield by 1.2 times, and increase the lifetime of the excited state by 1.5 times. It is shown that a strong bathochromic shift ~ 37.0–39.6 nm is observed in the fluorescence spectra. The effect of the metal nature on the UV/Vis spectra of palladium complexes of octaethylporphyrin in conjunction with literary data for metal complexes of porphyrin molecules of simpler structure is also analyzed.

This research was funded by the Russian Scientific Foundation (project № 19-73-20079) and performed with the use of equipment of the Shared Facility Centre "the Upper Volga Regional Centre of Physicochemical Studies".

Faustova M.R.[1], **Mollaev M.D.**[1], **Sokol M.B.**[2], **Nikolskaya E.D.**[2], **Zhunina O.A.**[2], **Lobanov A.V.**[3], **Shvets V.I.**[1], **Yabbarov N.G.**[2]

POTENTIAL APPLICATION OF PLGA PARTICLES WITH PORPHYRINS FOR TREATMENT OF NEOPLASTIC DESEASES

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[2]Biotechnology Laboratory Russian Research for Molecular Diagnostics and Therapy, Moscow, Russia,
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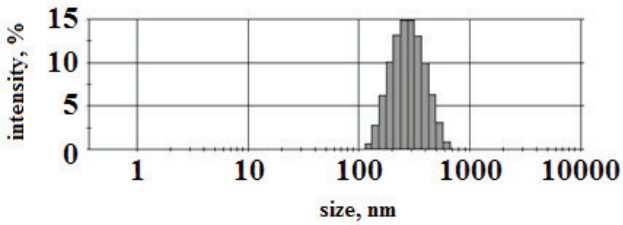
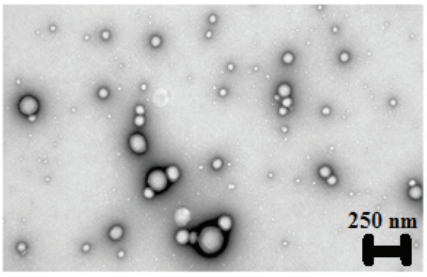
Nowadays, porphyrins and phthalocyanines are commonly used in the treatment of neoplastic diseases [1]. Cobalt-based phthalocyanines successfully serve as matrix for reactive oxygen species production. In present study, we have investigated Co^{II}-tetraphenylporphyrin (CoTPP) catalytic and cytotoxic properties in combination with ascorbic acid (AA). To increase the bioavailability of CoTPP, we developed a delivery system constituted of CoTPP in poly(*D,L* lactic-co-glycolic acid) particles. Nanoparticles were prepared by precipitation method and main particles parameters were optimized. The results demonstrated that entrapment efficiency was 61.30 %, CoTPP loading – 6.89 %, mean particles size – 273.3 nm, zeta potential was –15.6 mV and polydispersity index was 0.190. CoTPP catalytic activity was analyzed spectrophotometrically by recording data during oxidation-reduction reaction with ascorbic acid under physiological conditions. We noted that CoTPP nanoparticles attend longer in the reaction solution than free CoTPP. Higher stability of nanoparticles was probably due to sustained release of CoTPP. The results of MTT assay showed that nanoparticles in combination with AA exhibit antitumor activity against K562 cell line, probably due to the interaction of CoTPP and AA, which led to the reactive oxygen species formation. The results revealed that free CoTPP as well as free AA at the same concentration has no effect on the viability of the cells. As a positive control, K562 cell line was treated with 3-amino-1,2,4-triazole, a catalase inhibitor, which increased the cytotoxic activity of CoTPP with AA against K562 cell line.





Acknowledgements. *This work was supported by the Russian Foundation for Basic Research (project No 17-04-01009\19).*

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Fazlyeva A.M., Skvortsov I.A., Stuzhin P.A.

SYNTHESIS OF PORPHYRAZINES FROM ALKYL SUBSTITUTED 6,7-DIHYDRO-1*H*-1,4- DIAZEPINE-2,3-DICARBONITRILES

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Porphyrazines containing 1,4-diazepine fragments with two acceptor imino groups [1] and their tetrahydro derivatives with donor amino groups [2] are described in the literature. In this work, porphyrazines with 6,7-dihydro-1*H*-1,4-diazepine rings combining acceptor imino and donor amino groups were obtained for the first time.

By the condensation of diaminomaleonitrile with acetone or cyclohexanone, according to the method [3], 6,7-dihydro-1*H*-1,4-dicarbonitriles were obtained, which were used as precursor for porphyrazines. Their cyclotetrametization in the presence of magnesium amylate affords the Mg(II) complexes, while reaction with lithium amylate leads to the corresponding metal free macrocycles (Figure 1,3).

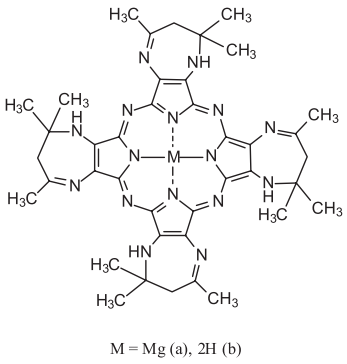

Fig. 1

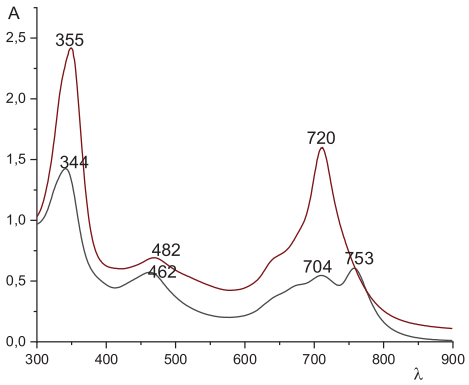

Fig. 2

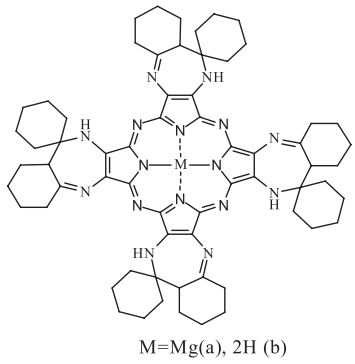

Fig. 3

The formation novel macrocyclic compounds was confirmed by MALDI-TOF spectra and ^{1}H NMR measurements. In the electronic absorption spectra the long-wavelength absorption band is observed in the near IR region at 700–750 nm (Figure 2). Therefore, the use of these compounds as photosensitizers for photodynamic therapy is promising.

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Fedotova M.K.[1], **Smirnova A.G.**[1], **Sivaev I.B.**[2], **Bregadze V.I.**[2], **Mironov A.F.**[1], **Grin M.A.**[1]

MULTIFUNCTIONAL PLATFORM BASED ON CHLORINE CONJUGATES WITH TETRAAZAMACROCYCLE FOR MRI AND BNCT APPLICATIONS

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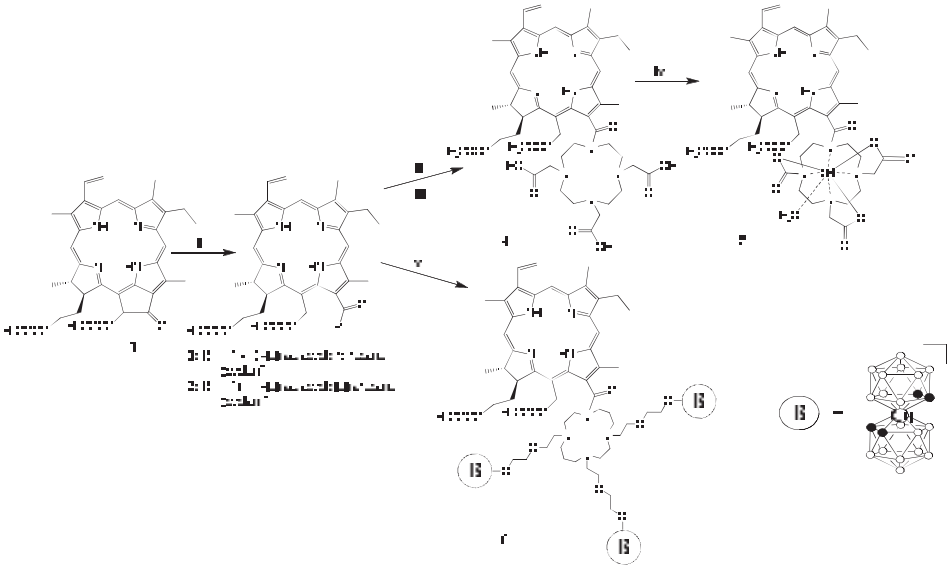

Scheme 1. *Modification of chlorine conjugates with tetraazamacrocycles. Reagents and conditions: i, cyclen/cyclam, piridyn; ii, $BrCH_2COOC(CH_3)_3$, CH_2Cl_2, DIPEA; iii, 80 % TFA; iv, $GdCl_3 \times 6H_2O$, CH_2Cl_2, CH_3OH, DIPEA; v, 1,4-dioxane-$(C_2B_9H_{11})Co(C_2B_9H_{10})$, $CH_3CN:C_2H_5OH$ (1:1)*

Introduction to the periphery of the chlorine macrocycle of other macrocycles capable of additional functionalization or complexation allows the creation of multifunctional conjugates with predetermined physicochemical and biological properties. In the present study, derivatives of natural chlorine with tetraazamacrocycles (cyclen and cyclam) were obtained as possible precursors for creating a contrast agent for MRT diagnostics, as well as for increasing the number of boron atoms in one chlorine molecule.

Into the previously obtained [1] dimethyl ether of chlorine e6 with tris-methylene (*tert*-butylcarboxy) substituted cyclen **4**, Gd^{3+} was introduced in the basic medium. Direct evidence of the presence of the Gd^{3+} cation in the metal complex **5** was implemented by atomic emission spectroscopy (AES). The T1 relaxivity of Gd^{3+} ions in an aqueous solution was determined by the ClinScan 7T magnetic resonance imaging system using the Inversion Recovery mode. The magnitude of T1 relaxivity was 1.8 $\mu M^{-1}s^{-1}$ (Dotarem® 4.2 $\mu M^{-1}s^{-1}$; Gadovist® 3.6 $\mu M^{-1}s^{-1}$).

The addition of cyclam to the methyl ester of pheophorbide *a* **1** took place in the same way as the reaction with cyclen. Three secondary nitrogen atoms in the cyclam unit of compound **3** are available for the opening of the dioxane ring and the addition of 1,4-dioxane-bis (dicarbolide) cobalt.

Acknowledgements. *The authors thank the support of grants RFBR №19-03-00255.*

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Fomina A.V., Marova A.A., Ivanova S.S., Stuzhin P.A.

BORON(III) SUBPHTHALOCYANINATE AND ITS ANALOGUES AS CHROMOGENIC SENSORS FOR ANIONS

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Subphthalocyanines are the lowest homologues of phthalocyanines, consisting of three isoindole moieties arranged around the boron atom. They were first obtained in 1972 by cyclotrimerization of phthalonitrile in the presence of boron trichloride. Subphthalocyanines show interesting spectral features and properties that reveal perspectives of their practical application in various fields, *i.e.* as pink dyes, photosensitisers, in organic photovoltaics, nonlinear optics, *ets*. [1]. Is was reported that dodecachlorosubphthalocyanine can be used as fluorochromogenic sensor for cyanide anions [2].

We have studied the influence of various anions (fluoride, bromide, hydroxide, cyanide, cyanate, thiocyanate, dihydrophosphate and acetate) on spectral properties of boron subphthalocyanine (SubPcB) and its analogue containing 1,2,5-thiadiazole fragments instead of benzene rings (SubPz(SN_2)B). Both dyes are highly sensitive to toxic cyanide anions, which cause an instantaneous discoloration of their pink solutions, and have more slow response for fluoride anions. In the presence of OH^- anions the pink solutions of the complexes turn blue with bathochromically shifted and widened Q-band, but after acidification by acetic acid the UV-Vis spectra get their initial form. As for other studied anions they have no effect of the spectral properties of subporphyrazines. Here, we try to look for the reasons and discuss mechanism of such sensing ability of the subporphyrazine structures.

This study was supported by Russian Science Foundation (17-13-01522).

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Glazkova M.E.[1], Rodina Yu.S.[1], Ageeva T.A.[1], Koifman O.I.[1,2]

METALLOISOPORPHYRINS IN MACROMOLECULAR CHEMISTRY

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Metalloisoporphyrins are the porphyrin tautomers. They are intermediate compounds in heme-oxidation, chlorophyll biosynthesis, and, therefore, have a catalytic potential and have prospects for widespread use in various fields [1]. The study of synthesis patterns of metalloisoporphyrins, as well as the determination of their role in macromolecular chemistry, in particular, in polymerization processes, is of great interest.

In this work the interaction of zinc and cobalt *meso*-tetraphenylporphyrins with benzoyl peroxide in methyl methacrylate was studied by the spectrophotometric method (Figure).

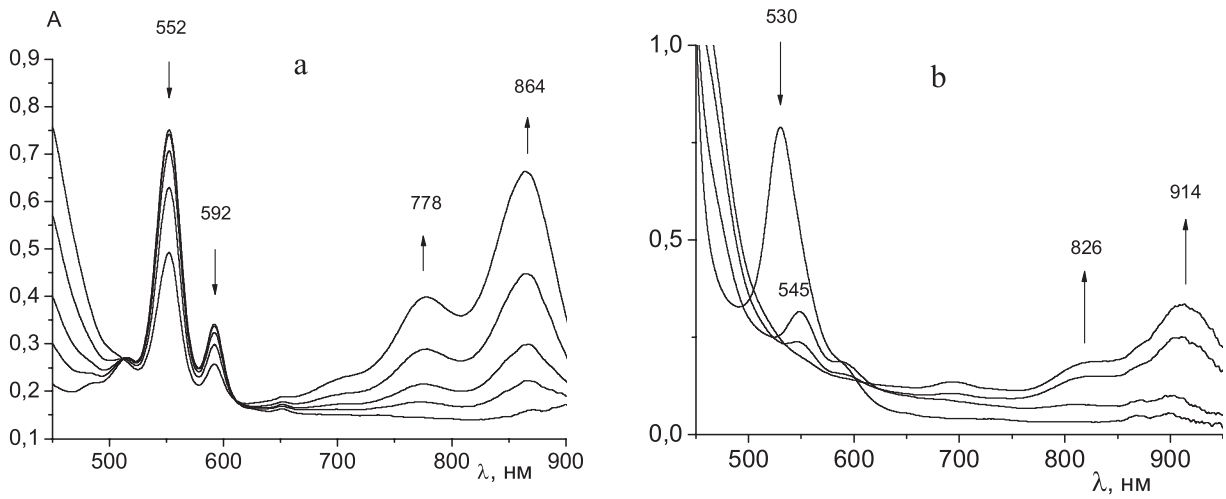

Fig. *Changes in the electronic absorption spectra of zinc meso-tetraphenylporphyrin (a) and cobalt meso-tetraphenylporphyrin (b) during interacting with an excess of benzoyl peroxide in methyl methacrylate*

It was established that the first stage of methyl methacrylate polymerization in the presence of these metal complexes included the formation of metalloisoporphyrins.

The study was carried out by using the Center for collective use of scientific equipment «ISUCT», in the framework of the State task (project № 4.9109.2017/7.8). This work was supported by the Russian Foundation for Basic Research (grant RFBR № 18-03-00986).

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Gornukhina O.V.[1], **Vershinina I.A.**[2], **Semeikin A.S.**[1]

STUDY OF THE DEPENDENCE OF THE COORDINATING PROPERTY OF POLYFLUOROALKYL SUBSTITUTED OF TETRAPHENYLPORPHYRIN FROM THEIR STRUCTURE

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As it is known, porphyrin compounds play a key role in many chemical and biochemical processes, and the possibility of introducing substitutes of different nature into the porphyrin cycle significantly expands the scope of their potential use. Therefore, the introduction of fluoroalkyl substituents into the porphyrin macrocycle attracts particular attention from researchers in connection with the development of FBS (*Fluorous Biphasic System*) technology, the development of photoelectroactive materials and the expansion of effective photosensitizers.

Also of no less interest is the study of the dependence of the coordination properties of polyfluoroalkyl-substituted porphyrins on the spatial structure of their macrocycle.

Therefore, we carried out a kinetic study of the coordination properties of polyfluoroalkyl-substituted tetraphenylporphyrin derivatives with d-metal salts (cobalt, copper, and nickel acetates) in non-aqueous media (acetic acid — benzene and pyridine).

The studies were carried out spectrophotometrically on a *Shimadzu UV-1800* scanning spectrophotometer. In parallel with these studies, a quantum-chemical calculation of porphyrin macromolecules was carried out taking into account the influence of the solvent used.

Quantum chemical calculations were performed using the Gaussian03 software package within the framework of the density functional theory (*DFT*). The RB3LYP functional and the 6-311G (d, p) basis set were used to optimize the geometry of the molecules.

When analyzing the kinetic data on complexation, the dependences not only on the nature of salt and medium, but also on the number of fluorine atoms and the length of the fluoroalkyl substituent were revealed.

There is also some cyclicity of the obtained kinetic parameters (porphyrin with odd and even number of carbon atoms in fluoroalkyl substituent), which is quite consistent with spatial changes in the structure of porphyrin molecules.

The work was performed in the framework of the State contract from the Ministry of Education and Science of the Russian Federation (project no. 4.7305.2017/8.9). The studies were conducted using the resources of the Center for collective use of scientific equipment of the «ISUCT».

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STUDY OF THE WOUND HEALING EFFECT OF TETRACARBOXYPHENYLPORPHYRIN IMMOBILIZED ON THE SURFACE OF NONWOVEN POLYPROPYLENE MATERIAL

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In recent years, the use of wound coatings based on polymers and drugs has become most relevant. The use of such complex materials can significantly improve the treatment of wounds, burns and trophic ulcers, which is especially important in terms of primary treatment of wounds to prevent bacterial contamination and tissue infection.

In order to create new wound coverings, the wound-healing effect of 5,10,15,20-tetrakis-(4'-carboxylphenyl)porphyrin (H_2P) immobilized on the surface of a modified nonwoven polypropylene material (NPP) was investigated. Since H_2P is a water-soluble cationic derivative of tetraphenylporphine and has high biological activity, it is a very promising compound in this case. However, one should take into account that the H_2P macromolecule is very voluminous (its dimensions considerably exceed the size of the elementary unit of the polymer) and its immobilization on the surface of the polymer carrier is significantly hampered due to the occurrence of steric obstacles. Therefore, a preliminary post-chemical modification of the surface of the NPP with polyvinyl alcohol was carried out, which made it possible to significantly facilitate the immobilization process and increase the sorption capacity of the polymer matrix. H_2P immobilization was carried out from its solution in DMF at 18 ± 2 ° C for 12 h.

The identification of the immobilized compound was carried out by ESPs at the following characteristic bands: λ_I=626 nm (Igε_I, = 3.26), λ_{II} = 575 nm (Igε_{II}=3.87), λ_{III} = 542 nm (Igε_{III} =3.73) and λ_{IV} = 509 nm (Igε_{IV} = 4.26), λ_{Sore} = 412 nm (Igε_{Sore} = 5.21) in DMFA. Using the obtained values of the optical density of the immobilized porphyrin layer, its concentration on the surface of the NPP was calculated: 0.508 × 1015 particles / cm^2.

To determine the wound-healing effect of modified H_2P materials, an in vivo study was conducted on 30 male rats of out-bred Wistar runoff with an assessment of the morphofunctional state of the wound defect. As a result of the studies, the staging of the wound process was shown and a histological study of the regenerate in the area of the wound defect was carried out (on the 3rd, 9th and 14th day). As a result of the study the reduction of reepithelisations terms in the experimental group in relation to the comparison group, as well as the formation of a more complete regenerate, which was accompanied by an increase in the thickness of the epidermis and a reliably large number of appendages of the skin localized in the area of regenerate. Focal points of lymphocytic infiltration on the obtained slices were not revealed, which is also an important indicator of successful healing of the skin. The results of the study showed that applications based on non-woven PP material with immobilized porphyrin have a well-defined wound healing effect.

The work was performed in the framework of the State contract from the Ministry of Education and Science of the Russian Federation (project no. 4.7305.2017/8.9). The studies were conducted using the resources of the Center for collective use of scientific equipment of the «ISUCT».

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PORPHYRINS METAL COMPLEXES AS ELEMENTS OF ELECTRET MATERIALS DESIGN

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A new approach of the electret materials creating is based on the intercalation of macromolecules with a significant dipole moment into a polymeric film matrix during polymerization in a constant electric field. Thus, the material with a constant potential difference is formed. At the same time, the large size of the macromolecule makes the dipole orientation arbitrarily change impossible. The polarity of the metal-porphyrin complexes molecules suggests that the materials with their inclusion can show a high pyroelectric and/or electret activity.

Bismuth iodine etioporphyrin II and bismuth iodine 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin were selected and synthesized as inclusion elements into a polymer matrix [1, 2].

Polyvinyl acetate polymer films with the bismuth porphyrin complexes intercalated in a constant electric field, were obtained. Using a magnetron sputtering method, a 100 nm thick layer of copper was applied onto both sides of the obtained films.

The dielectric properties (the dielectric permeability and the loss-angle tangent) of polymeric polyvinyl acetate films with intercalated metal complexes in the 100–450 K temperature range and 25–106 Hz frequency range were studied.

The obtained data confirm the existence of relaxation processes in the samples. These processes are due to reorientation of the side dipolar groups and the polymer chain segments, as well as to a phase transition. At low temperatures (up to 300 K), the dielectric permeability has a quite low value: $\varepsilon \approx 2.7$.

The thermostimulated depolarization currents dependences of the samples with bismuth porphyrins complexes are qualitatively similar to the thermostimulated depolarization currents dependence of the 100 % polyvinyl acetate sample. The first and the second systems of maxima (in the regions of 250 K and 325 K) qualitatively and quantitatively correspond to α- and β-relaxation processes occurring in the polymer matrix. However, the appeared third system of maxima (at 364 K), which was not observed for the 100 % polyvinyl acetate sample, rather sharply degrades with the frequency increasing and the decreasing of the bismuth porphyrin complex content in the film. So, it refers to the intercalated metal complex.

Thus, a pronounced electret effect was shown in the polymeric films of polyvinyl acetate with intercalated bismuth porphyrins complexes. The suggested new approach based on an intercalation of macromolecules with essential dipole moment into a polymer, opens the prospects of creating a novel family of electret materials.

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Gradov O.V.[1], **Gradova M.A.**[1], **Bychkova A.V.**[2], **Lobanov A.V.**[1]

PHOTOPHYSICAL PROPERTIES AND SUPRAMOLECULAR ORGANIZATION OF PORPHYRINS WITHIN POLYELECTROLYTE COMPLEXES

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Polyelectrolyte complexes (PECs) are the products of cooperative ionic binding between two oppositely charged polyions (interpolymer complexes) or polyelectrolytes and colloidal particles (polymer-colloid complexes). These supramolecular systems demonstrate sensitivity towards p*H* and ionic strength, and hence, are considered as the promising systems for controlled targeted drug delivery [1]. Charged porphyrin molecules can also participate in the formation of PECs and provide their photochemical activity and spectral response towards the changes of the local parameters in the surrounding medium due to the sensor properties of macrocycles [2–3]. This report considers aggregation state, spectral and luminescent properties of a number of cationic, anionic and neutral porphyrin derivatives within hybrid supramolecular systems based on the water-soluble non-stoichiometric polyelectrolyte complexes.

Interpolyelectrolyte systems based on biocompatible polymers are characterized by the accumulation of porphyrins in a fluorescent monomolecular form within the inner volume of the phase-separated microparticles (coacervate droplets). The accumulation efficiency and the distribution coefficient of the dye between the droplets and the liquid phase are determined both by the particle charge and the HLB value of the porphyrin molecules. In the polymer-colloid complexes obtained from synthetic polyelectrolytes and the oppositely charged surfactant micelles the aggregation state and the photophysical properties of macrocycles are mostly determined by the micellar component solubilizing the monomolecular form of porphyrins in the oppositely charged surfactant micelles resulting in the increased absorbance and fluorescence quantum yield. Ionic binding with the linear oppositely charged polyelectrolytes, in contrast, leads to the porphyrin fluorescence quenching due to the dipole-dipole interactions between the macrocycles bound to the ionic groups of the neighboring units in the polymer chain.

Thus, self-assembly of polyelectrolyte complexes with porphyrin derivatives allows to obtain hybrid photoactive supramolecular systems with emergent properties.

This work was financially supported by the Russian Foundation for Basic Research (Project 18-03-00539).

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Gradov O.V.[1], **Gradova M.A.**[1], **Lobanov A.V.**[1], **Kochervinskii V.V.**[2]

SPECTRAL AND ELECTROPHYSICAL PROPERTIES OF FERROELECTRIC POLYMER FILMS DOPED WITH TETRAPHENYLPORPHYRIN DERIVATIVES

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Poyvinylidene fluoride (PVDF) and a number of its copolymers with ferroelectric properties are promising materials for designing thin film sensors and coatings for photovoltaic devices. These applications require introduction of dyes into the polymer matrix, providing photosensitization and the optical response towards the changes of the certain parameters in the surrounding medium. In this casse, the interaction of the dopant molecules both with each other within the amorphous phase of the copolymer and with the functional groups in the polymer chain can lead to the significant changes in the photophysical properties of the dye molecules and the electrophysical properties of the polymer matrix. In this report we discuss the spectral and luminescent properties, as well as the high voltage conductance of the polymer films based on the copolymer of difluoroethylene and hexafluoropropylene doped with tetraphenylporphyrin (TPP) derivatives.

Using broadband low-voltage impedance spectroscopy it was shown that the introduction of TPP molecules into the ferroelectric polymer film results in a decrease of the Maxwell-Wagner polarization relaxation time due to the emergence of the additional current carriers. In addition, an increased electrical conductivity in the external high-voltage field was observed for the dye-doped film. Introduction of the porphyrin molecules changed not only the absolute current value up to two orders of magnitude, but also the kinetics of its changing after the pulse application (the time required for the current to reach the stationary value was tens of seconds). A similar effect was described earlier in paper [1]. It can be assumed that in this case the excess conductivity is provided by the protons. The introduction of the metal ions into the porphyrin macrocycle decreases the observed conductivity of the dye-doped polymer films.

The obtained polymer films with immobilized TPP are characterized by the optical response to the changing pH, particularly in the presence of ammonia and hydrogen chloride vapors due to the reversible addition of the protons to the inner nitrogen atoms in the porphyrin base and the corresponding changes in the symmetry and conformation of the macrocycle, resulting in the bathochromic shift of both the absorption and emission bands. The above findings allow to consider the porphyrin-doped ferroelectric films obtained as the promising materials for the thin film gas sensors.

This work was financially supported by the Russian Foundation for Basic Research (Project 18-03-00493).

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SYNTHESIS OF CHLOROBORON(III) SUBPORPHYRAZINES ON THE BASIS OF FUMARONITRILE AND TETRAFLUOROPHTALONITRILE

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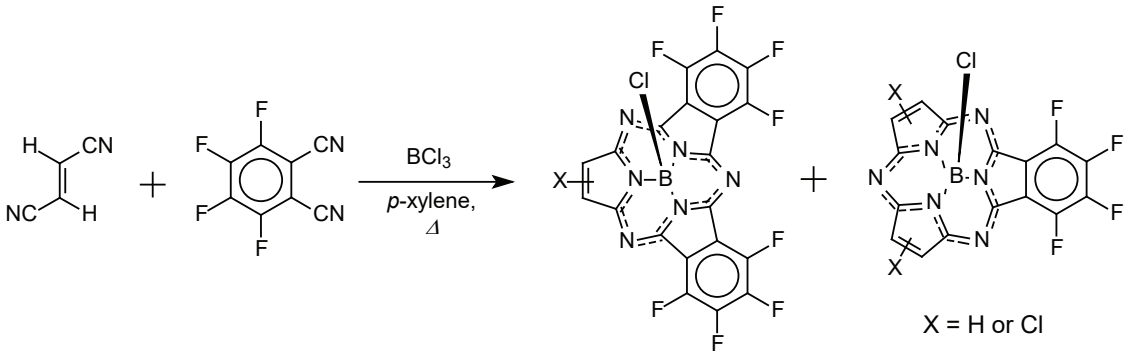
Mixed cyclotrimerization of fumaronitrile and tetrafluorophthalonitrile in the presence of BCl_3 in p-xylene affords a mixture of boron(III) subporphyrazines with one and two tetrafluorobenzene fragments. Chlorine evolving during reaction leads to partial chlorination of benzene rings and formation of mono- and dichlorosubstituted subporphyrazines.



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Ivanova Yu.B., Chizhova N.V., Mamardashvili N.Zh.

SYNTHESIS, BASIC AND COMPLEX-FORMING PROPERTIES OF NITROSUBSTITUTED TETRAPHENYLPORPHYRINES

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The study of new structures with a supposed chemical activity, carried out in a class of chemical compounds where substances with a certain direction of action have already been found, is an important aspect in understanding of the "chemical structure – chemical action" dependences. The variety of useful properties of porphyrins and their analogues is associated with the peculiarities of their structure. However, the successful solution of fundamental questions of practical application of this class compounds directly depends on the optimization of methods for the porphyrins synthesis and the possibility of their modification. Therefore, the study of the influence of the electronic and steric effects of substituents of the porphyrin macrocycle as a tool for the directed change in the coordination, acid-base and spectral properties of porphyrins seems to be an important and urgent task for creating the physicochemical bases for obtaining new materials.

In order to establish the influence of electron-withdrawing NO_2-groups on the basic and complex-forming properties of the 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**1**) and 5,10,15-tri-(4-nitrophenyl)-20-phenylporphyrin (**2**) the method of spectrophotometric titration was used to study the protonation and complex formation of these ligands with $Zn(OAc)_2$ in the systems acetonitrile (AH) – $HClO_4$ (1) and (AH) – $Zn(OAc)_2$ (2) at 298 K and 298–318 K respectively.

Analysis of our experimental results data showed that the introduction of the nitro groups into the porphyrin molecule reduces the basic properties of the ligands **1** and **2** compared with unsubstituted tetraphenylporphine. It was also determined that the measured kinetic parameters of the tetrapyrrolic compounds coordination reaction upon interaction with zinc acetate are in good agreement with literature data.

This work has been carried out with financial support of the Russian Foundation for Basic Research (grant № 19-03-00078 A) with the involvement of the equipment of the center for collective use of the Upper Volga Regional Center for Physical and Chemical Research.

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CONJUGATES OF DERIVATIVES OF NATURAL CHLORINS WITH FULLERENE C_{60}

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Unique electronic and photophysical properties of porphyrins and fullerenes lead to great interest in creation of hybrid structures based on them [1]. The photodynamic activity of porphyrin- and chlorin-fullerenes is studied in order to search for new effective photosensitizers for photodynamic therapy of cancer and antimicrobial photodynamic inactivation. The creation of hybrid structures based on porphyrins and chlorins, which intensively absorb in the visible spectral region, and fullerenes, which effectively generate reactive oxygen species, can allow to increase the photodynamic effect of photosensitizers. The lipophilicity of fullerenes facilitates the transport of conjugates across the cancer cell membrane.

We have synthesized conjugates of cycloimide derivatives of chlorin p_6 with fullerene C_{60}. The possibility of the introduction of fullerene moiety at various positions of the chlorin macrocycle (pyrrole rings A and D, as well as the imide exocycle) was studied. Chlorin- fullerenes were obtained by the reaction of the corresponding hydroxyiminomethyl substituted derivatives of chlorin p_6 cycloimides with (diacetoxyiodo)benzene and C_{60} [2, 3]. For synthesized chlorin-fullerenes, the parameters of electron transfer under photoexcitation were determined, and the generation of singlet oxygen was also studied.

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THE ROLE OF ELECTRONIC STRUCTURE OF PERIPHERAL DEPOSITS CO(II) PHTHALOCYANINES ON THE FORMATION OF ASSOCIATES IN SOLUTIONS

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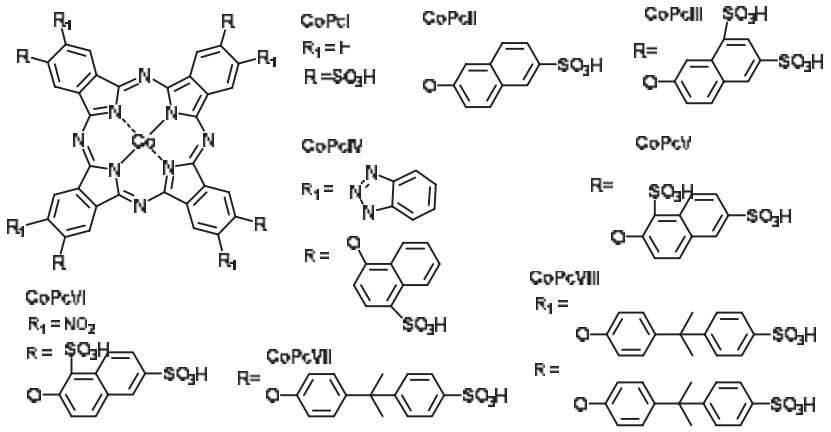
Metal phthalocyanines are capable of coordinating ligands of various natures on the central metal cation and forming ordered structures in the form of aggregates: H-, J-, T-type. By varying the central metal and substituents at the periphery of the phthalocyanine ring, it is possible to change the properties of the phthalocyanine metal complex in a directional manner. The study of physicochemical properties of phthalocyanine derivatives allows them to be used as catalysts, photosensitizers, dyes, photovoltaic solar energy converters. However, the aggregation of phthalocyanine macrocycles in solutions, especially aqueous ones, can significantly reduce the areas of their application, associated primarily with the processes of light excitation of macromolecules. From this point of view, the search for ways to control the aggregation of macroheterocyclic compounds in solutions is most appropriate.

In this work, the influence of the electronic structure of peripheral substituents of sulfonated Co (II) phthalocyanines derivatives (CoPcI-CoPcIII) on the association management processes by introducing small nitrogen-containing ligands (pyridine, piperidine) was evaluated.



It was shown that for the presented compounds, with the exception of CoPcIV and CoPcV, an increase in the stability of molecular complexes with nitrogen-containing ligands is observed during the transition from pyridine to piperidine, due to the presence of high electron density on the donor nitrogen atom of this ligand. The introduction of a benzotriazole fragment to the periphery of the metal complex leads to a redistribution, namely an increase, of the electron density in the macro ring, which promotes the formation of more stable complexes with an aromatic heterocycle.

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SYNTHESIS OF NEW MEMBRANOTROPIC CATIONIC CHLORINS BASED ON PHEOPHYTHINE *A* AND ESTIMATION OF THEIR PHOTODYNAMIC ACTIVITY

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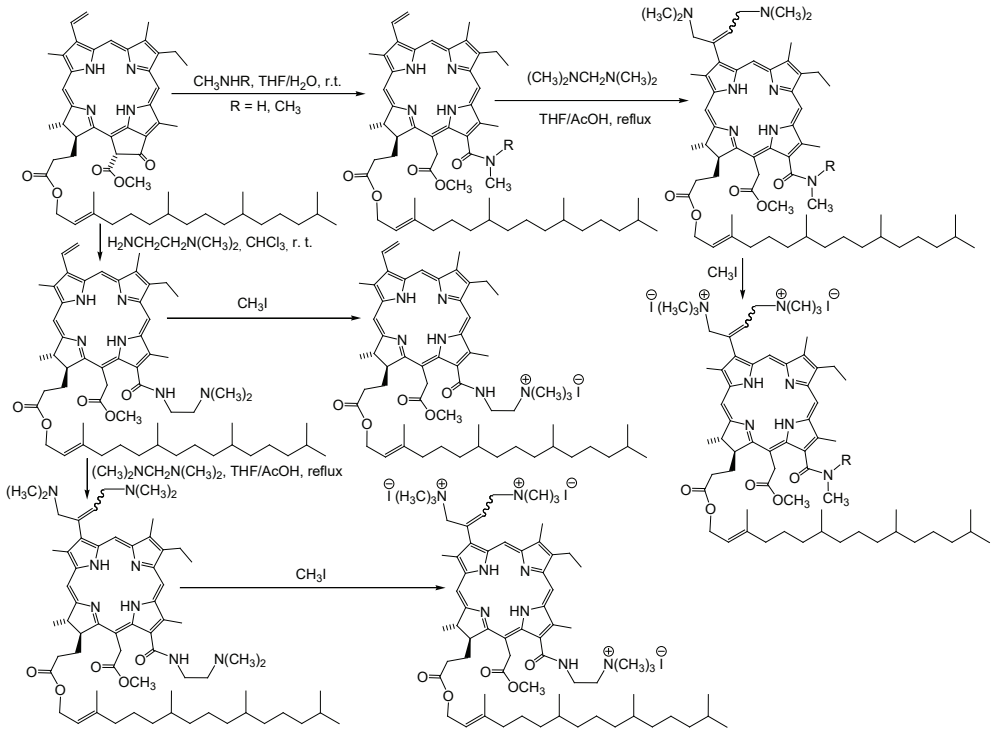
It is known that a fragment of phytol in chlorophyll a is involved in the interaction with chloroplast membranes. Therefore, the presence of such a fragment can increase the membranotropicity of the chlorophyll derivative, which, in the presence of hydrophilic groups, can enhance the efficiency of photodynamic action. Cationic groups can act as hydrophilic substituents, the presence of which not only increases the bioavailability of the compound, but also promotes interaction with mitochondria, the damage of which can lead to apoptosis. In this regard, a number of chlorins with cationic groups containing a phytol fragment was synthesized (Scheme 1). It was shown that all cationic derivatives obtained are capable of causing hemolysis of erythrocytes both in the dark and under illumination (LED, 660 nm), and the concentrations necessary for effective photohemolysis are at least an order of magnitude lower than those at which hemolysis is observed without illumination.



Scheme 1

This work performed using equipment of the CCU «Chemistry» at the Institute of Chemistry of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar) and CCU «Molecular Biology», the Institute of Biology of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar).
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SYNTHESIS OF DERIVATIVES OF NATURAL CHLORINS WITH GUANIDINE AND BI-GUANIDINE GROUPS

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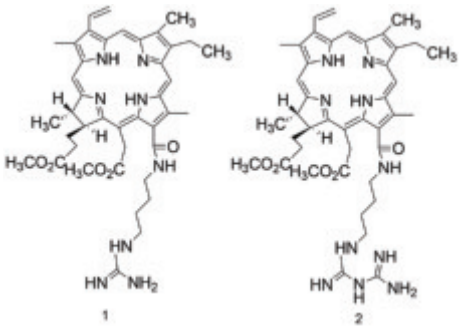
Photodynamic therapy of cancer (PDT) is rather new, perspective method of treatment of oncological diseases. However the drugs-photosensitizers applied now possess a number of shortcomings, including low accumulation in tumor cells. Therefore the purpose of this work is synthesis of multifunctional conjugates on the basis of natural chlorins with pharmacophoring guanidine and bi-guanidine groups which, according to literary data, increase accumulation of drugs in a tumor and their biological activity.

Guanidine is a fragment of many biologically active compounds and has a number of important physiological properties. In particular, he can act as a vector for delivery of drugs in tumor cells and itself is the pharmacophoring group showing cytotoxicity.

Bi-guanidine, in turn, is also pharmacophore of many drugs. On its basis Metformin - anti-diabetic drug which possesses as it became clear also antineoplastic activity is developed.

It is important to note that the range of biological effect of biguanides is very wide. They show antineoplastic activity, causing apoptosis and inhibiting activity of membrane proteins. Guanyl guanidines can suppress an angiogenesis, breaking food and growth of cells, blocking synthesis of ATP and AMP, interacting with AMPK (5'AMP the activated kinase).

In this work synthesis of guanidine and bi-guanidine derivatives of natural chlorins is provided. Synthesis was carried out according to the described technique. To initial substance- aminobutylamide of methyl ether of pheophorbide *a* an excess of pyrazole-1-carboxyamidine was added. As a result, after separation and chromatographic cleaning, guanidine derivative with a quantitative yield which was characterized by methods of mass-spectrometry and nuclear magnetic resonance of spectroscopy was received . Bi-guanidine derivative was received by action of excess of N-amidinopyrazole-1-carboxyamidine on the aminobutylamide of methyl ether of pheophorbide *a*. The received conjugate was also characterized by methods of mass-spectrometry and nuclear magnetic resonance of spectroscopy.



Kiselev A.N., Pogonin A.E., Kurochkin I.Yu., Otlyotov A.A., Voevodina E.A.

A COMPREHENSIVE STUDY OF THE STRUCTURE OF MACROCYCLIC COMPOUNDS

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Structural and physicochemical properties of porphyrin compounds were studied using gas electron diffraction (GED) method, mass spectrometry (MS), quantum chemistry (QC), infrared and electron spectroscopy. The main objects of this study are 5,10,15,20-tetrakis (4'-halophenyl) porphins (H_2P-$4C_6H_4X$, X = F, Cl, Br, I). This work is a continuation of the structural study described in the works [1–3] for different macrocyclic compounds.

DFT (B3LYP functional) quantum-chemical calculations were performed for H_2P-$4C_6H_4X$. The conformational diversity of these molecules was studied: the considered conformers differ in the positions of the $–4C_6H_4X$ groups relative to the macrocyclic core. According to the results of the calculations, the most energetically favorable structure of the $4C_6H_4X$-H_2P possesses C_{2v} symmetry. At the same time, relative energies of the other conformers are very low. Structural parameters of the molecules slightly differ from each other in the series. H_2P-$4C_6H_4F$ → H_2P-$4C_6H_4Cl$ → H_2P-$4C_6H_4Br$ → H_2P-$4C_6H_4I$. The exception is bond length C-X (from 1.349 Å (C–F) to 2.121 Å (C–I))

DFT calculations were used to simulate IR and UV-Vis spectra of H_2P-$4C_6H_4X$. Theoretical spectra are in good agreement with experimental data available in literature. However, UV-Vis spectra of H_2P-$4C_6H_4X$ slightly change in the considered series.

The combined GED-MS experiments for the compounds were performed with use of the EMR-100/APDM-1 setup. QC calculations predict structural parameters being in good agreement with the GED data.

The mass spectra of the H_2P-$4C_6H_4X$ were recorded and studied and the fragmentation path of the molecules was analyzed. For these investigations magnetic mass spectrometer MI 1201 modified for thermodynamic studies was used. The sublimation enthalpies were determined by the Knudsen effusion method: H_2P-$4C_6H_4F$ - 233 ± 4 kJ/mol, H_2P-$4C_6H_4Cl$ - 225 ± 4 kJ/mol, H_2P-$4C_6H_4Br$ - 243 ± 4 kJ/mol.

The reported study was funded by RFBR according to the research project № 18-33-01199.

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Kolarova M., **Mulaku A., Zimcik P.**

STUDY OF DEMETALLATION OF MAGNESIUM COMPLEXES OF PHTHALOCYANINES AND TETRAPYRAZINOPORPHYRAZINES IN ACIDIC MEDIA

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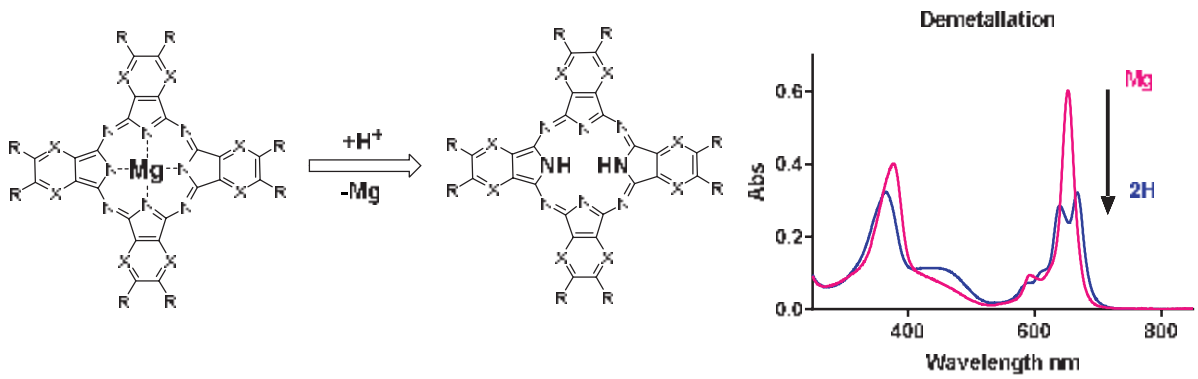
Magnesium complexes of phthalocyanines (Pc) and their azaanaloges (AzaPc) are well known for their interesting photophysical and photochemical properties, especially a strong emission of photons, which make them widely examined as potential diagnostic dyes.[1] Changes of the macrocycle relaxation pathways of the excited states are driven primarily by the incorporated central cation on the basis of heavy-atom effect.[2] Magnesium is the lightest stable central cation that explains strong fluorescence of such complexes; However, the instability of magnesium complexes in acidic environment (demetallation to metal-free ligands) is the main obstacle to wider utilization of these fluorescent dyes. Once a macrocycle is demetallated, it loses its strong fluorescent properties. In this work, we evaluated more closely the demetallation process of these compounds at various pH. The stability was monitored by absorption spectroscopy where characteristic splitting of the Q-band occurs after demetallation. Water-soluble compounds were tested in buffers at five different pH ranging 1 – 7.4. Lipophilic derivatives were tested in organic solvent (after addition of TFA) as well as after incorporation into two delivery systems (liposomes and microemulsions). Interestingly, liposomes as delivery system showed high level of protection where no changes in absorption spectra of AzaPc were detected after 24 h even at the most acidic pH. Experiments proved that the more acidic environment the faster process of the demetallation occurs and that magnesium complexes of Pcs are less stable than corresponding AzaPcs.



Acknowledgement. *The study was supported by Charles University (SVV 260401).*

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Kollár J.[a] **, Macháček M.**[b]**, Zimčík P.**[a]

EFFECT OF BOVINE SERUM ALBUMIN ON PHOTODYNAMIC ACTIVITY OF NEW ANIONIC AND CATIONIC PHTHALOCYANINES

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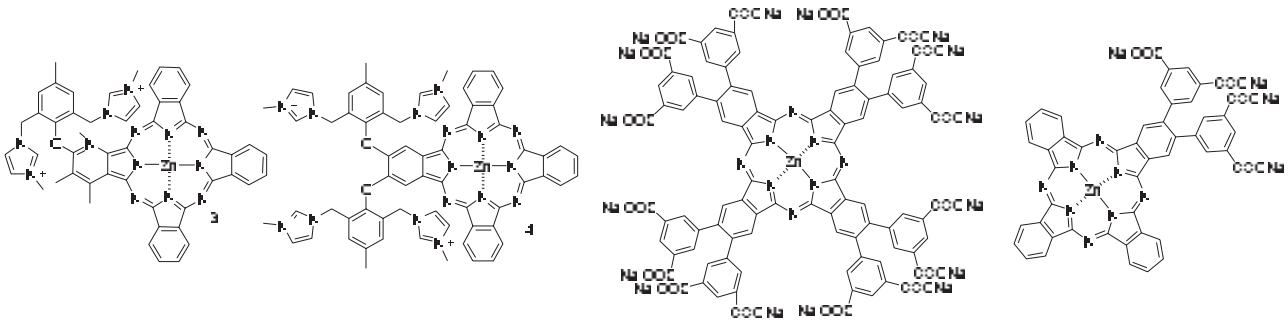
Phthalocyanines (Pcs) and their aza-analogues represent a promising group of organic dyes with interesting photophysical properties (strong absorption in area 600–750 nm and strong singlet oxygen production) highly suitable for the use in photodynamic therapy of cancer. Peripheral substituents may affect behavior in biological environment and may promote interaction with various biomolecules. One of the most important molecule that during application *in vitro* or *in vivo* can interact with Pcs is albumin, the most abundant serum protein. Interaction between Pcs and albumin can be positive, neutral or can lead to quenching of the excited states and to loss of the photodynamic activity. The aim of this work was synthesis of new symmetrical and unsymmetrical anionic and cationic Pcs and study of the effect of bovine serum albumin on their photodynamic activity.

Symmetrical Pcs were obtained by cyclotetramerization reaction (initiator magnesium butoxide) of one precursor while unsymmetrical Pcs were prepared by statistical condensation of phthalonitrile with 4,5-disubstituted phthalonitrile. Magnesium complexes were converted to metal-free ligands and then to zinc complexes. Basic hydrolysis of ester bonds was the last step of the synthesis of anionic Pcs. Quaternization of basic nitrogens was the last step of the synthesis of cationic Pcs.

Pcs were tested on photodynamic activity *in vitro* on HeLa cells with different results in serum free medium (SFM) and serum-containing medium (SCM). Photodynamic activity of anionic symmetrical Pcs was negatively affected by the presence of serum albumin. On the other hand, cationic symmetrical Pcs did not interact with serum proteins. Unsymmetrical amphiphilic cationic and anionic Pcs had better photodynamic activity because they could interact with biomembranes, which lead to better photodynamic activity.

Effect of binding to serum proteins was studied as change in absorption and fluorescence spectra of Pcs after addition of bovine serum albumin. Obtained results corresponded well with change in photodynamic activity of these compounds in SFM and SCM.



Acknowledgement. *The work was supported by GA UK 1060216, Czech Science Foundation, grant. No. 19-14758Y and SVV 260 401.*

Komarova I.M., Trifonova I.P., Burmistrov V.A.

INFLUENCE OF ELECTRONIC PROPERTIES SUBSTITUENT ON THE PHENYL RING ON THE REACTIVITY OF TETRAPHENYLPORPHYRINS

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The study of porphyrin reactions in solutions is an important task in terms of expanding the areas of application of these important compounds. The kinetics of zinc acetate complexation with 5,10,15,20-tetra (4-methoxyphenyl) porphyrin H_2TMPP, *meso*-tetraphenylporphyrin H_2TPP and 5,10,15,20-tetra (4-hexyloxycarbonylphenyl) porphyrin H_2THPPP was studied. Extreme dependences of the complex formation rate constant on the composition of the binary solvent are observed for all the porphyrins studied. Linear experimental dependences of the logarithm of the rate constant on the substituent Hammet's constant are obtained, confirming that the rate of complex formation depends on the nature of the substituent in the phenyl ring, and also the principle of linearity of free energies is fulfilled.

A series of reactivity of porphyrins in the complexation reaction has been established: $H_2TMPP > H_2TPP > H_2THPP$, according to reduction of the electron donor properties of the para-substituent. Considering the nature of the main stages of the complexation process, it can be concluded that the enhancement of the electron-donor properties of the substituent promotes an increase in the electron density on the pyrolenine nitrogen atom of the porphyrin cycles and an increase in the coordinating ability of the latter during the formation of a SAT complex with a metal ion. This experimental fact suggests that the limiting stage of the complex formation process under the experimental conditions is the formation of a transition state (SAT-complex).

Kostrova E.A., **Mikhaylova A.I., Vashurin A.S., Znoyko S.A., Malyasova A.S.**

OPTICAL PROPERTIES OF FLYING-SEED-LIKE PHTHALOCYANINES

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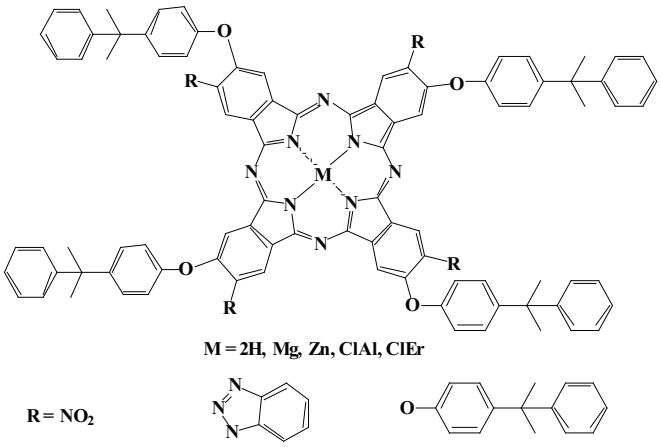
Authors [1–3] were investigated new phthalocyanines (named "flying-seed-like"), among which 2,9,16,23-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine and their metal complexes. These macrocycles exhibit liquid crystals, sensory and fluorescent properties. The purpose of this work – modification and synthesis new phthalocyanines containing additional electron-donor and acceptor substitutes in benzene rings, as well as use of different metals in the coordination cavity.



We have studied spectra luminescent of new phthalocyanines in $CHCl_3$ and THF medium and determined quantum yields of fluorescence. The calculated data showed a decrease in the fluorescent quantum yield during the transition from the ligand to the metal complexes. This fact can be explained aggregation process and additional heavy atoms.

The ability to generate singlet oxygen by laser irradiation was determined for all the compounds obtained on the equipment of the SEC MSU in Chernogolovka. According to the study, it can be concluded that metal complexes containing an aluminium atom in the central cavity of the macrocycle can be used as promising agents for fluorescent diagnostics and photodynamic therapy.

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PERHALOGENATED AZAANALOGUES OF SUBPHTHALOCYANINE AS A PERSPECTIVE ACCEPTORS FOR ORGANIC ELECTRONICS

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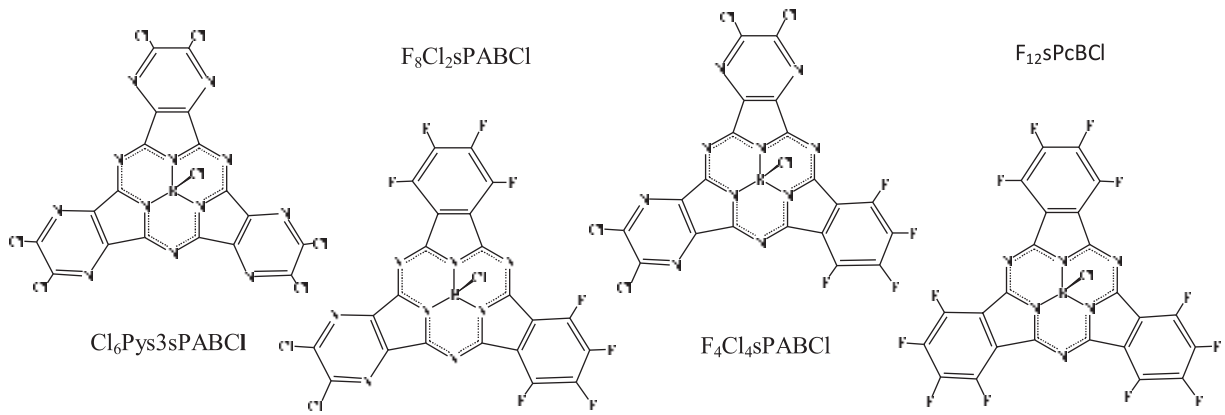
Introduction of different substituents in a subphthalocyanine molecule leads to considerable modification of its properties [1]. While subphthalocyanines behave as donor p-layers in hybrid organic solar cells, perfluorinated subphthalocyanine analogs have n-type conductivity and can be used as electron acceptors [2]. Moreover, not only halogenation, but also aza-substitution in benzene rings of subphthalocyanine may be used to enhance its acceptor properties. In our work we combined both modification methods: halogenation and aza-substitution. Thus, by co-condensation of tetrafluorophthalonitrile and 5,6-dichloro-pyrazin-2,3-dicarbonitrle in the presence of BCl_3 in a p-xylene we have obtained a set of perhalogenated porphyrazines, containing dichloropyrazine and tetrafluorobenzene fragments.



The structure of obtained porphyrazines was characterized by MALDI-TOF mass spectroscopy and NMR-spectroscopy (^{11}B, ^{13}C, ^{19}F). Preliminary results of DFT calculations and electrochemical measurements indicate that obtained compounds are perspective acceptor materials for organic electronics.

This work was supported by Russian Science Foundation (grant №17-13-01522)

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SYNTHESIS AND TRANSFORMATIONS OF THE AZOMETHINE DERIVATIVES OF B-ALKYL SUBSTITUTED PORPHYRINS AND CHLORINS

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In this work we suggested a new approach to the functionalization of the β-alkyl substituted porphyrins and chlorins based on the electrophilic substitution reaction [1,2]. β-Alkyl-substituted chlorins were prepared from the corresponding porphyrins by a reduction with sodium metal in isoamyl alcohol [3]. Methyl esters of the coprochlorins I and II (dihydro derivatives of the coproporphyrins) were obtained for the first time. The structure of the compounds was confirmed by UV-Vis, MS and NMR spectroscopy.

Using 2D NMR technique, we found that the electrophilic substitution reaction in β-alkyl substituted chlorins proceeded regioselectively at the *meso*-position of the tetrapyrrole macrocycle closest to the reduced pyrrole ring.

Ni(II) and Pd(II) complexes of the azomethine derivatives of β-alkyl substituted porphyrins and chlorins with hydrazine, methylamine and benzylamine were also obtained, and their thermal transformations were studied. In the case of the Ni(II) complexes of the azomethine derivatives of β-alkyl substituted porphyrins, derivatives with annelated cyclic fragments were formed, while the corresponding chlorines were oxidized to the porphyrins during the thermolysis.

We have demonstrated a new approach to functionalize Pd(II) and Ni(II) complexes of the β-octaalkyl chlorins affording a new class of the compounds namely β-octaalkyl chlorin azines where azine bridge links two aromatic chromophores. This approach gives high yields, and could prove useful for the creation of extended conjugated systems possessing significantly modified optical properties. In particular, we have synthesized a number of variously substituted arylazine chlorins and dyads of β-octaalkyl chlorin with pyropheophorbide-*a* and pyropheophorbide-*d* methyl esters with azine bridge.

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Kočiščáková L., Zimčík P.

SYNTHESIS OF PHTHALOCYANINE DERIVATIVES FOR SUPRAMOLECULAR INTERACTIONS WITH CUCURBITURIL

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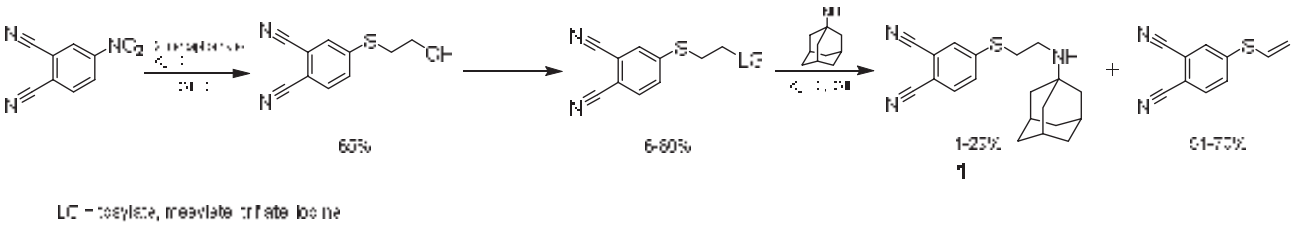
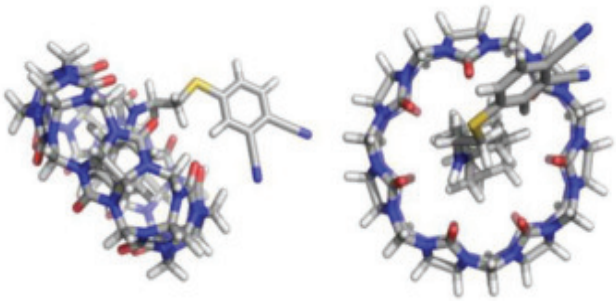
Phthalocyanines (Pc) are macrocyclic compounds structurally related to porphyrins, which are used e.g. as photosensitizers in photodynamic therapy in the treatment of tumor diseases. Their main disadvantage is their poor solubility in water and aggregation. Based on formation of a supramolecular complex with cucurbiturils (CB) we can potentially improve those properties. CB are pumpkin-shaped macromolecules composed of methylene bridged glycoluril oligomers.[1] In this project we used one of the strongest reported supramolecular interactions between CB[7] and 1-aminoadamantane[2] as substituent on the Pc ring.

Phthalocyanine precursor was prepared (**1**) and different synthetic approaches were used to optimize its synthesis. Universal method was developed which could allow easy preparation of different phthalonitrile and pyrazine-2,3-dicarbonitrile precursors. Crystal structure of the complex was also obtained and confirmed the predicted orientation of adamantyl moiety in the cavity of CB. Photophysical properties of final Pc after cyclotetramerization reaction of its precursor were measured. Biological tests on HeLa cells showed ten times higher photodynamic activity of Pc-CB supramolecular complex than Pc without CB.





Acknowledgement. *This work was supported by SVV 260 401 and Grant Agency of Charles University (1606119).*

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Kruchin S.O.[1], **Krest'yaninov M.A.**[1], **Batov D.V.**[1], **Kustov A.V.**[1,2], **Venediktov E.A.**[1], **Kudyarova T.V.**[2], **Berezin D.B.**[2]

PHOTOSENSITIZER FOR ANTIMICROBIAL PHOTODYNAMIC THERAPY BASED ON WATER-SOLUBLE DERIVATIVE OF DEUTEROPORPHYRIN-IX: SYNTHESIS, INTERPHASE DISTRIBUTION, AGGREGATION, MICROBIOLOGICAL TESTING

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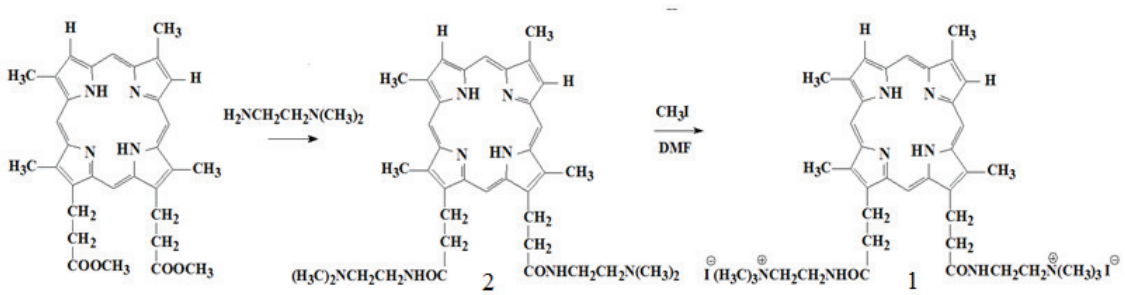
Photodynamic therapy is one of the fast growing direction in the treatment of antibacterial infections [1]. In this regard, the search for photosensitizers (PS) that meet the clinical requirements is of current interest. In this work we have synthesized diiodide 13,17-bis (trimethylammoniaethylamide)deuteroporphyrin-IX (PS, **1**), which has an antimicrobial effect due to the generation of reactive oxygen species under red light exposure (λ = 620 nm). PS **1** has been identified via UV-VIS, ^{1}H NMR- and MS-spectra. The ability of comp. **1** and its uncharged precursor **2** to generate singlet oxygen was studied. The quantum yield of $^1O_2$ value for PS **1**–**2** (~0.7) is found to be above the range observed for chlorin derivatives (0.4–0.6).



The distribution of comp. **1**–**2** between lipid-like and water phases in the system of 1-octanol and phosphate buffer (pH = 7.4) was studied. It was shown that the value of the distribution coefficient P does not change significantly with the temperature variation [2]. The solubility of PS **1** in water was determined using isothermal saturation method with spectrophotometric control of PS concentration. Measurements were carried out in a hermetic thermostatically controlled cell in the temperature range of 298–318 K.

Dynamic light scattering (DLS) and UV-VIS-spectroscopy were used to study aggregation of PS **1** in water and non-ionic surfactant (Tween 80) solutions. According to DLS porphyrin **1** is more exposed to aggregation in comparison with corresponding dicationic chlorin and stays associated even in diluted aqueous solutions. Moreover, the interaction constant of porphyrin **1** and Tween 80 is lower as compared to dicationic chlorin as well [3].

Comp. **1** reveals a stable positive photodynamic effect at the radiation dose of 80 J/cm^2 with respect to antibiotic-resistant strains of bacteria (*Escherichia Coli hemolyzing*).

This work was supported by the Russian Scientific Foundation (Grant 15-13-00096).

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Kudayarova T.V., Rogova E.A., Sinitsyn A.M.

PROSPECTS OF APPLICATION OF N-ALKYL TRIAZOLE DERIVATIVES

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Alkyl derivatives of heterocycles are widely used in the creation of devices operating on liquid crystals, as well as various antimicrobials.

1N-Alkyl derivatives of 1,2,4-triazole were obtained in accordance with the developed method and investigated for further study in the applied aspect.

An increase the ability to exhibit mesomorphic properties with an increase in the alkyl chain $C_{10}H_{21}<C_{12}H_{25}<C_{16}H_{33}$ was found in a series of 1N-alkyl-3,5-diamino-1,2,4-triazoles. We can assume the possibility of self-assembly due to intermolecular H-bond and the effect of this process on the mesomorphic and physical properties of the liquid crystal due to the presence in the structure of the studied compounds of electron-donating nitrogen atoms of the five-membered cycle and amphiproton amino groups.

The analysis of experimental and theoretical study results of synthesized mesogens will be the basis for the combinatorial development of supramolecular liquid crystals with predictable physical and mesomorphic properties, which will allow for the directed design of self-organizing liquid crystal compositions for various applications in the future.

Studies of antibacterial properties have shown that the compositions created on the basis of 1-decyl-3,5-diamino-1,2,4-triazole have high antibacterial activity and can be used as drugs immobilized on a textile carrier for the preparation of medicinal dressings, which are promising at the present. In addition, the manifestation of antimicrobial activity also makes alkyl-substituted triazoles promising objects for obtaining new antibacterial drugs on their basis. In particular, they are promising compounds for the production of bifunctional agents by covalent binding to molecules of macroheterocycles – porphyrins, chlorines or phthalocyanines.

Thus, the increase in the alkyl substituent to C_{16} contributes to the manifestation of promising properties in practical terms, which will allow in the future, to use such compounds to create organic materials with predictable characteristics.

The work was performed under the State contract (Project part), project No. 4.3232.2017/4.6. The research was performed using resources of the Center for Collective Use, Ivanovo State University of Chemical Technology "ISUCT".

Kulev V.A.

BIS-PHYTHALOCYANONATES AS SENSOR FOR DETERMINATION OF CHOLESTEROL CONCENTRATION

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Kirin and Moskalev firstly published the article about synthesis of bis-phthalocyaninates with lanthanides in 1965[1]. Further, this class of compounds has attracted the big attention of researchers because they demonstrated unique physicochemical properties and can used in different areas. In particular, they widely studied as electrochromic materials, liquid crystals and sensors for metal cations and in many other areas [2].

We firstly establish that these compounds could be use as sensors for the quantitative determination of biologically important compounds, for example Cholesterol, in organic solvents. We observed that absorption intensity linearly dependents in both UV and fluorescence spectra (fig.1).

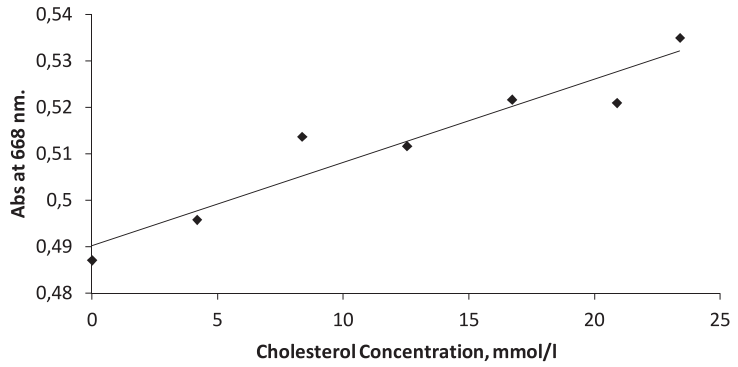

Fig. 1. *Absorbance dependence (λ_{max} = 668 nm.) for solution of $Gd(Pc)_2$ vs. concentration of cholesterol. Solution in CH_2Cl_2.*

This is probably because the bis-phthalocyaninate forms a donor-acceptor complex with a Cholesterol, which leads to the observed spectral changes. It was establish that the stability of these complexes depends from the nature of the metal cation. Therefore, the sensitivity of bis-phthalocyaninate depends on the size of the central metal cation. As we observed that the Gadolinium bis-phthalocyanine was a more effective as sensor in comparison with Lutetium one.

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Kurtikyan T.S.[1], **Hovhannisyan A.A.**[1], **Hovhannisyan G.Sh.**[1], **Lubimtsev A.V.**[2], **Ageeva T.A.**[2], **Koifman O.I.**[2]

SELF-ASSEMBLY OF 5-(PYRIDYL-4'-YL)-10,15, 20-TRIS(3,5- DI-TRETBUTYLPHENYL)-PORPHYRINATO IRON(II) IN SUBLIMED LAYERS. INTERACTION WITH DIATOMIC LIGANDS

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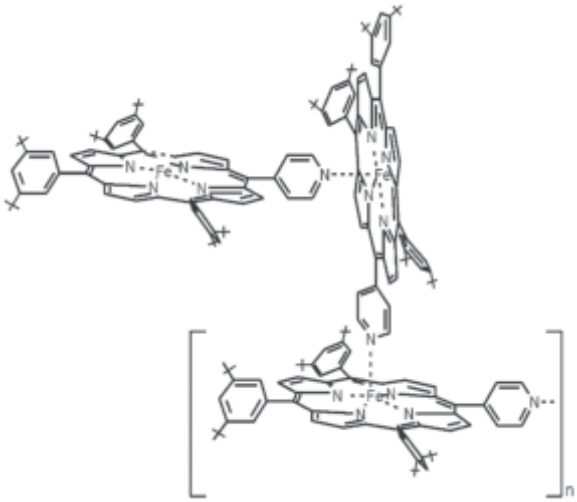

According to FTIR spectroscopy the low-temperature interaction of diatomic ligands (O_2, CO) with sublimed layers of Fe(II)-5-(pyridyl-4'-yl)-10,15,20-tris(3',5'-di-tertbutylphenyl)-porphyrin (**I**) leads to the formation of 2 types of complexes, evidencing that these films consist of coordination oligomers, the sixth coordination site of which is occupied by the pyridyl group of an adjacent molecule in the film (Scheme).

Reaction of O_2 gas with these films leads to the formation of two types of complexes: six-coordinate dioxygen complexes, in which the fifth site is occupied by the pyridyl group of the neighboring molecule in the film and the five-coordinate dioxygen complexes that terminate the oligomers. Upon storage of the films, the concentration of six-coordinate complexes increases at the expense of the five-coordinate indicating increasing degree of oligomerization. It should be mentioned that in these films there is no any evidences of Fe(II) to Fe(III) oxidation. It is likely, that in the solid state the bulky *tret*-butyl groups prevent the formation of Fe-O-O-Fe bridges that is believed should initiate the oxidation process.

Interaction of CO with layers of **I** leads to formation of the mixed CO-pyridyl complexes in the middle of coordination chain and formation of the di-carbonyl complexes (at low temperatures) at the end of the oligomers. From the ratio of intensities of the bands characterizing these species the degree of oligomerization can be estimated. This ratio markedly grows when the layer is warming to room temperature and continue to grow when is exposed under CO atmosphere. Spectral monitoring reveals that dynamic processes leading to the enhanced degree of oligomerizion continue for several days. Sublimed layers of **I** conserve their microporosity and ligand-binding ability upon standing at ambient conditions for a long time. Obviously, the bulky tert-butyl groups of **I** slow down the close packing of molecules in the films making metal ions accessible to different ligands for a long period.

It will be shown that when the mixture of dioxygen and carbon monoxide is supplied to this system at room temperature only CO is coordinated with the metal center. The bound CO can be eliminated from the film by pumping at about 40°C and the film may be used repeatedly. Hence the sublimed layers of **I** can be used for purification of O_2 from the trace quantities of CO.

This work was supported by the State Committee of Science RA (Grant № 18T-1D242).

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pH EFFECT ON AXIAL COORDINATION PROCESSES OF WATER-SOLUBLE ZINC AND TIN METALLOPORPHYRINS

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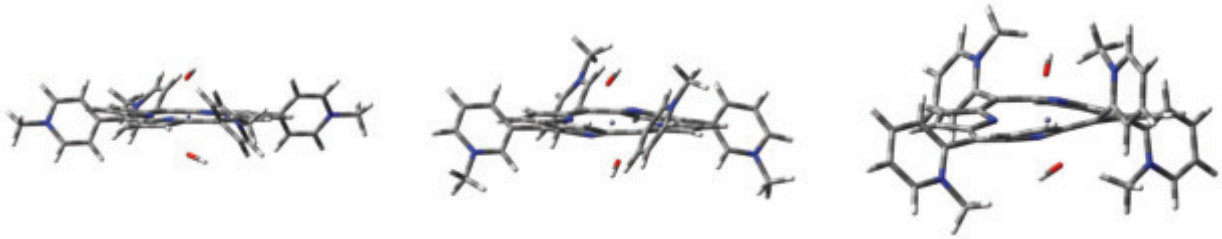
By means of synchronous UV-Vis, fluorometric and potenciometric titration technique and quantum-chemical calculations the comparative study of axial complexes formation between cationic water-soluble zinc and tin complexes of (tetra-N-methylpyridyl)porphyrins and small organic substrates were carried out.



ZnP(4'-MePy$^+$)$_4$-(OH$^-$)$_2$ **ZnP**(3'-MePy$^+$)$_4$-(OH$^-$)$_2$ **ZnP**(2'-MePy$^+$)$_4$-(OH$^-$)$_2$

Calculated geometry of Zn-porphyrins dihydroxo complexes, DFT B3LYP 6-31G(d,p)

As substrates for axial coordination on metalloporphyrins were chosen such bioorganic bases, as pyridine (Py), imidazole (Im), N-methylimidazole (MeIm), histamine (Hist), cysteamine (Cys), glutathione (Glu), theophylline (Theo), adenine (Ade), guanine (Gua) and nicotinic acid (NA). During the experiment it was found that studied cationic porphyrinates binds organic bases rather weak in aqueous solutions, significant ligand additives are required for the reaction proceeding. Besides, it was observed that even small amounts of added ligands significantly increase the pH of solution. With the aim to understand the influence of pH we investigated the interactions between Zn-(tetra-N-methyl-4-pyridyl)porphyrin **ZnP**(4'-MePy$^+$)$_4$, Zn-(tetra-N-methyl-3-pyridyl)porphyrin **ZnP**(3'-MePy$^+$)$_4$, Zn-(tetra-N-methyl-2-pyridyl)porphyrin **ZnP**(2'-MePy$^+$)$_4$ and hydroxide anions in water. In aqueous solutions, under conditions of a large excess of solvent molecules that can be coordinated on the central metal ion, the existence of hexacoordinated axial complexes of zinc porphyrinates with two water molecules is possible. Sequential alkalization of solutions leads first to the replacement of one and then the second water molecule with a hydroxide anion. Sequential addition of OH$^-$ anions is also confirmed by quantum-chemical calculations. Enthalpies of axial complexes formations with water and hydroxide anions were calculated in gaseous phase by means of DFT B3LYP 6-31G(d,p) method. These calculations are in good agreement with obtained from experimental data stability constants of mono- and dihydroxocomplexes of zinc porphyrinates. Investigations in buffer solutions have shown that buffer capacity is not enough for the required bases additives.

Studies of interactions between Sn-(tetra-N-methyl-4-pyridyl)porphyrin (OH$^-$)$_2$**SnP**(4'-MePy$^+$)$_4$ and cysteamine revealed the acidic pH changes during titration which means that protolytic equilibria of two axially-coordinated on porphyrin hydroxo-groups are preferable.

Presented work was supported by Russian Science Foundation (Project № 18-73-00234).

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NEW PLANAR AND SANDWICH TYPE PHTHALOCYANINE COMPLEXES OF PRASEODYMIUM AND NEODYMIUM: SYNTHESIS AND PROPERTIES

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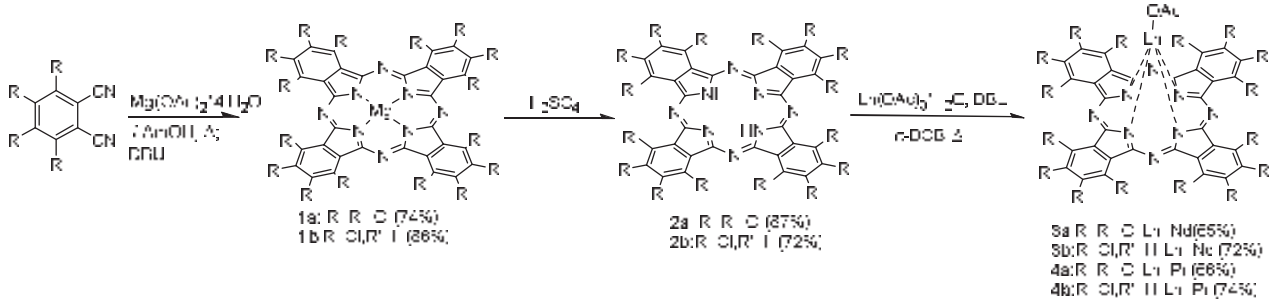
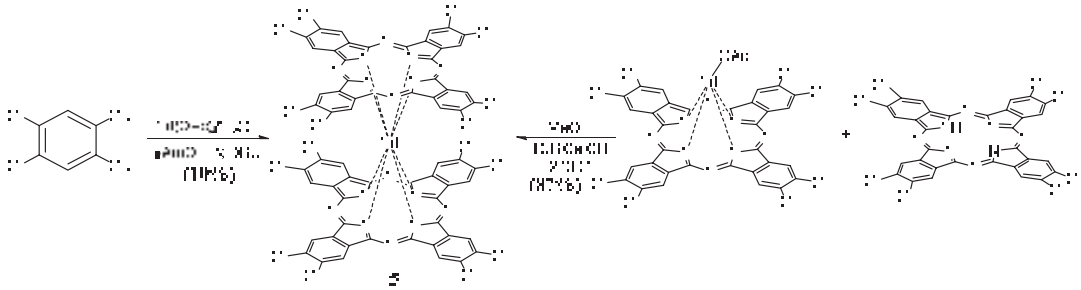
A selective method for the synthesis of new octa- and hexadecachloro substituted phthalocyaninates of praseodymium and neodymium was developed. The target compounds were obtained in three stages: template synthesis of magnesium complex **1**, demetallization with the formation of a free ligand **2** and metallization of the ligand with acetates of the corresponding lanthanides.



It was shown that when attempting template synthesis of complexes **3** and **4**, a mixture of mono and *bis*phthalocyanine complexes is formed from the corresponding nitriles. *Bis*phthalocyanine of neodymium **5** was isolated from the mixture in individual form by gel-permeation chromatography. It was shown that this complex formed as a stable reduced (anionic) form. The directed method of synthesis of complex **5** was carried out on the basis of ready synthetic blocks – monophthalocyanine complex and the corresponding ligand. The synthesis was carried out in a mixture of solvents 1,2,4-trichlorobenzene: cetyl alcohol, in the presence of catalytic amounts of lithium methylate, as a base.



All target compounds were characterized by mass spectrometry MALDI TOF, IR and ^{1}H NMR spectroscopy and electronic absorption spectroscopy.

This work was supported by the Russian Science Foundation (Grant 17-13-01197) and the Russian Foundation for Basic Research (Grant 16-02-00694).

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ACID-BASE EQUILIBRIA OF PHENYL-SUBSTITUTED PORPHYRINOIDS: SPECTROSCOPIC AND QUANTUM-CHEMICAL STUDY

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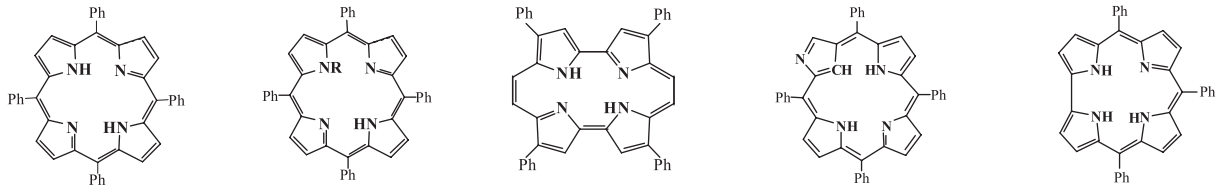
The constitution of the porphyrin macrocycle (MHC) has a significant impact on its acid-base properties. In this work we have studied the influence of the MHC structure, solvent polarity and basicity as well as the acid strength on the basic properties of a series of porphyrinoids: *ms*-tetraphenylporphyrin ($H_2\{ms\text{-Ph}\}_4P$, **1**), its N-substituted ($H[N\text{-Me}]\{ms\text{-Ph}\}_4P$, **2**) and confused ($[^2N,^{21}CH]H_2\{ms\text{-Ph}\}_4P$, **4**) analogues, as well as *ms*-triphenylcorrole ($H_3\{ms\text{-Ph}\}_3Cor$, **5**) and *β*-phenylsubstituted porphycene ($H_2\{\beta\text{-Ph}\}_4Por$, 3). Protonation processes were studied in non-polar benzene (C_6H_6) and polar acetonitrile (MeCN) in the presence of acetic (AcOH) and trifluoroacetic (TFA) acids.



*$H_2\{ms\text{-Ph}\}_4P$, **1*** *$H[N\text{-Me}]\{ms\text{-Ph}\}_4P$, **2*** *$H_2\{\beta\text{-Ph}\}_4Por$, **3*** *$[^2N,^{21}CH]H_2\{ms\text{-Ph}\}_4P$, **4*** *$H_3\{ms\text{-Ph}\}_3Cor$, **5***

MHC such as **1**, **2** and **3** with two basic pyrrolenine nitrogen atoms (=N–) inside of the coordination core (CC) are usually subjected to double protonation [1, 2] in the presence of strong acids to form mono- and dications.

$$\mathbf{H_3P^+_{(solv)} \leftrightarrows H^+_{(solv)} + H_2P_{(solv)};} \qquad \mathbf{H_4P^{2+}_{(solv)} \leftrightarrows H^+_{(solv)} + H_3P^+_{(solv)}}$$

CC (N_4H_3) of the corrole molecule **5**, being a monoacid N-base, in contrast to the porphyrin one has only one basic tertiary N-atom. Usually monocations of corroles (H_4Cor^+) are formed in solutions of medium acids (AcOH) or in dilute solutions of strong acids (TFA). The second protonation step takes place at the C_{ms}-atom in the presence of strong acids. Corrole dications H_5Cor^{2+} are registered in the UV-Vis spectra in 4–13 M TFA in C_6H_6 or MeCN [3].

Confused porphyrinoid can exist as one of two tautomers [4]. In tautomer **b** both =N- atoms are located in the CC, when in tautomer **a** one of them migrates to the periphery of the molecule **4**. The later tautomer undergoes to stepwise protonation with an attachment of the first proton to the external N-atom. The monocation is formed in a solution of 4M AcOH in benzene and 0.46M AcOH in MeCN or in the presence of $3.3 \cdot 10^{-5}$–$4.7 \cdot 10^{-5}$ M TFA in these solvents. The second protonation on the inner-cyclic N-atom is completed in 17 M and 9 M AcOH in C_6H_6 and MeCN, respectively.

Basicity of porphyrinoids increases in the series: **3** < **1** < **5** < **4** < **2**. Basicity and proton location in MHC **1**–**5** is confirmed by quantum-chemical calculations.

This work was supported by the Russian Scientific Foundation (Grant 15-13-00096).

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SOLVATION OF INVERTED PORPHYRINOIDS ACCORDING TO SPECTRAL, CALORIMETRIC AND QUANTUM-CHEMICAL DATA

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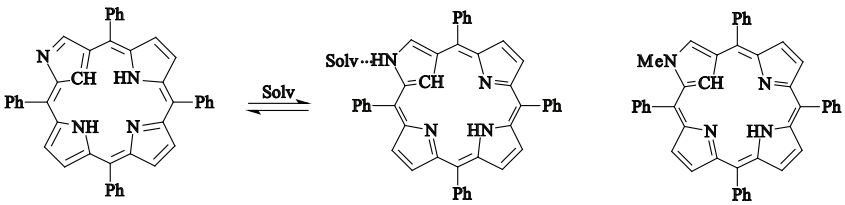
Tetrapyrrolic macroheterocycles (MHC) with the reactive NH-bonds demonstrate a number of intriguing properties [1–3]. For instance, solvent-dependant tautomerism of inverted porphyrin analogs found to regulate an oxidation state of metallocenter inside the coordination cavity of such porpyrinoids at their complexation [2].

Here we firstly present enthalpy characteristics of inverted MHC **I-II** solution in organic solvents of different polarity and acid-basic nature (C_6H_6, $CHCl_3$, DMF) as well as the spectral (UV-Vis) and quantum-chemical data (DFT, B3LYP, CC-pVDZ, NBO-analysis).

Known that inverted porphyrinoid **I** and others can exist in solution in tautomer form *a* or *b*. Parameters of the organic solvents for the former tautomer to appear are DN ≤ 15 and ε ≤ 5; for the later these characteristics are ε ≥ 30, μ > 3.5 D, DN > 25 and DN ≥ AN [4]. When MHC **I** in tautomeric *a* form shows typical non-electrolyte behavior, the solution enthalpy ($\Delta_{sol}H$) of compound **I***b* in DMF is noticeably concentration dependant. Similar behavior in electron donating solvents is inherent to corroles [5] and other MHC with reactive NH-bonds. In contrast, MHC **II** does not represent any concentration dependence of $\Delta_{sol}H$ value. Because of the outer cyclic N-methylation of MHC **II** this inverted porphyrinoid is locked in tautomeric *b* form, but it does not have external NH-proton and therefore not able to interact with coordinating solvents at the periphery of the molecule.



I*a* I*b* II

UV-Vis-spectra and quantum-chemical calculations are in agreement with the calorimetric data discussed. According to the NBO-analysis data compound **I***b* forms the most stable H-bonded associate with DMF molecule among tautomers studied. The energy of stabilization of non-bonding orbital of NH-proton within this associate is 80 kJ/mol with a charge transfer equal 0.037 ch.u. [6].

More details on the experimental and conclusions are given in a poster.

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Lomova T.N., Korolev V.V., Ramazanova A.G., Balmasova O.V., Mozhzhukhina E.G.

IRON(III) PORPHYRIN BASED PARAMAGNETS: SPIN CROSSOVER AND MAGNETOCALORIC BEHAVIOR

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DMF ligated six-coordinated iron(III) mesoporphyrin IX dimethyl ether, $[(DMF)_2FeMP]^+Cl^-$ and chloride ligated penta-coordinated iron(III) 5,10,15,20-tetraphenylporphin, (Cl)FeTPP have been synthesized using porphyrin base coordination with iron(III) chloride to investigate the presence of a room-temperature magnetocaloric effect (MCE) in them and to observe thermodynamic parameters of their magnetization. Direct determination of MCE/magnetization thermodynamic parameters in aqueous suspensions and specific heat capacity (C_p) in a solid at 283–330 K for the iron(III) complexes in comparison with the Mn^{III} analogs [1–6] was performed by the microcalorimetric and DSC methods respectively.

Specific spin-admixed S = 5/2, 3/2 state of $[(DMF)_2FeMP]^+Cl^-$ and pure high-spin state of (Cl)FeTPP were established by temperature-depended ^1H NMR spectrometry. The sharp rise of the C_p values at the low temperatures and its deceleration in the high-temperature area was established and interpreted because of the iron(III) porphyrin spin state changing. The S = 5/2 contribution increase in the spin-admixed S = 5/2, 3/2 state in the $[(DMF)_2FeMP]^+Cl^-$ solid with the temperature growth.

$[(DMF)_2FeMP]^+Cl^-$ and (Cl)FeTPP display positive MCE of 0.028 and 0.020 K at the magnetic induction of 1.0 T and the temperature of 283 and 278 K, respectively. MCE values are associated with both the Fe^{III} spin state and redistribution of spin density between the spin carrier and the macrocycle π-electron system, which are controlled by macrocycle *meso*/peripheral substitution. Macrocycle functional substitution in the iron(III) porphyrins is useful as the way of improving magnetocaloric properties of molecular paramagnets of this class promising in a magnetic cooling and in a diagnostic/therapeutic hyperthermia.

It was done with support of the Russia Foundation for Basic Research, № 18-43-370022.

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MODIFICATION OF MAGNESIUM SILICATE WITH CATIONIC CHLORIN E_6 DERIVATIVES

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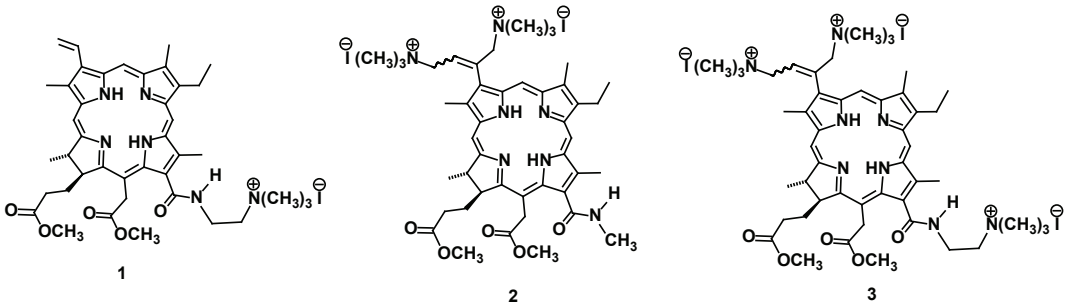
Layered silicates as dispersed carriers are known to prevent porphyrin molecules from aggregation [1] and improve their photochemical stability [1] and fluorescent properties [2]. In this work synthetic layered magnesium silicate with the hectorite composition was used. The aggregation state of mono-, di- and tricationic chlorin e_6 derivatives in water was studied: chlorin e_6 13(1)-*N*-(2-*N*',*N*',*N*'-trimethylammonioethyliodide)amide-15(2),17(3)-dimethyl ester (**1**), 3(1),3(2)-bis-(*N*,*N*,*N*-trimethylaminomethyliodide)-chlorin e_6 13(1)-*N*-methylamide-15(2),17(3)-dimethyl ester (**2**) and 3(1),3(2)-bis-(*N*,*N*,*N*-trimethylaminomethyliodide)-chlorin e_6 13(1)-*N*'-(2-*N*'',*N*'',*N*''-trimethylammonioethyliodide)amide-15(2),17(3)-dimethyl ester (**3**), respectively.



Only (**1**) was found to form a stable colloidal system in water, while the other compounds failed to produce stable colloidal particles. The aggregation stability of colloidal particles in water for (**1**) was found to decrease upon the dilution due to the decreasing of zeta potential. Therefore, in order to provide the conditions under which compound (**1**) interacts with magnesium silicate in the form of individual molecules, it was necessary to carry out the reaction in conditions of maximal dilution. Magnesium silicates modified with the monomolecular form of (**1**) were synthesized by means of the thermal treatment method in aqueous medium. The same approach was applied for obtaining the magnesium silicate particles modified with the monomolecular form of compounds (**2**) and (**3**). The possibility of magnesium silicate modified with compounds (**1**), (**2**) and (**3**) to generate reactive oxygen species (particularly, singlet oxygen) under visible light irradiation was demonstrated. These findings make such hybrid materials promising for further research as heterogeneous photocatalysts.

This work was carried out using the equipment of the core shared research facilities "Chemistry" of the Institute of Chemistry, Komi Scientific Centre of the Ural Branch of the Russian Academy of Sciences.

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THE SYNTHESIS OF NON-METAL SYBSTITUTED IN PHENYL RINGS β-OCTAFENYLPORPHYRASINES

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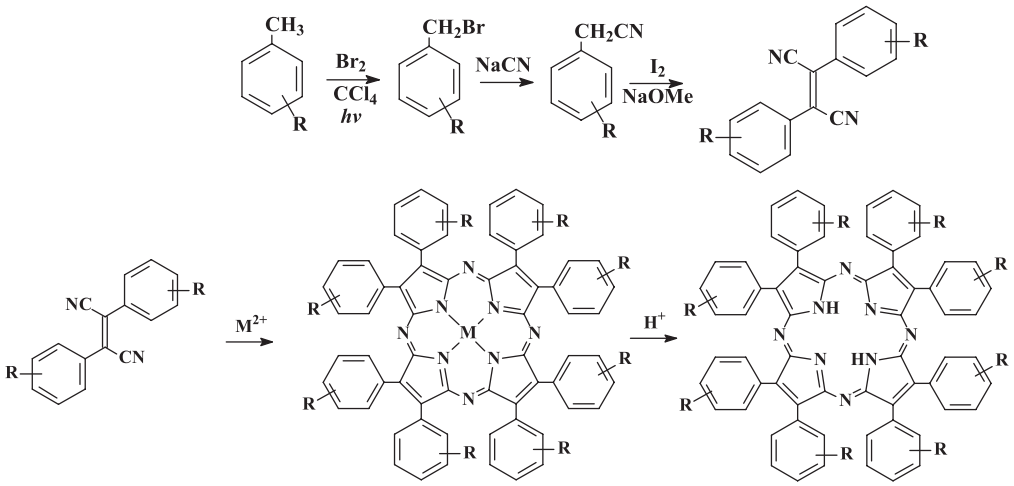
The methods of the synthesis of non-metal *β*-octafenylporphyrasines obtained by the condensation of 1,2-diarylfumaronitriles in different conditions were studied. The precursor fumaronitriles were obtained from substituted toluene by its bromination with further nucleophilic substitution of bromine on the cyano-group and the oxidative condensation (scheme).



M = 2Li; Mg; Pb R = H, tBu, F, Cl, Br, CF_3

It was determined, that the best results of the non-metal *β*-octafenylporphyrasines synthesis were obtained by the reaction in refluxing ethylene glycol in the presence of lead salts or magnesium with the following demetalation of obtained labile metal complexes in the mixture of acetic-trifluoroacetic acids. The obtained compounds may be used for the further modification of substitutes in phenyl rings, and for the preparing stable metal complexes with d-metals and for the conversion into octaphenyltriazacorroles.

All the synthesized compounds were characterized by spectrum methods.

The work was carried out within the framework of State assignment of the Ministry of Education and Science of the Russian Federation № 4.1929.2017/4.6

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COMPLEXATION OF MONO D-LEUCYL SUBSTITUTED TETRAPHENYLPORPHIN WITH ZINC AT AIR - WATER INTERFACE AND OPTICAL PROPERTIES OF LS-FILMS OF THE COMPLEX

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Recently it was shown that zinc complexes of porphyrin-amino acid conjugates have a higher ability to generate singlet oxygen than their metal-free analogs. [1]. The study of their interactions with membrane-forming compounds is also important [2]. Usually, the complexation of porphyrins with metal is carried out in organic solvents at high temperatures. The objective of the present work is to carry out the reaction of formation of the zinc complex of 5-(4′-N-*tert*-butyloxycarbonyl-D-leucylamidophenyl)-10,15,20-triphenylporphine (Zn(D-LeuPh)TPP) at the air-water interface, at the room temperature and to study UV-vis spectra of Langmuir-Shafer (LS) films obtained from the formed layers.

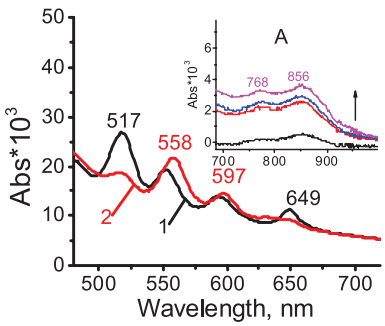

Fig. 1. *UV-Vis spectra of the LS- films formed from the layers at subphase: 1 – water, 2 – zinc acetate water solution)*

The floating layers of (D-LeuPh)TPP were formed on the Langmuir trough "KSV-NIMA" from the solution of the compound in dichloromethane ($C=5\cdot10^{-5}$ M) and at the initial surface coverage degree c_{face}=2–20 %. To carry out the complexation, the solution of (D-LeuPh)TPP was applied on the surface of zinc acetate water solution. The structure of the floating layers was analyzed within the framework of an original model [3].

It was show that the structural unit of the floating layer of (D-LeuPh)TPP at low surface pressures (up to 1 mN/m) at the both subphases is 2D-nanoaggregate. The molecules in nanoaggregates are parallel to the water surface.The structure of monolayers formed on the water surface and on the zinc acetate water solution is the same. Monolayers are characterized by a large diameter of the aggregates (19–80 nm). For comparison, the diameters of the previously studied azaporphyrin derivatives are 10–13 nm [4].

LS-films were formed from face-on monolayers. It was shown that spectra of (D-LeuPh)TPP LS-films differ from the spectrum of the solution. The main bands are red shifted: the Soret band by 4 nm, the Q band by 2–3 nm. The spectra of the LS-films formed from the layers at the zinc acetate water solution indicate the formation of the zinc complex of (D-LeuPh)TPP (Fig.1). It was shown that films of Zn(D-LeuPh)TPP absorb in the near infrared range (768 nm, 856 nm, Fig.1A).

The work is performed in the framework of tasks of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018/4.6).

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Maiorova L.A.[1], Orena M.[2], Shumilova I.A.[1], Koifman O.I.[1,3]

FORMATION OF SUPRAMOLECULAR STRUCTURES FROM A CHIRAL γ-LACTAM DERIVATIVE USING LANGMUIR-SCHAEFER TECHNIQUE

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In recent years, non-protein-induced analogues of natural amino acids and composite materials based on polymers, including supramolecular ones, have attracted considerable interest [1,2]. They are used to obtain new drugs that show better binding to specific receptors and stronger inhibition. 5-Oxopyrrolidine-3-carboxylic acids(γ-lactams) and related compounds with this structure are widely studied for use in medicine, in bio- and nanotechnologies.

The objective of this work is formation and study the nanostructured monolayers and Langmuir-Schaefer (LS) films of 3-*tert*-butoxycarbonyl-1-(1-(4-methoxyphenyl)ethyl)-5-oxopyrrolidine. The floating layers were formed on the Langmuir trough «KSV-NIMA» from the solution of the compound in chloroform ($C=9.39\cdot10^{-5}$ M) with compression rate v= 2.2 $cm^2\cdot min^{-1}$. The structure of the floating layers was analyzed within the framework of an original model and method for quantitative analysis of compression isotherms of nanostructured M-monolayers [3,4].

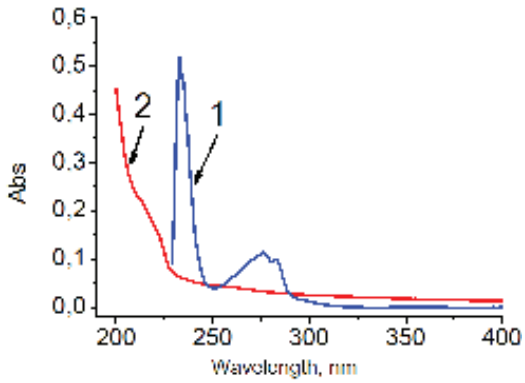

Fig. 1. *UV-Vis spectra of the 5-oxopyrrolidine-3-carboxylic acid derivative solution (1) and the LS-film (2).*

It was shown that the compound at the air-water interface at the initial surface coverage degree c_{face}=20 % and low surface pressures (from 0 to 0.4 mN/m) forms stable M-monolayers. Molecules of 5-oxopyrrolidine-3-carboxylic acid derivative in nanoaggregates are parallel to the water surface. The surface area per molecule in a nanoaggregate is 0.54 nm^2, the number of molecules in an aggregate is 4140. M-nanoaggregates are characterized by a large size. The area per molecule in the nanoaggregate is less than the area per molecule in a densely packed monolayer. Compressibility of the layer is 167 m/N.

Langmuir-Schaefer (LS) films were prepared from the floating polylayers (π_{tr}=9.8 mN/m). Spectra of the film and the solution are shown in figure 1. Formation of supramolecular polymers with non-covalent intermolecular interactions from monomers of 3-*tert*-butoxycarbonyl-1-(1-(4-methoxyphenyl)ethyl)-5-oxopyrrolidine is proposed.

The work is performed in the framework of tasks of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018/4.6).

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Maiorova L.A.[1], Mamardashvili N.Zh.[2], Mamardashvili G.M.[2], Kharitonova N.V.[1], Shumilova I.A.[1], Koifman O.I.[1,2]

AXIAL COORDINATION OF COBALT TETRAPHENYLPORPHINE WITH IMIDAZOLE AT THE AIR-WATER INTERFACE AND OPTICAL STUDY OF LS-FILMS OF THE COMPLEX

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Porphyrins are able to coordinate different kind of organic molecules, including various drugs. The aim of this work is investigation a possibility of formation of axial complexes of cobalt(II) tetraphenylporphine (CoTPP) in the layers at air-water interface.

The floating layers of CoTPP (Sigma-Aldrich) were formed with the use of the NT-MDT Langmuir trough (Zelenograd, Russia) from a solution of the compound in dichloromethane ($C=1.4\cdot10^{-4}$ M) at the initial surface coverage degree c_{face}=20 %. To carry out axial coordination, the solution of CoTPP was applied onto the surface of imidazole (Sigma-Aldrich) water solution. The structure of the layers at air–water interface was analyzed by using quantitative analysis of compression isotherms of a M-monolayer [1,2].

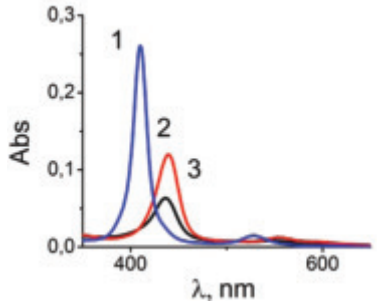

Fig. 1. *UV-Vis spectra of the CoTPP solution (1), the LS-film of CoTPP (2), and the LS-film of axial complex of CoTPP with imidazole (3).*

It was shown that the structural unit of the floating layer of CoTPP at low surface pressures (up to 1 mN/m) at the both subphases is 2D-nanoaggregate. The molecules in nanoaggregates are tilted to the water surface. The structure of monolayers formed on the water surface and on the imidazole water solution is different. The surface area per molecule in a nanoaggregate is 1.7 nm^2 and 2.0 nm^2, number of molecules in an aggregate is 200 and 125, for CoTPP and the complex of CoTPP with imidazole, respectively. The diameter of the aggregates is the same (18–20 nm).

Langmuir-Schaefer (LS) films were prepared by deposition of edge-on monolayers onto quartz plates. It was shown that the spectra of CoTPP LS-films differ from the spectrum of the solution. The main bands are strongly red shifted: the Soret band by 26 nm, the Q band by 20 nm (Fig. 1, lines 1, 2). The spectra of the LS-films formed from the layers at the imidazole water solution differ from the spectrum of the LS-films formed from the layers at the water. The main bands are red shifted: the Soret band by 3 nm, the Q band by 6 nm (Fig.1, lines 2, 3). Thus, mono-axial complex of cobalt tetraphenylporphine with imidazole was formed at room temperature at the air-water interface and in Langmuir-Schaefer films.

The work is performed in the framework of tasks of the Ministry of Science and Higher Education of the Russian Federation (project № 4.1929.2018/4.6, in the part of the Langmuir-Schaefer films formation) and Russian Science Foundation (project № 19-73-20079, in the part of synthesis and identification of the porphyrinate-imidazole complex).

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Makarov V.V.[1], **Rybenkova A.A.**[1], **Shukhto O.V.**[1], **Aleksandriyskiy V.V.**[1], **Khodov I.A.**[2], **Khudyaeva I.S.**[3], **Belykh D.V.**[3], **Kustov A.V.**[1,2], **Berezin D.B.**[1]

AGGREGATION OF CHLORIN E_6 TRICATIONIC DERIVATIVE IN AQUEOUS SOLUTIONS IN THE PRESENCE OF SURFACTANTS

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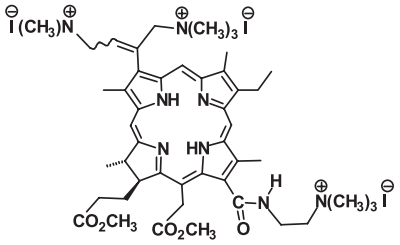
An important problem of pharmaceutical chemistry is the development of methods for the preparation of water-soluble dosage forms of drugs. In the case of preparations for photodynamic therapy (PDT), usually low water solubility causes the aggregation of photosensitizers (PS), reduces the efficiency of the singlet oxygen generation and PDT effect.



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One of the ways to increase it is to encapsulate the drug in an appropriate surfactant micelle or polymer structure, which also can be used for the PS delivery to target cells. Here we used a set of methods (DLS, UV-Vis, ^{1}H NMR, 2D DOSY) to study the aggregation behavior of chlorin e_6 derivative **1** [1] with three quaternary alkylammonium groups in water and aqueous surfactant solutions (Tween 80, PVP, m_{PS} from 10^{-5} to 10^{-3} mol/kg).

According to DLS study the formation of big aggregates with average diameter of 200 nm is observed at m_{PS} over $1.2\cdot10^{-3}$ mol/kg) [2]. Addition of even small amounts of surfactant (PS – PVP = 3 – 1) results in elimination of nano-sized aggregates. Meantime, UV-Vis spectra of comp. **1** demonstrate that even in millimolar solutions PS is associated in water-alcoholic solutions above 60 % of H_2O. Addition of about 100-fold excess of surfactant leads to the complete PS monomerization. PS – Tween 80 and PS – PVP binding constants are calculated and compared.

The features of comp. **1** aggregation in aqueous solutions were studied in details by one- and two-dimensional NMR spectroscopy ($m_{PS} = 10^{-3}$–10^{-4} mol/kg). The proton signals of PS **1** in ^{1}H NMR are shifted downfield with the addition of PVP and Tween 80 owing to the partial disaggregation and micelle binding. The chemical shift is changed up to the $m_{TWEEN\ 80} = 5\cdot10^{-3}$ mol/kg (5-fold excess) and $m_{PVP} = 4\cdot10^{-2}$ mol/kg (40-fold excess). Broad proton signals demonstrate the complete formation of molecular PS form is not observed at these conditions, presumably, because of the ionic nature of PS molecules. As the polymer or surfactant concentration increases the most noticeable downfield shifts are found for amide $^{13(1)}$NH-, *meso*-^{5}CH- and vinyl $^{3(2)}$CH= protons, the dependence on the nature of solubilizer is very little. Apparently, protons mentioned are involved in the interaction between PS **1** and surfactant molecules. 2D DOSY investigation of PS **1** surfactant solutions partially supports this suggestion. Details are given in a poster.

This work was partially supported of Russian Science Foundation (project No. 15-13-00096).

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Makarov V.V.[1], **Savonin P.V.**[1], **Belykh D.V.**[2], **Shukhto O.V.**[1], **Krest'yaninov M.A.**[3], **Kustov A.V.**[1,3], **Kudayarova T.V.**[1], **Berezin D.B.**[1]

MS-ARYLSUBSTITUTED CORROLES: SYNTHESIS, INTERPHASE DISTRIBUTION, AGGREGATION, MICROBIOLOGICAL TESTING

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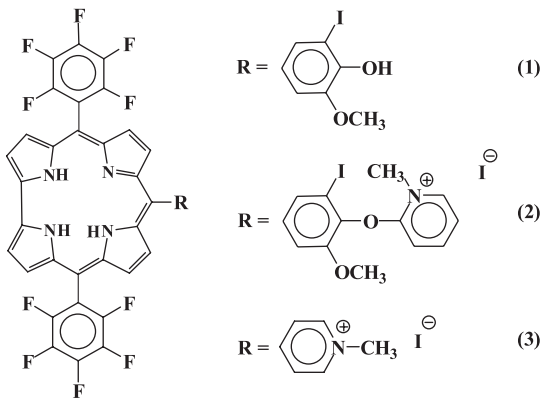
Low-symmetry corroles can be used as photosensitizers (PS) in photodynamic therapy (PDT) for fighting cancer and photoinactivation of microorganisms [1].

This work presents an approach to the synthesis of A_2B-type *meso*-substituted corroles containing both hydrophobic and hydrophilic fragments (comp. **1**–**3**). All the compounds synthesized has been identified using UV-Vis, 1D (^{1}H, ^{13}C) and 2D (HSQC, HMBC, COSY) NMR-spectroscopy as well as mass spectrometry.

Porphyrinoids **1**–**3** are found to be hydrophobic and exposed to aggregation in water-ethanolic solutions at $m_{PS} = 7.3\cdot10^{-6}$ mol/kg from 52 to 70 % of H_2O. Addition of non-ionic surfactant Tween 80 does not result in effective disaggregation, observed earlier for chlorins and other mactoheterocycles (MHC) [2]. Little disaggregation of PS **1** is confirmed by its low binding constant to Tween 80 ($K_b = 0.59\pm0.07$) and slight fluorescence in aqueous surfactant solution.



To evaluate quantitatively the hydrophilic-lipophilic balance (HLB) of corrole PSs the interphase distribution coefficients (P) in the octanol-water system were determined at 298–318 K. The strong temperature dependence of lg*P* values found is common for mainly hydrophobic compounds [3,4]. Because of the poor solubility of PS **1** in both 1-OctOH and H_2O the surfactant Tween 80 was added in molar ratio with PS equals 10–1 and 100–1. In this case lg*P* values found to decrease reasonably as the concentration of surfactant increased demonstrating higher hydrophilicity of PS in the solution.

The results of the study of comp. **1** antimicrobial phototoxicity when exposed to antibiotic-resistant strains of *E. Coli* demonstrate the high PDT effect at the irradiation dose of 80 kJ/cm^2 and $m_{PS} = 5\cdot10^{-4}$ mol/kg. Details are presented in a poster.

This work was supported by the Russian Scientific Foundation (Grant 15-13-00096).

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF FUNCTIONALLY SUBSTITUTED COMPLEXES OF TETRAPYRIDYLPORPHINE

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The Co- and Cu-complexes of *5,10,15,20*-tetrakis(1`-methyl-pyrid-4 and 3-yl)porphin tetratosylates are synthesized. Metallocomplexes are characterized by electronic spectroscopy and mass spectrometry.

Their redox properties have been studied by cyclic voltammetry. The influence of the heteroatom position in pyridyl fragments, the influence of the nature of the metal in the porphyrin molecule on the character of cyclic *I,E*–curves, the values of redox potentials and the electrocatalytic activity of compounds in the molecular oxygen reduction reaction are shown.

The spectral properties of the ligands H_2(1'-methyl-Py-3)$_4$P (Ts$^-$)$_4$ and H_2(1'-methyl-Py-4)$_4$P (Ts$^-$)$_4$ before and after reduction at the corresponding potentials, as well as the metal oxidation process in the composition of Co(1'-methyl-Py-4 - and -3)$_4$P (Ts$^-$)$_4$ were estimated.

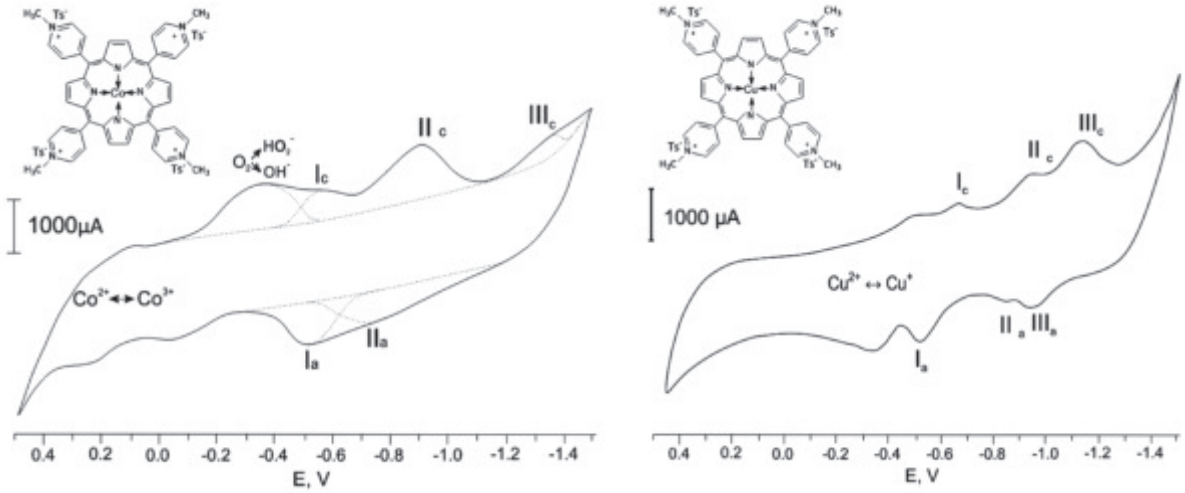

Fig. *Current-voltage curves for electrodes with application: a) Co(1`-methyl-pyrid-3-yl)P (Ts$^-$)$_4$; b) Cu(1`-methyl-pyrid-3-yl)P (Ts$^-$)$_4$ in 0.1M KOH in the atmosphere of Ar. υ=0.02 V·s^{-1}*

The depolarization effect $\Delta E_{1/2}(O_2)$ for Co(1'-methyl-Py-3)$_4$P (Ts$^-$)$_4$ and Co(1'- methyl-Py-4)$_4$P (Ts$^-$)$_4$ is 0.14 and 0.16 V, respectively, which is slightly more than for unsubstituted Co(Py-3)$_4$P (0.15) and Co(Py-4)$_4$P (0.12); for Cu(1' - methyl-Py-3)$_4$P (Ts$^-$)$_4$ and Cu (1' - methyl-Py-4)4P (Ts$^-$)$_4$ is 0.10 V, for unsubstituted complexes of Cu(Py-3)$_4$P (0.11) and Cu(Py-4)$_4$P (0.14) and for (Cl)Fe(1' - methyl-Py-4)$_4$P (I$^-$)$_4$ is Δ0.05 V.

Studied Co-complexes of tetraphenylporphyrin are quite effective system that can be of interest when using them as heterogeneous and homogeneous catalysts of oxidation processes with participation of molecular oxygen.

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NOVEL HYDROPHILIC CHLORIN E_6 DERIVATIVES WITH GALACTOSE FRAGMENTS: SYNTHESIS AND PHOTOTOXIC ACTIVITY

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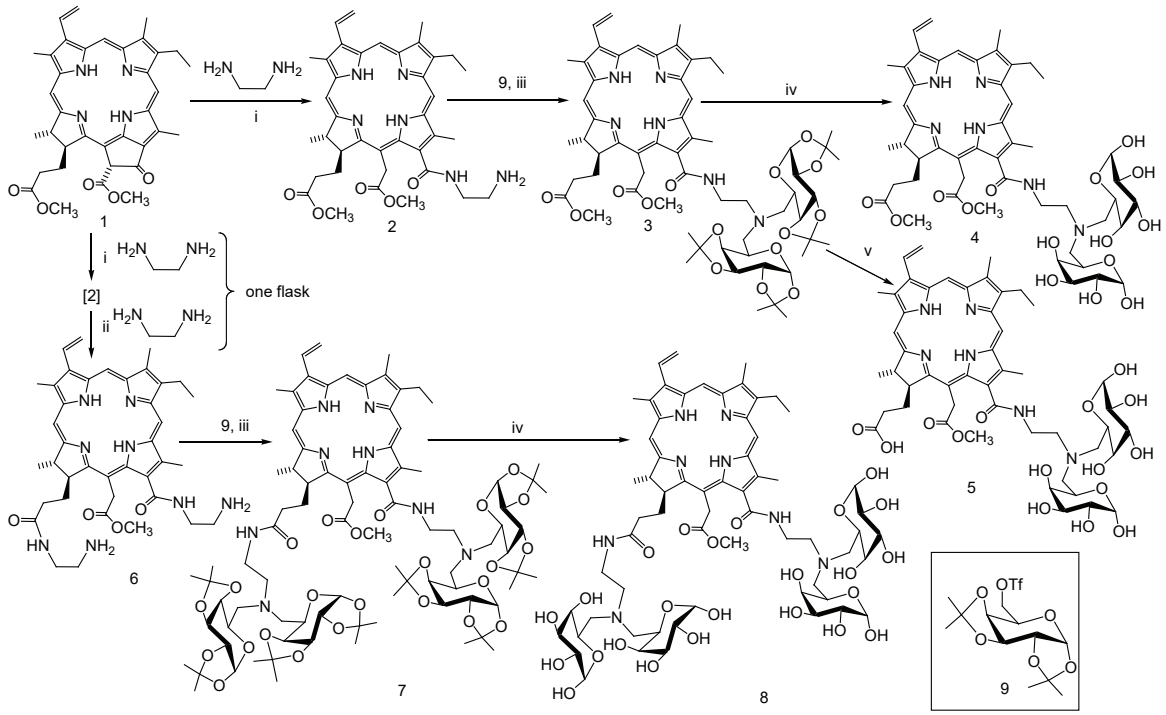
Promising from the point of view of further improvement of photosensitizers for photodynamic therapy of oncological diseases and diagnostic preparations based on chlorophyll *a* derivatives is their conjugation with carbohydrates. A galactose fragment significantly increases the bioavailability of the PS molecule, contributes to an increase in the affinity for malignant tumors and the active transport of such conjugates through the cell membrane. In the present work, chlorin e_6 derivatives with two (compounds **4** and **5**) and four (compound **8**) galactose fragments on the periphery of the macrocycle linked through a carbon atom at position 6 of the galactose molecule were synthesized (Scheme 1). It was shown that the synthesized compounds have intense red fluorescence inside the HeLa cell and exhibit phototoxic properties with respect to the cells of this line (irradiation with a LED with a wavelength of 660 nm).



i: $CHCl_3$, r. t., 2 h; ii: r. t., 20 h; iii: THF, reflux, 3 h (yield: **3** (48 %), **7** (22 %)); iv: TFA(90 %)-H_2O, 3–4 h (yield: **4** (81 %), **8** (76 %)); v: TFA(90 %)-H_2O, 48 h (yield of **5** (35 %)).

Scheme 1

This work performed using equipment of the CCU «Chemistry» at the Institute of Chemistry of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar) and CCU «Molecular Biology», the Institute of Biology of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar

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SYNTHESIS AND PROPERTIES METAL-ORGANIC FRAMEWORK BASED ON *P*-TETRAKIS-4-CARBOXYPHENYLPORPHYRIN COBALT (II) AND ALUMINUM NITRATE

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At present, more attention is paid to the study of organometallic coordination polymers (Metal-Organic Framework, MOF). The directional synthesis of new ligands, on the basis of which new organometallic framework structures (MOFs) are being created, is gaining an increasing role. MOFs are comprised of a central metal or metal complex that binds to organic ligands. The organic ligands that make the framework structure are known as linkers (salts and acids). Since porphyrins are structurally stable molecules with functional groups with terminal pendants, while demonstrating a relatively rigid geometry and high thermal stability, they can easily be built in the pores of the organometallic framework structure. Porphyrin MOFs have interesting properties that are used in photonic devices, conducting polymers, chemical sensors and selective catalysis [1].

The aim of this work is the getting of MOF, by condensation of p-tetrakis-4-carboxyphenylporphyrin cobalt (II) and nonahydrate aluminum nitrate in a solvent media (N,N-dimethylformamide). For purity of MOF, p-tetrakis-4-carboxyphenylporphyrin cobalt (II) was tested using mass spectrometry, IR, and UV-visible spectroscopy. The physics-chemical properties of MOF were verified using IR spectroscopy and thermogravimetric analysis of TGA/DSC. A number of characteristic bands are observed in the IR spectrum of the synthesized material, which are responsible for the stretching vibrations of C=O bonds in carboxyl groups and the bands characteristic of the porphyrin macrocycle. It should be noted that, according to the obtained thermal analysis data, MOF at a temperature of 18 °C to 300 °C under inert and oxidative conditions lost less than 35 % of its mass, which makes it possible to propose an organometallic coordination polymer as a photocatalyst and an redox catalyst.

The prospect of further research is the study of the obtained MOFs as a catalyst for the oxidation of organic substrates such as ascorbic acid, morin and β-carotene, since it is known that representatives of this class of MOF compounds possess suitable physics-chemical properties for these purposes: high porosity, metals and functional groups, high thermal stability, as well as a large surface area [2].

This work was supported by the RFBR (grant No. 18-03-00986). The study was conducted using the resources of the Center for the collective use of scientific equipment FSBEA HE "ISUCT".

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Motorina E.V., Ovchenkova E.N., Mozhzhukhina E.G., Lomova T.N.

NEW MOLECULAR SENSORS BASED ON NB(V) 5,10,15,20-(TETRA-*P*-*TERT*-BUTYLPHENYL)PORPHIN TO DETECT VOCS

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The reactions of niobium(V) 5,10,15,20-(tetra-p-*tert*-butylphenyl)porphyrins, (A)NbT^{t}BPP (A = Cl_3 or OCl) with pyridine (Py) and pikoline (Pic) were studied by chemical thermodynamic/kinetic technique using the author's method of simultaneous registration of the data in the concentration and time fields. The chemical transformations were used as a self-assembly model towards niobium(V) porphyrin – 1′-N-methyl-2′-(pyridin-4-yl)pyrrolidino[3′,4':1,2][60]fullerene, PyC_{60} systems (Figure).

The systems were investigated in toluene at 298 K and invariable concentration of metal porphyrine C_{MP}=2.45×10^{-6} M in the wide concentration regions of Py and Pic. The initial niobium(V) porphyrins were synthesized and isolated as individual compounds according to original technique [1]. The stoichiometry, nature and number of stages were determined, the equilibrium constants and rates were calculated for each reaction.

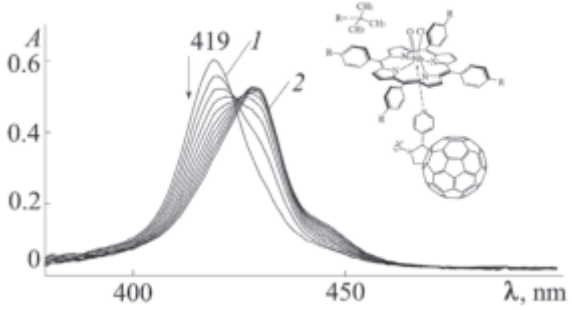

Fig. *UV-visible spectra of (OCl)NbT^{t}BPP in toluene–PyC_{60} mixture ($C_{PyC_{60}}$ = 8.75×10^{-5} M) immediately after preparation (1) and after 24 hours (2). The other lines correspond to intermediate moments of time*

The complexes niobium(V) were established to be the perspective detectors of pyridine and pikoline in solutions. They can be practically used for detection of alcohols, hexylamine, octylamine as well as other volatile organic compounds (VOCs) [2]. The self-assembling metal porphyrin – pyridyl-substituted fullerene systems are promising in formation of donor-acceptor complexes displaying the properties of PET.

Carried out with the help of «The upper Volga region centre of physic-chemical research», funded by Russian Foundation for Basic Research and the government of the region of the Russian Federation, № 18-43-370023 (the synthesis of PyC_{60}).

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Nikitin I.A.[1], **Skvortsov I.A.**[1], **Stuzhin P.A.**[1]

SYNTHESIS AND STUDY OF UNSUBSTITUTED TRIPYRAZINOSUBPORPHYRAZINE

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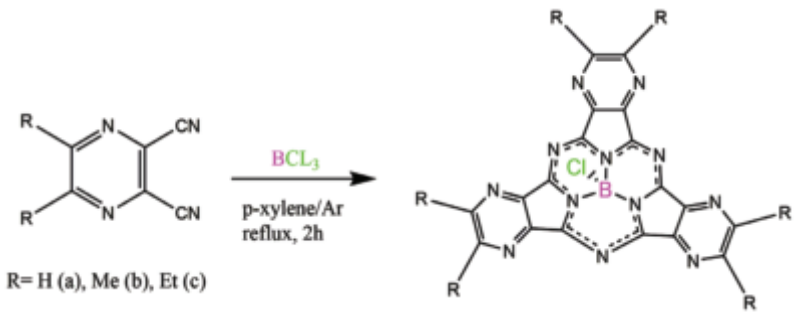
Subphthalocyanines are macroheterocycles in which three isoindole fragments are arranged around a boron atom bound to some axial ligand. They are used in organic electronics. It is known that the electron-acceptor properties can be increased with the replacement of CH groups in the aromatic molecules by nitrogen atoms N.

The aim of the work is the synthesis and study of the properties of aza-analogues of subphthalocyanines containing, instead of benzene rings, π-deficient pyrazine fragments.



In the work, unsubstituted tripyrazinosubporphyrazine was synthesized. The structure of the macrocycle was established on the basis of mass spectrometry MALDI-TOF. Its spectral properties were studied (UV-VIS, ^{1}H NMR). According to quantum chemical data, this compound can be an electron acceptor and can be used in organic electronics devices as n-type semiconductors.

Methyl and ethyl substituted subporphyrazines were obtained only in trace amounts that were not isolated and characterized.

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Nikolaeva O.I., Ageeva T.A., Koifman O.I.

EFFECT OF POLYMERIC ENVIRONMENT ON REACTIVE ABILITY OF PORPHIRINS IN COMPLEXATION REACTIONS

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The multifaceted nature of the use of tetrapyrrole macroheterocyclic compounds (MHCC) of various structures in recent decades has stimulated an increased interest in research towards obtaining new porphyrinpolymer (PP) systems. Two well-known methods are used as methods for incorporating porphyrins into the polymer matrix – radical copolymerization with vinyl monomers of non-porphyrin nature and immobilization of porphyrins and their analogues on the finished polymer, accompanied by polymer-analogous transformations. Synthetic MHCC with amino, hydroxy and carboxy groups and natural ones with a vinyl group on the periphery of the molecule act as porphyrins. Comonomers with different types of functional groups – methylacrylate, methylmethacrylate (MMA), glycidylmethacrylate (GMA), vinylpyrrolidone, etc. act as polymeric carriers.

We have obtained various functional polymers containing macrohetero-cyclic units in the side chain of the macromolecule.

One of the main properties of MHCC is the ability to form coordination compounds with various metal ions - metalloporphyrins, which have various structural and chemical features. Synthesis and study of metalloporphyrinpolymer systems with different metals in the coordination center of the MHCC represents one of the most important stages in the design of effective functional supramolecular systems. However, in the literature there is practically no information about the reactivity of porphyrins related with polymers. These data are of interest from the point of view of establishing the influence of the macro-molecular chain of a polymer on character of the resulting coordination centers, their structure, the nature of the bond, and the reactivity of macromolecules.

The complexing properties of porphyrinpolymers based on methylphaeophorbide *a* (MPP) with Cu (II) acetates in DMF and THF at different temperatures were studied for the first time. The MMA and GMA acted as the vinyl comonomers of the MPP. The kinetic and activation parameters of the reaction showed that for free porphyrin, the reaction rate of complexation in DMF and THF is almost the same, and the activation energy in the latter case is twice as high. The nature of the solvent significantly affects the kinetic parameters of complexation of porphyrins in the copolymer. In DMF, the rate of formation of metal complexes, while remaining independent of the copolymer composition, decreases by an order of magnitude during the transition from porphyrin to its copolymers. The rate constants of the complexation reaction acquire an obvious dependent on the concentration of the copolymer in the solution only with increasing temperature.

The kinetics of complexation of PP immobilizates with Cu (II) acetates in DMF has also been studied. PP immobilizates differ in the nature and length of the spacer. The larger the spacer size, the more mobile and more active the porphyrin is in the reactions with metal salts.

Thus, it was shown that the kinetic parameters of the complexation reaction upon immobilization on the carrier polymers can be influenced by the nature and composition of the polymer-carrier, the participation of the polymeric environment of the ligand in its solvation. The structure of the porphyrin determines the orientation of its immobilized molecules in solution and the availability of a coordination center for metal ions.

This work was supported by the grant of the RFBR, project № 18-03-00986.

Ostroverkhov P.V.[1], Zakurinov Y.E.[1], Kirin N.S.[1], Mironov A.F.[1], Grin M.A.[1]

PHOTOSENSITIZERS ON THE BASIS OF DERIVATIVES OF BACTERIOCHLOROPHYLL A WITH RESIDUES OF AMINO ACIDS

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Photodynamic therapy (PDT) is rather soft noninvasive method of therapy of oncological diseases. The main advantages of PDT are: locality of action at which healthy tissues are unaffected, a possibility of out-patient treatment, a lack of postoperative complications at preservation of function of the struck body, decrease in a system adverse effect on an organism.

Now photosensitizers (PS) of various classes are applied in clinic or these are at different stages of clinical tests but a natural chlorophyll and their derivatives with intensive absorption in distant red and near IR-area of a range are of special interest.

The main problems of modern photosensitizers are their hydrophobicity and low selectivity of accumulation in cancer cells. It dictates the need of creation of steady photosensitizers on the basis of chlorins and bakteriochlorins with improved spectral characteristics, the increased hydrophily for solubility in the polar solvents and water possessing a considerable definition to tumors.

It is known that biogenic amino acids are necessary for many metabolic processes in tumor cells. For example, recent researches showed primary accumulations of conjugates of PS with amino acids in mitochondria of tumor cells, and, as a result, there is significant increase in efficiency of PS.

Other target of amino acid derivatives of PS on the basis of poly-S-lysine and meso-tetraarylporphyrine is the membrane of bacterial cells. It was shown that similar drug effectively has phototoxicity in relation to antibioticresistant gram-positive and gram-negative bacteria [1]. Thus amino acid derivatives of PS are perspective candidates for PDT.

In this work derivatives of backteriochlorins from the residues of methyl ethers of a L-lysine and L-arginine were received by method of the activated ethers. Substances were cleaned and the structure was confirmed with methods of nuclear magnetic resonance spectroscopy and mass- spectrometry.

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Ovchenkova E.N., Bichan N.G., Ksenofontov A.A., Lomova T.N.

SPECTROSCOPIC INVESTIGATION OF THE NOVEL FLUORINATED MANGANESE(III) PHTHALOCYANINE – FULLERENE DYADS WITH PHOTOINDUCED ELECTRON TRANSFER

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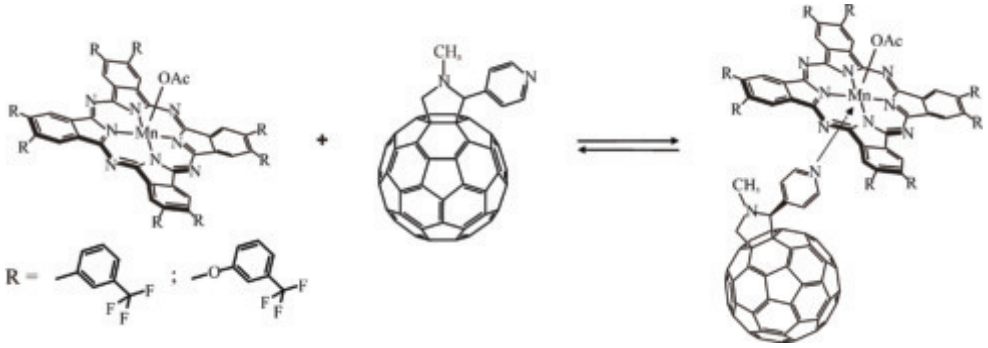
In recent years, the fluorinated porphyrinoids are actively studied because of number of advantages and additional features due to the introduction of fluorine atoms or fluorocarbon substituents into the structure macrocycle. So, they have an intense absorption at 600–750 nm and good solubility in different solvents. The special attention is paid to studying electrochemical behavior of fluorinated porphyrins/phthalocyanines and their metal complexes [1]. It has been shown that the introduction of fluorine atoms or fluorocarbon substituents significantly increases the oxidation potential of the molecule by compared with non-fluorinated analogues [2].

The data on the self-assembly of donor-acceptor complexes based on m-trifluorometylphenyl/m-trifluorometylphenoxy-coated phthalocyaninato manganese(III) and 1′-N-methyl-2′-(pyridin-4-yl)pyrrolidino[3’,4’:1,2][60]fullerene are presented in the report.



The structure of the obtained dyads was established by means of chemical thermodynamics/kinetics, UV-vis, IR, ^{1}H NMR spectroscopy. The phthalocyanine-fullerene dyads showed an efficient property of intramolecular photoinduced electron transfer as confirmed by fluorescence and DFT study. The substantial quenching of the fluorescence emission of the manganese(III) complexes by axially bonded [60]fulleropyrrolidin gives the positive result that shows prospects of the studying dyads as the active layers in solar energy conversion devices.

Carried out with the help of «The upper Volga region centre of physic-chemical research», funded by Russian Foundation for Basic Research and the government of the region of the Russian Federation, № 18-43-370023 (the synthesis of PyC_{60}).

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Petrov O.A., Osipova G.V., Khelevina O.G.

KINETIC CONTROLLED PROCESSES OF SLOW INTERMOLECULAR PROTON TRANSFER OF NH-GROUPS β-SUBSTITUTED AND β, β-ANNELATED PORPHYRAZINES

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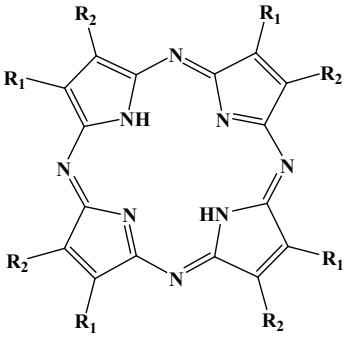
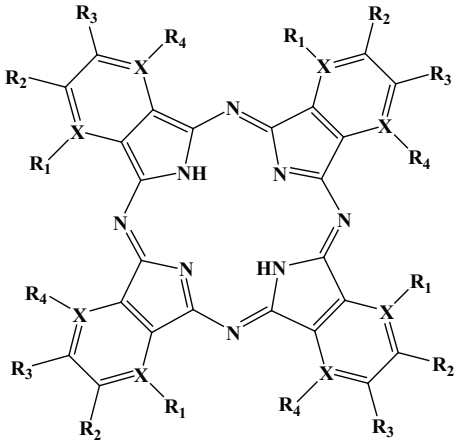
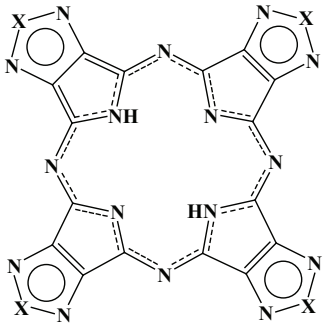
Due to pronounced acidic properties of intracyclic NH-bonds, porphyrazines enter into uncharacteristic for porphyrins kinetically controlled acid-basic interactions with pyridine, 2-methylpyridine, *n*-butylamine, *tret*-butylamine, diethylamine, triethylamine piperidine, morpholine, dimethylsulfoxide and diethylsulfoxide in benzene (chlorobenzene).



R_1=H; R_2=Br
R_1=H; R_2=Cl
R_1=R_2=$C_6H_4NO_2$
R_1=R_2=C_6H_4Br
R_1=R_2=$C_6H_4CF_3$



X=H; R_1=R_4=H; R_2=NO_2; R_3=Bu^t
X=H; R_1=NO_2; R_2=R_4=H; R_3=Bu^t
X=N; R_1=R_3=R_4=H; R_2=Bu^t
X=N; R_1=R_4=H; R_2=R_3=Et
X=N; R_1=R_4=H; R_2=R_3=Ph



X = S, Se

Reactions are characterized by unusually low values of the rate constants (10^{-2}–10^{-6} l/mol s), which is not characteristic of the overwhelming generality of relatively simple liquid-phase acid – base systems. Acid-base interactions lead to the formation of proton transfer complexes with different stability, which have D_{4h}-symmetry of the π-chromophore molecule.

The kinetic equations of the process are established and a possible scheme for the intermolecular transfer of the protons of the porphyrazines NH-groups to nitrogen- and oxygen-containing bases is proposed.

In the case of tetrahalogenporphyrazines, a correlation was found between the values of k^{298} and pKa (PA) of nitrogen-containing bases, which have a sterically unshielded nitrogen atom in the molecule.

It established that bulky substituents in the porphyrazine macrocycle and / or in a nitrogen-containing base prevent optimal spatial orientation of the partner molecules during the acid-base interaction and inhibit the intermolecular transfer of protons of NH-groups.

It is shown that an increase in the dielectric constant of the environment favors the acid-base interaction of the porphyrazine macrocycles with bases.

Petrova D.V., Semeikin A.S.

THE SYNTHESIS AND MODIFICATION OF *MESO*-MONOSUBSTITUTED ON PHENYL RINGS CORROLES

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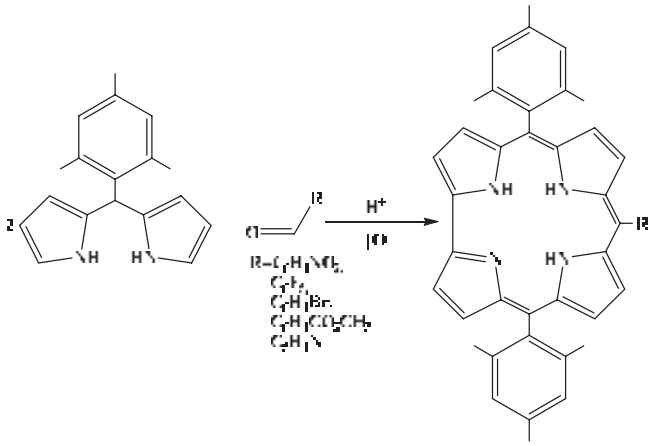
The corroles are aromatic analogs of the porphyrins, which haven't one methane bridge. As a result, the corroles have a distortion reaction center and their properties significant differ from porphirins properties. Currently these compounds are actively studied.

The corroles of A_2B-type, containing mesityl groups in 5-,15-positions and phenyl rings with active groups in 10-position, were synthesized by the condensation of substituted benzaldehydes and 5-mesityldipyrromethane (scheme).



Scheme

These compounds were used for the caring out of modification reactions of substitutes of phenyl rings of corrole's macrocycle:

1. for the reduction of nitro-group of nitrophenylcorrole, with the following acylation and the diazotization of the obtained aminophenylcorrole with the further conversions of the diazo groups;
2. for the nucleophilic substitution of fluorine in the pentafluorophenylcorrole;
3. for the palladium-catalyzed reaction of the brominephenylcorrole.

The obtained compounds were characterized by the spectrum data, which prove their structure.

The work was carried out within the framework of State assignment of the Ministry of Education and Science of the Russian Federation № 4.7305.2017/8.9.

Petrova D.V., **Berezina N.M., Bazanov M.I., Semeikin A.S.**

THE INFLUENCE OF THE METAL NATURE AND THE FUNCTIONAL SUBSTITUTION OF CORROLES ON THEIR ELECTRO CATALYTIC PROPERTIES IN WATER-ALKALINE SOLUTION

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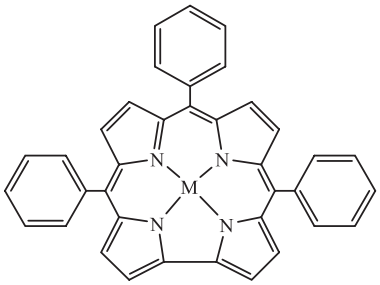
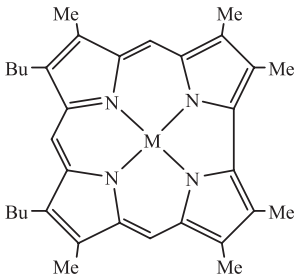
The corroles are aromatic analogs of porphyrins, which differs by the lacking of one methane bridge. As a result, the corroles have a distortion reaction cavity, and its properties differ from porphyrins' properties in a significant grade.

In this research the electrochemistry characteristics of *meso*-threephenylcorroles **1** with the silver {Ag^{III}(*ms*-Ph)$_3$Cor}, the antimony {(Py)Sb^{III}(*ms*-Ph)$_3$Cor}, the cobalt {(PPh_3)Co^{III}(*ms*-Ph)$_3$Cor}, and of the β-alkylsubstituted corroles **2**: {H_3(Me_6Bu_2)Cor}, {Cu^{II}(Me_6Bu_2)Cor}, {(Py)Sb^{II}(Me_6Bu_2)Cor} have been studied.



M=Ag, Sb(py), Cu, Co(Py), Co(PPh_3)

1



M= H_3, Sb(py), Cu

2

Here it is shown the influence of the metal, the effect of extracoordination on the example of cobalt complexes, the effect of *β*-substitution on the characteristics of the cyclic voltammograms (CVA) and on the activity of compounds in the reaction of the electroreduction of the oxygen at the interface "electrode - electrolyte solution".

It has been determined, that in the atmosphere of the argon the *meso*-phenylcorroles undergo a single process of the electroreduction of π-conjugated system and a single process of the reduction in the cases of the complexes with the silver and the antimony(III), and a single of process of oxidizing in the case of cobalt complex. The studied metalcorroles have the maximum of electrocatalytic activity in the form of the cobalt(III) complexes. For a number of the alkyl-substituted corroles in the atmosphere of the argon on the CVA curves one process of the electroreduction of macrocycle is observed.

As the result it has been determined, that the introducing of *β*-alkyl substitutes in the corroles molecule by comparison with *meso*-threephenylcorroles, shown on the example coordination compounds of antimony, has a positive effect on the electro catalysis of the oxygen reaction of the reduction. In its turn, the extra coordination on the cobalt atom (L = PPh_3) in the composed of (PPh_3)Co^{III}(*ms*-Ph)$_3$Cor, also leads to a noticeable improvement in the electrocatalytic properties of the complex (by 40 mV), compared to (DMF)Co^{III}(*ms*-Ph)$_3$Cor [1].

The work was carried out within the framework of State assignment of the Ministry of Education and Science of the Russian Federation № 4.7305.2017/8.9

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Petrova M.V.[1], **Maiorova L.A.**[1], **Ageeva T.A.**[1], **Koifman O.I.**[1,2]

STRUCTURE OF M-MONOLAYERS OF POLY(4-VINYLPYRIDINE) AT THE AIR-WATER INTERFACE

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Intensive study of polymers and composite materials based on polymers and macroheterocyclic compounds has led to significant advancements in different fields [1,2]. Polymers and copolymers of vinylpyridines belong to macromolecular chelates, which, due to the presence of pyridyl fragments, are able to bind metal ions and metal-containing compounds, such as the metal complexes of tetrapyrrole macroheterocyclic compounds [1].

The objective of this work is to study the structure of floating layers of poly(4-vinylpyridine) (P4VP) at the air- water interface. The studies were carried out on the Langmuir trough (NT-MDT, Zelenograd, Russia) from a solution of P4VP in chloroform (C = $4.15 \cdot 10^{-6}$M) at the initial surface coverage degree c_{face} = 40 %. The structure of the floating layers was analyzed within the framework of an original model and method for quantitative analysis of compression isotherms of nanostructured M-monolayers [3]. The surface area per monomer unit of P4VP in a nanoaggregate (A_{mol}) and the aggregation number were determined by approximating the πA–π plot using a linear function. The maximum error values for characteristics of the layer are described in [4]. Molecular model was built using the HyperChem 7.01 software package (MM+ calculation method).The projection area of the molecular unit of P4VP is 0.38 nm^2.

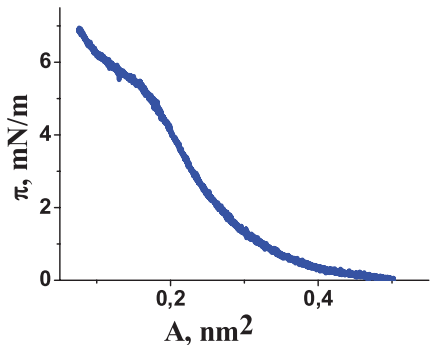

Fig. 1. *π-A Isotherm of P4VP, c_{face} = 40 %*

It was shown that P4VP at the initial surface coverage degree c_{face} = 40 % and at low surface pressures (up to 0.3 mN/m, Fig. 1, A-area per unit) forms stable monolayers. The area per molecular unit in the nanoaggregate (A_{mol}) is 0.4 nm^2, which corresponds to the area per molecular unit in the closest package. The main characteristics of the monolayer were determined. The aggregation number is 5105, the pressure extent of the stable state is from 0.04 mN/m to 0.3 mN/m, the water content per molecular unit in M-aggregates ($w_{in\text{-}M}/A_{mol}$) is 5 %, the surface area of a nanoaggregate is 2042 nm^2, the diameter of an aggregate is 51 nm, the distance between aggregate boundaries is 5.5 nm. Compressibility of the monolayer is very high (B = 595 m/N).

The work is performed in the framework of tasks of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018/4.6 and №4.9184.2017/7.8).

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NANOSTRUCTURE OF MONOLAYERS OF HEPTAMETHYL ESTER OF AQUACYANOCOBIRINIC ACID AT AIR-WATER INTERFACE

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Cobalamins are the most important biocomplexes. Cobalamins are derived from corrin and consist of a central cobalt atom surrounded by a corrin ring and an intramolecular nucleotide bounded to cobalt ion. The properties of ensembles of similar macroheterocyclic compounds are determined by the formation conditions of the ensembles [1,2].

The objective of this work is investigation the possibility of formation of nanostructures of a derivative of vitamin B_{12}, namely, heptamethyl ester of aquacyanocobirinic acid (NC-Co-OH) at the air-water interface. The floating layers were formed on the Langmuir trough "KSV-NIMA" from the solution of the compound in dichloromethane ($C = 2.4 \cdot 10^{-5}$ M, compression rate is 4.4 $cm^2 \cdot min^{-1}$). The structure of the layers was analyzed within the framework of an original model and method for quantitative analysis of compression isotherms of nanostructured M-monolayers [1].

It is established that at the air-water interface, at the initial surface coverage degree c_{face} = 19 %, structural elements of the monolayer are two-dimensional M-nanoarchitectures NC-Co-OH. The molecules in nanoaggregates are parallel to the water surface. The main characteristics of stable monolayers are determined. The area per molecule in the nanoaggregate (A_{mol}) is 10 nm^2; the number of molecules in an aggregate (n) is 254; the water content in M-aggregates ($w_{in\text{-}M}/A_{mol}$) and between them (per molecule, at the initial point of the stable state) is 80 % and 0.4 nm^2, respectively; the distance between the aggregates in the layer at initial point of the stable state is 1.2 nm; the pressure region where the stable state exists is 1.3 mN/m, the region of surface coverage degree where the state exists is 1.5 %, compressibility of the layer is low (56 m/N).

A specific feature of this compound is the formation of face-on monolayers with very large nanoaggregates (57 nm in diameter), with low density of these aggregates (ρ_{aggr}=0.2) and a very large distance between the molecules in the aggregate (2 nm). For comparison, the diameter, the density, and the distance for the previously studied derivatives of azaporphyrins are 10–13 nm, 0.8, and 0.3 nm, respectively [3,4]. At the same time, the monolayer density of NC-Co-OH, determined by the surface coverage degree by M-aggregates at the initial point of the stable state, is very high (c_{aggr} = 96 %, instead of 75–87 % for azaporphyrins).

The work is performed in the framework of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018/4.6).

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APPROACH TO THE SYNTHESIS OF MOLECULAR ASSEMBLIES ON THE BASIS OF HEMIHEXAPHYRAZINES

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Last decad molecular ensembles based on phthalocyanines, subphthalocyanines and fullerens, carbon nanotubes and graphene are the objectives of intensive research in the new photovoltaic devices creation [1].

There are several ways to gain access to the molecular ensembles. The main methods are based on condensation of various macrocycles or their precursors by replacing a halogen atom or modification of cyano groups, located in the *ortho*-positions, for the subsequent assembly of an additional macrocyclic system.

The most interesting method of molecular ensembles synthesis is replacing of a halogen atom using palladium catalyst under conditions of Sonogashira cross-coupling reaction. As a halogen-substituted phthalonitrile, 4-iodophthalonitrile is most often used in the preparation of molecular ensembles including phthalocyanines and their analogues [2].

The hemihexaphyrazines are of great interest to design such architectures. However, to the best of our knowledge, an application of hemihexaphyrazines to preparation of molecular ensembles has not yet to appear in literature. For this purposes, asymmetrically-substituted macroheterocyclic compounds of ABABAB'-type, containing the functional groups for the construction of molecular ensembles and bulky substitutes to supply with solubility, could be applied. Therefore, the main purpose of this work is to search for approaches to the synthesis of asymmetrically-substituted hemihexaphyrazines and studying of their applicability to build out molecular ensembles building blocks.

Acknowledgements. *This work was supported by the Russian Foundation for Basic Research (Grant No. 18-03-00888).*

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SYNTHESIS AND CATALYTIC ACTIVITY OF OCTASUBSTITUTED PALLADIUM (II) PHTHALOCYANINES

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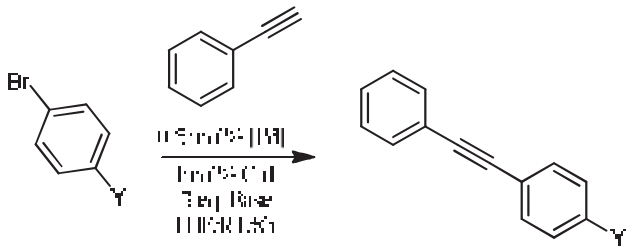
The Sonogashira cross-coupling is a very potent reaction and it have been widely used in the fine organic synthesis, convenient approach for the construction of multiple bonds. The most effective compounds among a wide variety of catalysts in Sonogashira coupling are palladium alkene complexes, phosphine ligand complexes, and metallocycles.

At the first step of our research we have synthesized the palladium complexes of octaalkoxy- and octaphenoxysubstituted phthalocyanines. Palladium complexes of phthalocyanines were prepared through cyclotetramerisation of phthalonitriles in benzonitrile at 190°C with use excess of palladium chloride. These reactions were controlled by TLC and products were purified by column chromatography (silica, dichloromethane). The formation of palladium complexes were confirmed by UV-Vis spectroscopy, MALDI-TOF mass spectrometry and ^{1}H NMR spectroscopy.

After successful synthesis of palladium complexes we began investigations aimed at evaluation of catalytic activities in Pd-catalysed Sonogashira cross-coupling reaction of phenylacetylene with various p-substituted arylbromides. First, we have investigated Pd/Cu-catalyzed Sonogashira reaction of bromobenzene with phenylacetylene under various conditions.

With the optimized conditions for the formation of diphenylacetylene from bromobenzene, we have examined the scope of the Sonogashira reaction for the synthesis of diverse alkyne-functionalized benzenes using various terminal alkynes [1].



Y H, Me, OMe, CHO, CN, NO_2, NH_2

In summary, firstly we have successfully used the palladium complexes of substituted phthalocyanines as novel efficient catalyst of Sonogashira coupling of the different p-substituted aryl bromides with phenylacetylene under mild conditions (25°C).

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COORDITIONAL AND PHYSICAL AND CHEMICAL PROPERTIES OF 5,10,15,20-TETRAPHENYL-21-TIA- AND 5,10,15,20-TETRAPHENYL-21-OXOPORPHYRINES

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The fundamental task of modern chemistry is to create new materials for highly sensitive optical sensors. The use of macroheterocycles - unique compounds with extended pi-electron conjugation contours, functional heteroatoms and groups, allows you to create materials with the necessary set of spectral and photophysical characteristics necessary for the practice [1–2].

The porphine macrocycle can be trans-formed via two main ways: substitution of hydrogen atoms in the β- and *meso*-positions of the macrocycle as well as at the transannular nitrogen atoms and the introduction of heteroatoms in the macrocycle. Replacement of the pyrrolic nitrogen atom by other donor atom such as O, C, results in the appearance of new macrocyclic systems known as porphyrinoids or heterosubstituted porphyrins.

This paper presents the results of the synthesis and analyzes the spectral and acid-base properties of mono-heterosubstituted porphyrins in comparison with their structural analogue, tetraphenylporphine. It is shown that such substitutions have a great influence on the electronic structure of the macrocycle, thereby changing the physical and chemical characteristics of compounds while maintaining the aromatic character.

For the first time, the features of the complex formation reactions of 5,10,15,20-tetraphenyl-21-thia- and 5,10,15,20-tetraphenyl-21-oxo-porphyrins with transition metal salts (Cu (II) and Zn (II)) were studied in solvents of various nature. Studies have allowed to establish the relationship between the structure and properties of organic ligands. The reactivity of the free bases was found to increase in the series: 5,10,15,20-tetraphenyl-21-thia-porphyrin < 5,10,15,20-tetraphenylporphine < 5,10,15,20-tetraphenyl-21-oxoporphyrins Thus, modification of the porphyrin core leads to compounds with very interesting properties that differ significantly from the properties of classical porphyrins.

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SYNTHESIS AND ANTIRADICAL ACTIVITY OF PORPHYRINS WITH A DIISOBORNYLPHENOL FRAGMENT AT THE MACROCYCLE PERIPHERY

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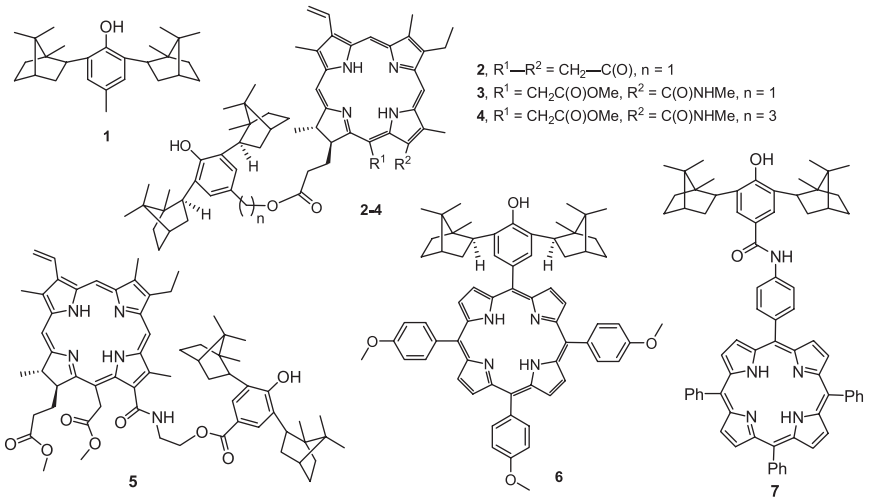
We have previously shown that tetra(*meso*-aryl)porphyrins as well as derivatives of chlorophyll *a* with 2,6-diisobornylphenol fragments on the periphery of the macrocycle exhibit radical scavenging activity (AOA) and antioxidant activity (RSA) [1, 2]. In this paper we presents the synthesis and investigate the RSA (in the model reaction of ethylbenzene oxidation initiated by azoisobutyric acid dinitrile) 2,6-diisobornyl-4-methylphenol **1** of natural and synthetic porphyrins **2–7** containing 2,6-diizobornilfenolny fragment differing in the structure of the macrocycle as well as the location and mode of conjugation. The study has shown that the electronic effects of the groups directly related to the 2,6-diisobornylphenol fragment exert the predominant influence both on the reactivity of the phenolic hydroxyl group in interaction with free radicals and on the antiradical activity of the molecule as a whole.



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M-MONOLAYERS AND LANGMUIR-SCHAEFER FILMS OF COBALT TETRA(P-METHOXYPHENYL)PORPHYRIN

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Study of *porphyrin systems* has gained special attention in the recent years *due* to *their unique physical*, *chemical*, and spectroscopic *properties*. They can be used as objects for formation of the nanostructured thin-film materials. The conditions of the formation of the nanostructures determine the properties of the material [1,2].

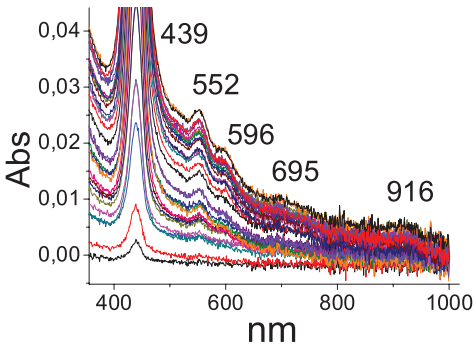

Fig. 1. *Absorption spectra of LS-films formed from M-monolayers of CoTMPP.*

The main objective of this work is to study the structure of M-monolayers and spectral properties of Langmuir-Schaefer (LS) films of cobalt tetra-(p-methoxyphenyl)porphyrin (*CoTMPP*). The floating layers of *CoTMPP* were formed with the use of the NT-MDT Langmuir trough (Zelenograd, Russia) from a solution in chloroform (C=3.6 10^{-5} M). The structure of the floating layers was analyzed by using quantitative analysis of compression isotherms of a nanostructured M-monolayer [3,4].

It is shown that *CoTMPP* at the air-water interface, at the initial surface coverage degree c_{face} from 3 to 25 % and low surface pressures (up to 1.0 mN/m) forms stable M-monolayers where molecules in nanoaggregates are parallel to the water surface. The surface area per molecule in a nanoaggregate (A_{mol}) is in the range of 26–3.4 nm^2. M-nanoaggregates are characterized by a large size (the diameter of the aggregates is 8–100 nm). The water content in aggregates ($w_{in\text{-}M}/A_{mol}$) is 93–49 %, the density of nanoaggregates is 0.07–0.5 and density of the layer, determined by aggregate surface coverage degree, is 80–90 %.

LS-films of *CoTMPP* were prepared by deposition of floating layers onto quartz substrates. The layers for transfer onto substrates were formed at c_{edge} values of 50 % (bilayer) and 8 % (monolayer), and at surface pressure of 44 and 0.9 mN/m, respectively. The spectra of both LS-films, with respect to the spectrum of the solution (Sore – 414 nm, Q – 531 nm), are characterized by strong red shifts of the Soret bands (by 32 and 25 nm) and of the Q bands (by 21 and 25 nm), and new bands at 593 and 596 nm, respectively. Moreover, films formed from M-monolayers absorb in near IR region (695 and 916 nm, Fig.1, Number of the layers is 2–60).

The work is performed in the framework of the State tasks of the Ministry of Science and Higher Education of the Russian Federation (4.1929.2018 / 4.6 and 4.9184.2017/7.8).

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INTERACTION OF CYANOCOBALAMIN WITH POTASSIUM HYDROXIDE IN NON-AQUEOUS MEDIA

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Chemistry of cobalamins (vitamin B_{12}) has attracted considerable attention due to their important role in living organism and the possibility of synthesis of modified vitamin B_{12} with new unique properties [1]. Non-aqueous media provide broad possibilities in synthesis of a wide range of derivatives of cobalamins. We carried out a comparative study of the interaction of cyanocobalamin (CNCbl) with a potassium hydroxide in dimethyl sulfoxide (DMSO) and isopropyl alcohol (^{i}PrOH).

In the first step of the reaction a complex of CNCbl with KOH is formed, which then decomposes to carbanion ($CNCbl^{-}$) and water (H_2O). At the absence of excess of potassium hydroxide the carbanion decomposes to form the reduced complex (Co^{2+}) and dicyanocomplex ($(CN)_2Co^{3+}$) in a 1:1 ratio. This process is accompanied by changes in the structure of cobalamin and leads to the formation of a dehydrocyanocobalamin containing a lactone ring. At the presence of excess of potassium hydroxide, $CNCbl^{-}$ reacts with KOH to form a super-reduced Co^{1+}. In both solvents (DMSO and ^{i}PrOH), dehydrocyanocobalamin containing an unsaturated amide side chain is formed.

The kinetic and activation parameters of reaction steps are determined. The rate of the accumulation of carbanion increases in order DMSO > iPrOH. This step is characterized by negative activation entropy, which supports an associative reaction mechanism.

The formation of Co^{1+} and decomposition of the carbanion do not depend on the solvent. These reactions are characterized by a positive value of entropy of activation, which supports a dissociative reaction mechanism.

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SYNTHESIS AND SPECTROPHOTOMETRIC STUDY OF DEMETALLIZATION OF METMPYP4 (ME = MG, FE) IN AQUEOUS SOLUTIONS

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Metalloderivatives of porphyrin TMPyP4 (5,10,15,20-tetrakis-(1-methyl-4-pyridyl)-21H,23H-porphyrin) are being intensively studied as promising antitumor compounds, as well as in connection with the possibility of using them as photocatalysts and fluorescent probes.

In this communication the results of NMR, UV-Vis absorption spectroscopy and spectrofluorometry study of intramolecular complexes of metalloporphyrins $[Me(X)TMPyP_4]^{n+}$ Me = Mg(II), Fe(III); X = H_2O, OH^-, Br^-, ADP^{2-} – (adenosine diphosphate) in solution, which were synthesized in Ivanovo State University of Chemistry and Technology.

A distinct feature of metal-free porphyrin TMPyP4 is its ability to form water-soluble complexes with a number of metals in a wide range of pH. This allows studying the simultaneously proceeding photolytic reactions and reactions of acidocomplex formation. The characteristics of UV-Vis absorption and luminescence spectra of metalloporphyrins were determined depending on the pH and the nature of the supporting electrolyte. Based on the data of acid-base titrations using chemometric procedure of multivariate curve resolution - alternating least squares MCR-ALS, pure spectra of intramolecular complexes of metalloporphyrins were calculated. An analysis of pure chemical forms spectra has shown that the intramolecular complexation leads to a noticeable bathochromic shift of the Soret band and the luminescence attenuation.

Transformations of UV-Vis spectrum of metalloporphyrin indicate either replacement of axial ligand and the leaving of the metal ion from ring. For instance the increase pH from 1.3 to 8.5 in solution of $[Fe(Cl)TMPyP4]^{4+}$, leads to the replacement of the axial ligand. In the case of a magnesium derivative in an acidic solution, demetallization and simultaneous protonation of the porphyrin base were observed. The ^{31}P NMR spectra indicate the coordination of the ADP^{2-} ligand to the metal in the center of the porphyrin via phosphate groups.

For compounds formed in the equilibrium complexation processes the types of coordination polyhedrons was considered with helps of a new matrix model.

The work was performed using the equipment of the Science Park Resource Educational Center of Chemistry

Shilov I.V., Pechnikova N.L., Lyubimtsev A.V., Ageeva T.A.

USAGE OF VINYL-CONTAINING PORPHYRINS OF DIFFERENT FUNCTIONALITY FOR THE SYNTHESIS OF WATER-SOLUBLE POLYMER COMPOUNDS

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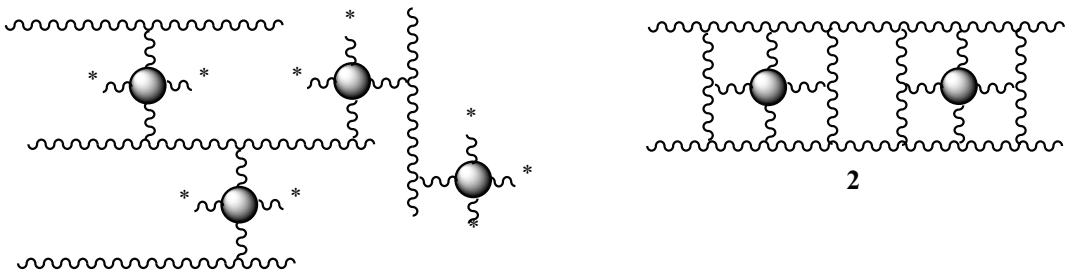
The tetrapyrrole macroheterocyclic compounds immobilization possibility on water-soluble polymers significantly expands the fields of their application. The copolymerization reaction of vinyl monomers with porphyrins having functional groups at the periphery of the molecule is one of the methods for producing such hybrid compounds. The use of a porphyrin monomer with one vinyl group on the periphery of the molecule in the copolymerization reaction allows to obtain only linear porphyrin polymers and eliminates the formation of cross-linked structures. Not only linear macromolecules **1**, but also branched and crosslinked structures **2** are formed by increasing the number of functional groups on the periphery of the tetrapyrrole macroheterocycles under certain conditions:



1 **2**

The water-soluble porphyrin-containing acrylamide-based polymers were synthesized by microwave radiation conditions. The radical copolymerization reaction was carried out in 1,4-dioxane, dinitrile azobisisobutyric acid was used as an initiator. Tetra- and mono-*meso*-vinyl-substituted porphyrins with different availability of vinyl groups were applied as the second comonomer. The reaction by microwave heating conditions afforded the water-soluble acrylamide-based porphyrin-polymers in good yields. The use of thermal heating to obtain water-soluble porphyrin-containing polymers with the same ratios of the starting components did not lead to the expected results: neither a homopolymer nor a copolymer is formed during the reaction. The porphyrin-polymers preparation under thermal heating conditions is possible only by increasing the initiator amount. However, this leads to a deterioration of the molecular weight characteristics of the synthesized compounds.

The applying of porphyrin monomers with different amounts of vinyl groups on the macrocycle periphery allows to receive water-soluble porphyrin-containing polymers of different composition, and the use of microwave heating provides great opportunities for the synthesis of new functional porphyrin polymer compounds.

The research was performed by using the resources of the Centre for Joint Use of Scientific Equipment "ISUCT", in the framework of the State Task (project No. 4.6938.2017/7.8).

This work was supported by the Russian Foundation for Basic Research (Grant No. 18-03-00986).

Simonova O.R.[1], **Zdanovich S.A.**[1], **Koifman O.I.**[1,2]

THE EFFECT OF THE CATION NATURE ON CATALASE ACTIVITY OF TETRAKIS-(2,5-DIHIDROXIPHENYL)SUBSTITUTED PORPHYRINATES OF COBALT AND MANGANESE

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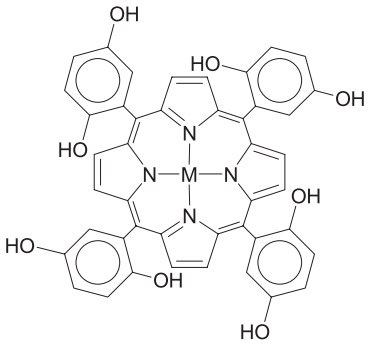
The change of the intracellular redox state occurs due to the oxidation of biologically active molecules by peroxides. The stable redox state provides the complex combination of enzyme with redox regulators. Therefore, the creation of biomimetics of redox regulators based on metalloporphyrinates is one of the important tasks in the field of biochemistry, pharmacology and medicine. In view of this task, cobalt and manganese porphyrinates having additional redox activators (2,5-dihydroxyphenyl fragments) as peripheral substituents are of interest.

The reactions of cobalt and manganese porphyrinates with hydrogen peroxide were investigated by spectral methods. The kinetic characteristics of the processes were obtained. The influence of the nature of the central cation and its coordination environment on the mechanism and rate of redox-transformations were noted. Varying the peroxide concentration has been established to lead to a change of nature of intermediates and products of the reactions. The presence of three active centers in the complex (metal cation, macrocycle, and 2,5-dihydroxyphenyl fragments) has shown to significantly affects its catalase activity.



M = Co, Mn

The results obtained can be useful for a detailed understanding of the processes of activation of free radical oxidation and for the search for ways to regulate them.

This work was supported by the Russian Foundation for Basic Research [grant number 18-03-00369-a] with the help of the center of the scientific equipment collective use «The upper Volga region centre of physic-chemical research».

Starikov A.S., Kazachenko V.P., Pushkarev V.E.

NOVEL ALKYL SUBSTITUTED SANDWICH LANTHANIDE(III) PHTHALOCYANINATES. ORIGINAL APPROACH TO SYNTHESIS

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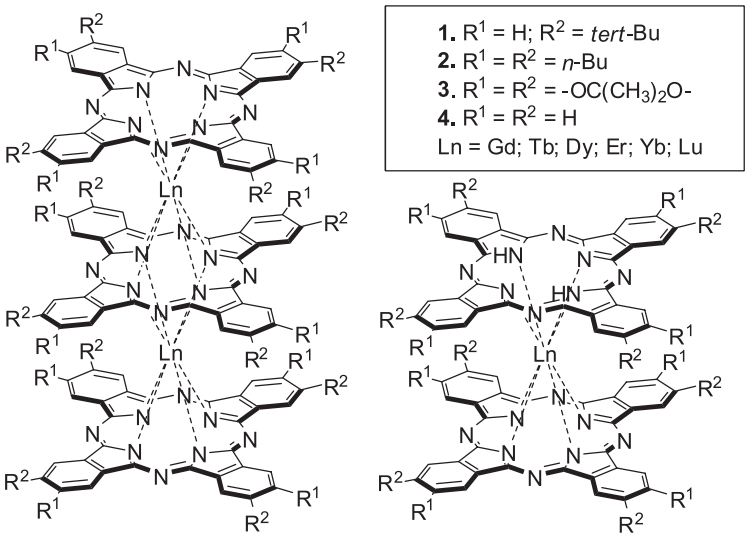
Sandwich phthalocyanine complexes of rare-earth elements (REE) are characterized by a set of unique optical, electrochromic, semiconductor and magnetic properties, which makes them extremely promising for research. Development of simple synthetic methods for such compounds is one the most important problems in tetrapyrrole chemistry [1].

In this work, we offer an efficient method for the preparation of sandwich REE phthalocyaninates based on the approach earlier reported by Ishikawa, which consisted in heating of the monophthalocyaninate under reduced pressure [2]. We found that the formation of sandwich complexes from monophthalocyaninates occurs at atmospheric pressure in the temperature range of 290–430 °C. Thus in the case of alkyl substituted ligands (types **1** and **2**), the selective formation of triple-decker complexes in 86–94 % yield is observed. In the case of alkoxy substituted ligand **3**, double-decker phthalocyanines are formed in 60–82 % yield. In turn, unsubstituted REE phthalocyaninates based on ligand **4** form a mixture of double-decker and triple-decker compounds with yields of the order of 20 and 70 %, respectively.



Within the current work, new representatives of alkyl substituted sandwich phthalocyaninates were synthesized, namely, double-decker and triple-decker complexes of Gd(III), Tb(III) and Yb(III) with ligand **2**.

This work was supported by the Russian Science Foundation (Grant 17-73-10413), Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grant MD-3847.2019.3), and performed within the framework of the State Assignment of 2019 (Theme 45.5 Creation of compounds with given physicochemical properties)

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OBTAINING OF PIROPHEOFORBIDE *A* DIETHYLENE GLYCOLIC ETHER FROM FEOPHITIN *A*

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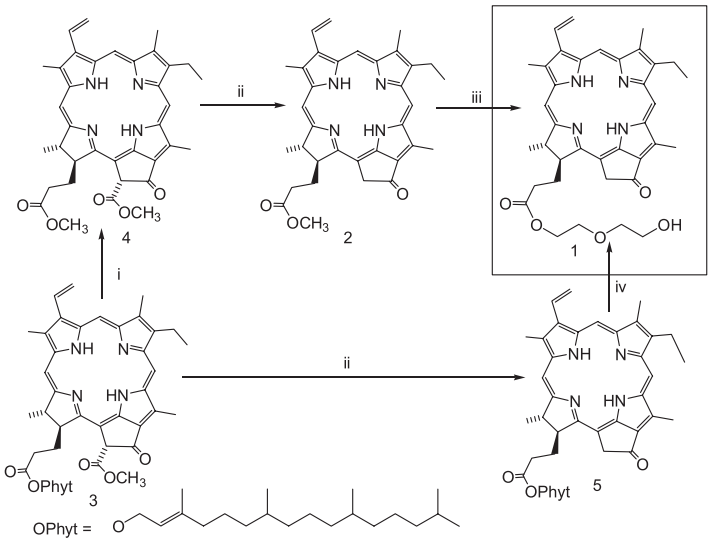
Chlorophyll *a* derivatives with oligoethylene glycol fragments were previously investigated by us as potential antitumor photosensitizers (PS). As a result, pyropheophorbide *a* diethylene glycol ether **1** was chosen as the substance with the best ratio of dark and photoinduced toxicity [1]. Further study of this compound requires optimization of its obtaining processes for its production in large quantities. Initially, **1** was obtained by transesterification of methylpyropheopheorbide *a* **2** ester group by diethylene glycol (DEG) in the presence of H_2SO_4 (scheme). In the present work, **1** was obtained directly from pheophytin *a* **3**, bypassing the stage of methylpheophorbide *a* **4** production.



i: CH_3OH - H_2SO_4 (5 % by volume), reflux for 1 hour, 60 % yield; ii: collidine, reflux for 40 min, 80 % yield (for 2), 70 % yield (for 5); iii: DEG – H_2SO_4 (5 % by volume), r.t., 12 h, 24 % yield; iv: DEG – H_2SO_4 (5 % by volume) 80 °C, 2 h, 40 % yield.

Scheme 1

The best way to obtain **1** is decarboxylation of **3** followed by transesterification of the ester group of the formed pyrotheophytin *a* **5** by the action of DEG in the presence of H_2SO_4 (Scheme).

This work performed using equipment of the CCU «Chemistry» at the Institute of Chemistry of the Komi Scientific Centre of the Ural Branch RAS (Syktyvkar)

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1. Dark and Photoinduced Cytotoxic Activity of the New Chlorophyll-a Derivatives with Oligoethylene Glycol Substituents on the Periphery of Their Macrocycles. Yana I. Pylina, Dmitry M. Shadrin, Oksana G. Shevchenko, Olga M. Startseva, Igor O. Velegzhaninov, Dmitry V. Belykh, Ilya O. Velegzhaninov **Int. J. Mol. Sci.** 2017, 18, 103; doi:10.3390/ijms18010103.

Stepanova A.A., Eliseeva A.S., Golovashova E.S., Ageeva T.A., Kudrik E.V.

CATALYTIC OXIDATION OF PLAIN SUGARS IN THE PRESENCE OF ORGANOMETALLIC FRAME CONNECTION BASED ON OCTARCARBOXYPHTHALOCYANINATE COBALT

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Metal-complex compounds, which include vital metals – copper, zinc, manganese and others, with nitrogen-containing ligands, are promising biocatalysts. In the life of living organisms, an important place is occupied by the oxidation of sugars. Increased interest in these processes is associated both with attempts to create a number of drugs, as well as with ideas about the radical mechanism of oxidation reactions. An important fact is that glucose oxidation products are in demand and used in the pharmaceutical, food and other industries. In this work, we synthesized an organometallic skeleton compound based on cobalt octacarboxyphthalocyanine, studied its physicochemical properties, and studied the possibility of using this nanomaterial as a heterogeneous catalyst in monosaccharide oxidation reactions such as glucose and fructose under mild conditions.

Glucose oxidation is a well-studied process, since gluconic acid produces commercially. In contrast to glucose, fructose oxidation has been studied to a much lesser extent. We investigated this process under the conditions given for glucose. The data obtained unequivocally indicate that during the oxidation, the formation of new carboxyl groups occurs, therefore, the newly obtained catalyst is able to oxidize fructose with the formation of its carboxy-derivatives under mild conditions with atmospheric oxygen.

From the data set it can be assumed that it is likely that the oxidation process proceeds at the tertiary atom of the furanose form of fructose.

It is shown that this material is an effective catalyst for these processes. Based on the data obtained, it can be concluded that the rate of the limiting stage of the process is the formation of reactive oxygen forms at the catalyst metal centers

The advantage of the material obtained is the fact that it fully retains its activity for at least three catalytic cycles and can be easily regenerated, and high catalytic activity in combination with the availability of the catalyst determine the prospect of its use.

Work Supported by RFBR 18-33-00456 мол_а

Suvorov N.V., Bondareva E.A., Evtushkova P.P., Cheshkov D.A., Mironov A.F., Grin M.A.

APPLICATION TETRAZINE-ALKENE ADDITION FOR MODIFICATION OF NATURAL CHLORINS

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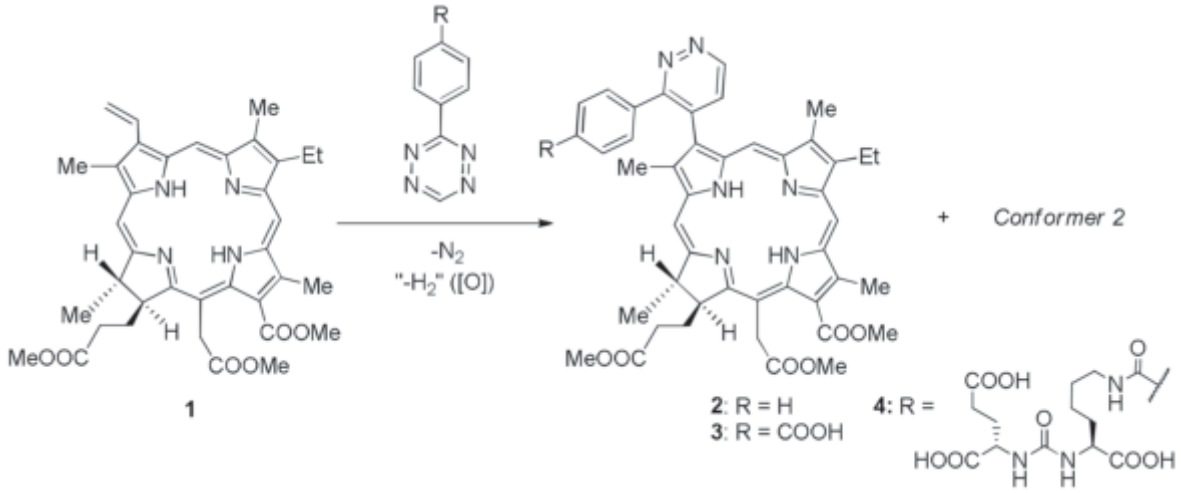
A special place among clickreactions belongs to tetrazine–alkene addition (IEDDA reaction) that does not require a catalyst. The accessibility of a vinyl group in chlorophyll *a* derivatives makes it possible to use this reaction in a series of natural chlorins. The purpose of this work was to study the IEDDA reaction between chlorin e_6 trimethyl ester and aryltetrazines, as well as to introduce a complex biologically active molecule into the macrocycle. 3Phenyl1,2,4,5tetrazine and 4(1,2,4,5tetrazine3yl)benzoic acid were reacted with chlorin **1**.



The structure of the products was studied by NMR spectroscopy. The ^{1}H NMR spectrum showed two different sets of signals corresponding to the *meso*proton at the 20position of the macrocycle and also two different sets of signals assigned the pyridazine ring. Analysis of ^{1}H, ^{13}C COSY, NOESY and HSQC spectra revealed the presence of two conformers in 1 : 1 ratio. The study of spectral properties of the compounds **2** and **3** revealed insignificant changes in the absorbance and fluorescence spectra as compared to those of chlorin.

Such functionalization of chlorin allowed the introduction of the PSMA ligand at position 3 of the macrocycle. The phototoxicity of conjugate **4** was evaluated on prostate cancer cell lines 22Rv1 (PSMA +) and PC-3 (PSMA-). A significant increase in the phototoxicity of compound **4** was observed compared with the clinical drug.

Thus, we have shown that the click-reaction of tetrazine-alkene addition is an effective way of regioselective introduction of rather complex molecules into chlorophyll *a* derivatives.

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SPECTROPHOTOMETRIC STUDY OF THE ACID-BASE PROPERTIES OF SULFO DERIVATIVES OF 5,10,15,20-TETRAPHENYL-21-TIA- AND 5,10,15,20-TETRAPHENYL-21-OXOPORPHYRINES IN ETHANOL–SULFURIC ACID SYSTEM

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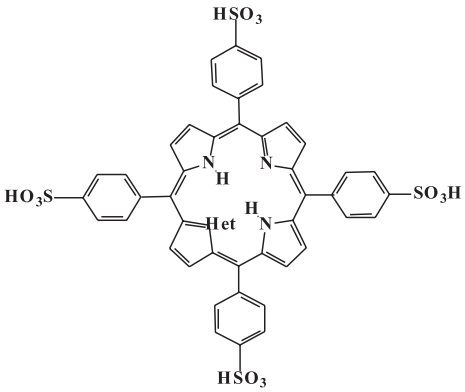
Spectrophotometric titration method was used to study the spectral and basic properties of heterosubstituted anionic porphyrins in comparison with their structural analogue, tetraphenylporphine tetrasulfonic acid.



I Het =N, $H_2T(4\text{-}SO_3HPh)P$;
II Het =S, $HT(4\text{-}SO_3HPh)SP$;
III Het =O, $HT(4\text{-}SO_3HPh)OP$**;**

The formation of mono-and doubly ionized forms upon protonation of the tetrapyrrole core of the macrocycle changed the symmetry of the molecule and led to substantial spectral changes, as in the case of the N4-porphyrins. The parameters of the electronic absorption spectra and the concentration ranges for the existence of mono- and diprotonated forms of the corresponding ligands, as well as their basic dissociation constants, were determined.

A comparative analysis of the effect of modification of the reaction site and the medium composition on the basicity of the compounds was carried out.

Based on the obtained data, the basicity of the porphyrins in the $C_2H_5OH–H_2SO_4$ system decreased in the $H_2T(4\text{-}SO_3HPh)P > HT(4\text{-}SO_3HPh)OP > HT(4\text{-}SO_3HPh)SP$ series. However, the difference in the constants of acidic dissociation of the cationic forms of the investigated ligands did not exceed one order of magnitude. The so small difference in the basicity of compounds **I–III** was likely due to the levelling effect of the solvent: pK_{b2} and $pK_{b1,2}$ included the equilibrium constants of the protonated forms interaction with the solvent, which could affect the value of the basicity constants [1]

This research was funded by the Russian Science Foundation (project № 19-03-00214 A) and performed with using of equipment of the Shared Facility Centre, the Upper Volga Regional Centre of Physicochemical Studies

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Teletsky Z.A.[2], **Pogonin A.E.**[2], **Kiselev A.N.**[1,2], **Petrov O.A.**[2], **Syrbu S.A.**[1]

SYNTHESIS AND PROPERTIES OF BENZOTHIAZOL-CONTAINING NITRILE

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Nitriles are important building blocks in organic synthesis. These compounds can serve as the key precursors for the synthesis of amines, amidines, tetrazoles, aldehydes, amides and carboxylic acids. Macroheterocyclic compounds with aza-bridges, for example, porphyrazines can be synthesized via the condensation of dinitriles. The classical methods for the synthesis of nitriles include Sandmeyer and Rosenmund-von Braun reactions, as well as the dehydration of aldoximes and amides. In recent years, transition metal-catalyzed cyanation reactions of aryl halides have been developed for the preparation of nitriles.

Various dinitriles are needed for synthesis of new functional materials based on porphyrazines. Dinitriles are modified using ipso-substitution of nitro groups, alkylation and arylation of the thio-, hydroxyl-, and carboxy groups; via cross-coupling reactions: Heck, Negishi, Sonogashira, Suzuki [1]. The development of new methods for the synthesis and modification of dinitriles is of considerable interest and allows expanding the range of symmetric and asymmetric porphyrazines synthesized from them.

In our work, we propose the synthesis of dinitrile, still undescribed in the literature, using palladium-catalyzed C-H-functionalization. 5,6-bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile was originally synthesized, which was introduced into the reaction of hetarylation with benzothiazole. The product 5,6-bis(4-(benzo[d] thiazol-2-yl)phenyl)pyrazin-2,3-dicarbonitrile was obtained in 73 % yield. This technique opens up prospects for the appending of a variety of acidic heterocyclic residues in dinitrile molecules.

As part of this work, quantum chemical calculations of the structure and harmonic vibration frequencies of 5,6-bis(4-(benzo[d]thiazol-2-yl)phenyl)pyrazine-2,3-dicarbonitrile were carried out using the Gaussian 03 program in the framework of DFT (B3LYP functional) method. Quantum chemical calculations were performed using the pVTZ basis function sets. According to the results of calculations, the molecule has three conformers that differ from each other in the orientation of sulfur atoms in space. The magnitudes of the relative energies of the conformers do not exceed 0.6 kJ / mol.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 18-33-01199.

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Tikhomirova T.V., **Fedotova A.E.**, **Nikitina T.G.**, **Maizlish V.E.**, **Shaposhnikov G.P.**

TETRA-4-(4-ARYLOXY)PHTHALOCYANINES OF COPPER AND ZINC AND THEIR SULFONIC ACIDS

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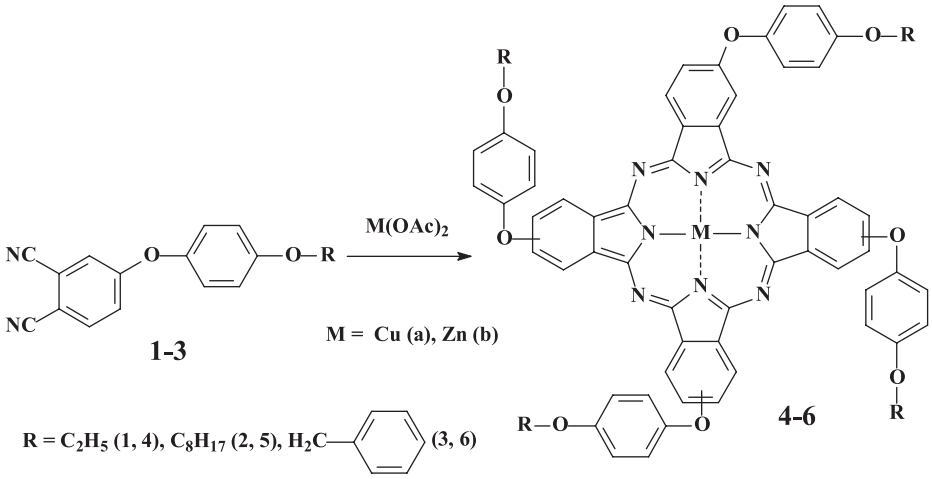
The low solubility of unsubstituted phthalocyanines (Pc) in most solvents limits their possible application. Due to the introduction of functional substituents in benzene rings, they can be dissolved in organic or water-alkaline media. It allows to significantly expand the area of their practical usage. In this regard, the aim of this work was to synthesize and to study spectroscopic properties of copper and zinc tetra-(4-aryloxy) phthalocyanines and their sulfonic acids.



Synthesis of tetra-4-(4-aryloxy)phthalocyanines (**4-6**) were carried out by nitrile method by means of interaction of substituted phthalonitriles (**1-3**) with copper and zinc acetates at a temperature of 185-190°C. The phthalocyanines obtained (**4-6**) were sulfochlorinated with a mixture of thionyl chloride and chlorosulfonic acid and then hydrolyzed to the corresponding sulfonic acids. Phthalocyanines (**4-6**) are soluble in chloroform and DMF, and their sulfonic acids are dissolved in water. By means of it, the spectral characteristics of complexes synthesized in these solvents were studied. The structure of all compounds obtained was confirmed by MALDI-TOF mass spectrometry, IR, NMR and electronic spectroscopy.

The work was carried out within the framework of the state assignment of Ministry of Education and Science of Russian Federation [grant number 4.1929.2017/4.6] using the resources of the Center for collective use of scientific equipment of «ISUCT».

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THE OBTAINING OF METHYLPHEOPHORBIDE *A* 13(2)-ESTERS WITHOUT ACTIVATING AGENTS

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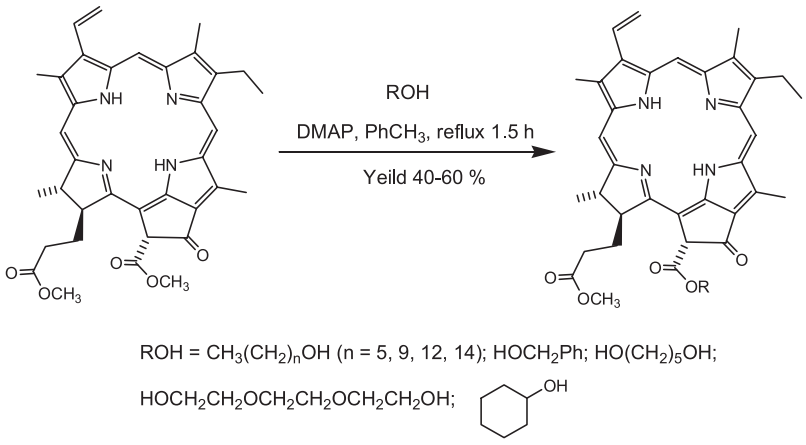
Methylpheophorbide *a* is one of the most accessible and convenient chlorophyll *a* derivatives used as starting materials in the synthesis of macroheterocyclic compounds. The formation of an ester bond is one of the most common ways of introducing fragments of a given structure to the periphery of the chlorin macrocycle; therefore, it is widely used in the chemical modification of *a*-row chlorins, including methylpheophorbide *a*. For the synthesis of methylpheophorbide *a* 13(2)-esters (Scheme 1), the Mukayama reagent (CMPI, N-methyl-2-chloropyridine iodide) [1,2] ore iodine are [3] successfully used when boiling with the corresponding alcohol in toluene in the presence of DMAP (dimethylaminopyridine).



Scheme 1

In this work, we studied the interaction of methylpheophorbide a with various alcohols in toluene in the presence of a base (DMAP) during boiling of the reaction mixture. It has been shown that under these conditions the transesterification of the esocyclic esocycle group can be chemoselectively carried out without the use of an activating agent (N-methyl-2-chloropyridinium iodide). The necessary conditions for the success of the reaction and obtain acceptable yields of the transesterification products are the presence of a base, providing exocycle enolization, and a substantial excess of the esterifying alcohol.

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Tyulyaeva E.Yu.[1], **Zaitseva S.V.**[1], **Kudrik E.V.**[2], **Koifman O.I.**[1,2]

DIRECTED OXIDATION OF M-CARBIDO DIRUTHENIUM PHTHALOCYANINE BY ^{T}BUOOH: CHEMICAL MODULATION OF OXIDANT PROPERTIES

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The compounds of ruthenium, as well as their oxidized species, are highly charged analogues of iron and suitable models of synthetic macrocycles, which allow generating and significantly stabilizing mimetics of one- and two-electron-oxidized intermediates responsible for oxygen transfer in the catalytic cycle of cytochrome P450 or peroxidases. The study of μ-carbido bridged macrocycle compounds is of great interest due to their significant catalytic activity [1–4].

μ-Carbido-bis[*tetra*-tert-butyl-phthalocyaninatoruthenium(IV)], $[Ru^{t}BuPc]_2C$ (**1**), was prepared according to the literature report [5] and identified by different techniques. Yield 25 %. UV-visible (C_6H_6): λ_{max}, nm (log ε) 648 (5.29), 627 (5.07), 572 (5.16), 407. IR (C_6H_6): ν, cm^{-1} 1007 (ν_{as} Ru=C=Ru). ^{1}H NMR ($CDCl_3$) δ ppm: 8.45 s ($8H_{Pc}$), 7.72–7.51 m ($16H_{Pc}$), 2.26–1.94 (72H ^{t}Bu). ESI-MS: *m/z* $[Ru^{t}BuPc]_2C^+$ 1688.2. E_{ox1} = 0.689 V. Generation of a π-cation radical species (**2**) of $[Ru^{t}BuPc]_2C$ was observed under interaction of **1** with ^{t}BuOOH in degassed benzene resulted in changes in absorption spectra with isosbestic points. The reaction between bis-imidazole derivative $[ImRu^{t}BuPc]_2C$ (**3**) (UV-visible (C_6H_6): λ_{max}, nm 649, 630, 578, 549, 417. ESI-MS: *m/z* = 1823.0. E_{ox} = 0.739 V) and ^{t}BuOOH led to resulting high-oxidized species (**4**) which UV-vis spectrum was different from that of **2**. Both the **2** and **4** species were competent in β-carotene oxidation. However, the rate constant of carotene oxidation was less in the presence of **4** than in the presence of **2**. It is in agreement with the obtained electrochemical oxidation potentials of **1, 2** and β-carotene. The conditions, rate constants and mechanism of the studied oxidation reactions, as well as nature of active intermediates **2** and **4** are presented in the report. Modification of coordination sphere composition of the compound **1** was shown to vary its oxidant properties. The data obtained contribute to the study of ruthenium μ-carbido dimer derivatives as the new catalytic systems.

This work was supported by the Russian Foundation for Basic Research [grant number 18-03-00617-a] with the help of the center of the scientific equipment collective use «The upper Volga region centre of physic-chemical research».

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Tyulyaeva E.Yu.

GENERATION OF Π-CATION RADICAL SPECIES BY PORPHYRIN COMPLEXES OF NOBLE AND RARE METAL

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The development of catalysts for the oxidation of organic substances based on metalloporphyrins requires easy participation of MP in redox-reactions combined with their coordination non-saturation. Chemical generation of oxidized species occurring due to the interaction of the coordination center with molecular O_2, was observed for the complexes of ruthenium, osmium, palladium, rhodium, iridium and the rare element rhenium with H_2TPP, H_2OEP, as well as with *meso*-phenyl-substituted analogs of H_2OEP, under the action of atmospheric oxygen with the assistance of protons in aerated HOAc, H_2SO_4, CF_3COOH and HOAc–H_2SO_4 mixtures.

Based on the characterization of UV-visible spectra of π-cation-radical species of MP, UV-visible spectroscopy was used for monitoring the rate of MP oxidation reactions and to identify the reaction intermediates. The nature of the latter, as well as the reaction products, was confirmed, when it was possible, by additional studies using IR and ^{1}H NMR and 2D ^{1}H NMR spectroscopy.

The reasons for the difference between the reaction centers during the oxidation of the Os(II) and Ru(IV) complexes are explained. The stability of the compounds depending on the donor – acceptor properties of the macrocycle was investigated for palladium (II) complexes. The high resistance of PdP to oxidation of their aromatic part is due to the strong σπ-binding of the central atom. The modification of the *meso*-positions of the ligands can be considered as a way of changing the electron-donating properties of the complexes that is important for oxidation reactions and partial proton transfer from the environment. For isostructural tetraphenylporphin complexes of rhodium(III) and iridium(III), the oxidation of which is preceded by an axial substitution reaction for ions and molecules of the reaction medium, the dependence of the charge localization site on single-electron oxidation on the central cation and nature of the mixed solvent (for $Ir^{III}P$) was shown. The position of the mixed-ligand complexes $O{=}Re^{V}(X)$ in the row of stability to oxidation in concentrated H_2SO_4 is fueled by the combination of the electron-donor-acceptor effects of the coordination environment Re(V), which determines the redox potentials of the reaction intermediates.

The data on the existence and behavior of oxidized species in various media allow to modulate transformations with the catalytic participation of natural and synthetic MP, resolve the mechanisms of such transformations, as well as to expand the list of studied technical processes and biochemical reactions.

It was done under the Program of Russian State Academies of Sciences (subject No. 0092-2014-0002) with the help of the center of the scientific equipment collective use «The upper Volga region centre of physic-chemical research».

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Yakovenko P.O., Hamdush M., Stuzhin P.A.

SYNTHESIS AND STUDIES OF 1-PHEHYL-DIAZABOROLIN-2,3-DICARBONITRILE

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Tetrapyrrol macroheterocyclic copmositions are the subject of intensive researche in a modern coordination and organic chemistry. The scientific and practical interest in them resulted from the fact that their natural representatives porphyrins (hematoglobulins, chlorophyls, cytochromes – are widely-spread natural pigments. Their most accessible synthetical analogues – phthalocyanines are used as pigments, dye-stuffs, materials for organic electronics and in other fields.

Lately the heterocyclic analogues of phthalocyanines which contain aromatic heterocycles instead of benzene rings are investigated. For such porphyrazines it is possible to obtain dinitrile precursors based on DAMN. So it is easy to obtain dicarbonitriles with 6-membered pyrazine cycle, 5-membered imidazole, triazole, 1,2,5-chalcogenadiazole. In this paper, for the first time we obtained dinitrile containing a boron atom in a heterocycle.

By reacting phenylboronic acid with diaminomeleonitrile, 1-phenyl-diazaborolin-2,3-dicarbonitrile was obtained. A new compound was characterized by IR, 1H, 11B, 13C NMR spectroscopy and studied by cyclic voltammetry.

The report also presents the results of the research in macrocyclization reactions.

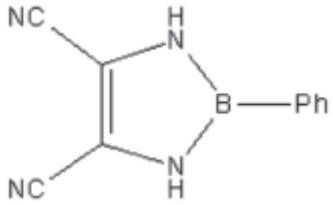

Fig. *2,3-dicyano -1phenyl-diazaborolin*

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SINTHESIS AND REDOX PROPERTIES OF HETEROLEPTIC IRON(IV)-RUTHENIUM(VI) HETEROMETALLIC μ-CARBIDO COMPLEX

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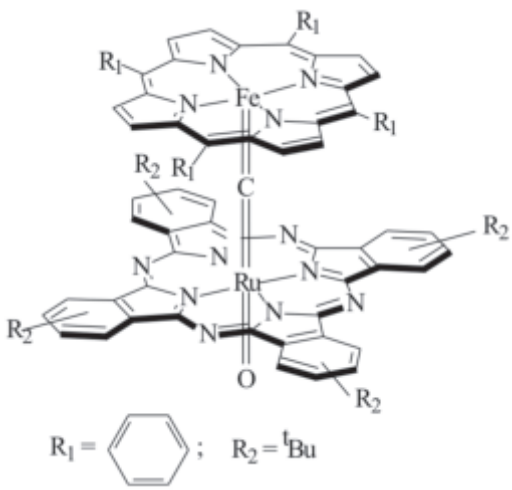
Biomimetic studies using synthetic models of catalases and peroxidases based on porphyrins and their analogues for generating the active species, provide valuable information about the fundamental properties of enzymes and the influence of various factors on the mechanism of catalytic reactions with their participation. According to studies on the modeling of natural heme oxidoreductase enzymes, the formation of high-valence oxo-complexes following the cleavage of the O – O bond in peroxides is a prerequisiteis for the manifestation of enzyme-like catalytic activity of compounds.



In order to create models of the active centers of synthetic biocatalysts, a heteroleptic iron(IV)-ruthenium(VI) heterometallic μ-carbido complex has been synthesized. Its redox properties in the reaction with ^{t}BuOOH have been studied. Intermediates and reaction products were identified by spectral methods. Kinetic characteristics of oxidation were obtained and a possible mechanism of the redox process under study was proposed. The peroxidase activity of the heterobimetallic complex was estimated. The presence of imidazole in the internal coordination sphere of the complex was shown to decrease the value of oxidative potential of the studied compound. As a result, rapid formation of a highly oxidized form, which is different from the oxo-species without imidazole, was observed spectrometrically. This power species is characterized by high reactivity and is capable of oxidizing peroxide with the dioxygen release.

This work was supported by the Russian Foundation for Basic Research [grant number 18-03-00617-a] with the help of the center of the scientific equipment collective use «The upper Volga region centre of physic-chemical research».

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SYNTHESIS, COORDINATION AND CATALYTIC PROPERTIES OF WATER SOLUBLE ZINC(II) PHTHALOCYANINATE

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Due to its unique electronic and optical properties, phthalocyanines are used as photosensitizers, chemical sensors, liquid crystals, materials for nonlinear optics, Langmuir-Blodgett films, polymers of various structures, etc. Search and creation of biomimmetic systems acting as effective catalysts for redox reactions is one of the most important areas in modern chemistry. Despite numerous studies in this area, the study of the influence of the structure and coordinating ability of a synthetic system on its catalytic properties and possible transformations during chemical reactions remains relevant. Metallophthalocyaninates can successfully act as an active component of such a system.

The synthesis and study of the coordination and catalytic properties of water-soluble zinc(II) complex with sulfo- and tert-butyl substituted phthalocyanine are presented. It was established that the complex under study possesses substrate specificity with respect to biologically active bases, the coordination binding of which is characterized by a clear spectral response. The composition and stability of the donor-acceptor complex was shown to depend on the nature of the substrate.

The catalytic activity of water-soluble zinc phthalocyaninate in the oxidation of organic pollutants with hydrogen peroxide is noted. Varying the composition of the coordination environment by introduction of various substrates affects the redox properties of the complex and can be considered as a way of regulating the oxidation process.

Intermediates and products of the studied reactions were identified by UV-visible, IR-spectroscopy and mass spectrometry techniques.

This workt was done under the Program of Russian State Academies of Sciences (subject No. 0092-2014-0002) with the help of the center of the scientific equipment collective use «The upper Volga region centre of physic-chemical research».

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SPECTRAL-KINETIC PROPERTIES AND MAGNETIC CIRCULAR DICHROISM OF STERICALLY HINDERED Pd-OCTAETHYLPORPHYRINS WITH MESO-PHENYLS

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In a lot of cases the formation of multiporphyrin complexes where molecular subunits are covalently (or non-covalently) linked via side bulky spacers leads to steric interactions of molecular fragments, which may be accompanied by static and dynamic distortions from planarity in porphyrin macrocycles. Thus, in addition to the analysis of photoinduced processes in these complexes, it is necessary to take into account the direct influence of bulky substituents on the deactivation of excited electronic S_1 and T_1 states of tetrapyrrole macrocycles (steric factors, spatial distortions, effects of the conformational dynamics of macrocycles, *etc.*).

In contrast to previous studies, we have shown for the first time that mono- and di-*meso*-phenyl substitution in octaethylporphyrins (OEP and Zn-OEP) leads to the drastic shortening of triplet lifetimes at 293 K (from ~1.5 ms down to 2-5 μs in degassed toluene solutions). In the case of Pd-octaethylporphyrin molecules (Pd-OEP) we have succeeded to compare spectral-kinetic results for pump-probe and phosphorescent measurements giving us the unique direct information concerning the influence of the non-planarity increase in a wide temperature range on all parameters of triplet states and their variation: i) T-state position in the energy scale; ii) direct phosphorescence lifetime in comparison with parallel T_1-T_n transient absorption decay; iii) phosphorescence quantum efficiency; iv) conformational and temperature change of the energy gap $\Delta E=E(S_1) - E(T_1)$; v) activation energy of temperature dependent phosphorescence rate constant for planar PdOEP and non-planar Pd-OEP-*meso*$(Ph)_n$ molecules. The transition from planar Pd-OEP molecule to the sequential set of sterically hindered compounds (last one, Pd-5,10,15,20Ph-OEP) manifests itself in the noticeable shortening of T-states and drastic decrease of the efficiency of singlet oxygen generation. We found also that the increase of the non-planar deformations of π-conjugated tetrapyrrole macrocyle manifests itself in noticeable changes of magnetic circular dichroism (MCD) spectra. To explain the experimental MCD findings the so-called Michl's perimeter model was used. Using the results of semiempirical CI calculations (INDO/S (DZDO) of the Faraday terms in MCD spectra it was concluded that MCD peculiarities can be described by perimeter model with an excellent accuracy. The evaluation of the positive-hard character of the compounds under study and their behavior with a sequential addition of *meso*-phenyls allowed us to predict the sign and intensity of B terms as well as absorption bands ratios for meso-phenyl substituted PdOEP molecules.

Based on the whole set of steady-state and time-resolved results (absorption, fluorescence, phosphorescence, T_1-T_n transient absorption, MCD) together with the quantum chemical analysis (DFT, and TD-DFT calculations) the detailed picture of steric interactions between bulky meso-phenyl and side β-alkyl substituents of pyrrole ring as well as the reasons of T-state drastic shortening have been evaluated for compounds under study.

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SYNTHESIS OF CATIONIC MESO-ARYLPORPHYRINS AND INVESTIGATION OF THEIR PHOTODYNAMIC ANTIMICROBIAL ACTIVITY

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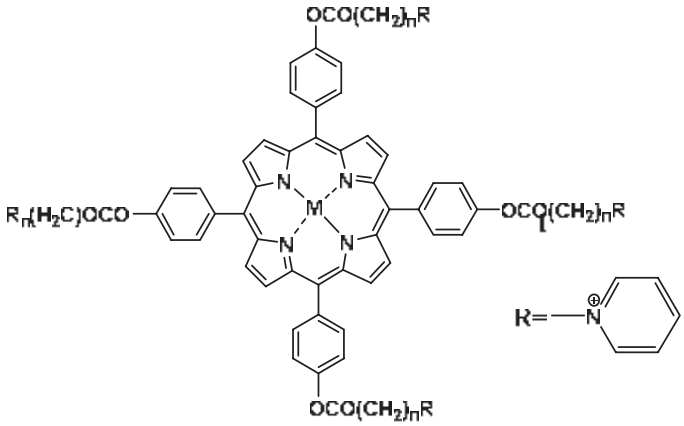
Currently, the use of photodynamic antimicrobial therapy (PACT) is being actively investigated. PACT kills bacteria, causing oxidative stress in several cellular targets. Synthetic porphyrins can be use as photosensitizing agents in PACT due to their high extinction coefficients, ease of synthesis, low cost, and possibility of macrocycle modification to produce compounds with desired properties.

Target compounds were synthesized according mixed-aldehyde monopyrrole condensation of pre-functionalized benzaldehydes according to the method of Lindsey [1]. Further, terminal bromo-containing groups of porphyrins were converted into pyridinium cationic groups.



The dark toxicity and photodynamic activity of compounds **1–2a,b** against E. coli and S. aureus strains were also investigated. Compounds **1a,b**, **2a** have been shown to quite strongly inhibit the growth of gram-positive S.aureus bacteria in aqueous solutions of compounds containing the Pluronic F-127 solubilizer without irradiation with light. Light exposure leads to an increase in S.aureus inhibition compared with the dark control only in the case of compound **1a**. In the case of the use of solutions in Pluronic, compounds **1a,b**, **2a** inhibit the growth of E.coli bacteria at high concentrations without irradiation with light; however, the MIC was not achieved in the investigated concentration range of 0.3–40 μM. The PD activity of the compounds against the biofilms of the E.coli and S.aureus bacteria was also examined. For compounds **1a, b**, 100 % inhibition of viable bacteria was achieved at concentrations of 10 and 20 μM **1a** and **1b**, respectively. The most effective on the E.coli biofilms under irradiation are compounds **1a** and **2a**.

This work was supported by the Russian Science Foundation (grant No. 17-73-10470).

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SYNTHESIS AND INDIFICATION OF MACROHETEROCYCLE BASED ON 2-AMINO-4-IMINO-2-THIADIAZOLINE HYDROCHLORIDE

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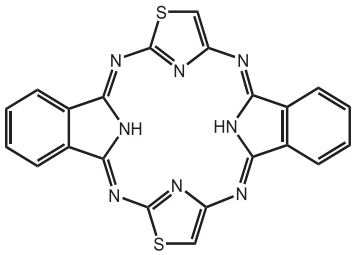
Currently, macroheterocycles containing fragments of 1.3-thiazole remain almost unstudied. Thus, the research of these compounds is interesting.

In most causes macroheterocyclic compounds (Mc) are prepared by reacting phthalonitrile or its derivatives with carbo- or heterocyclic diamines. 2,4-Diamino-1,3-thiazole is sensitive to the action of air oxygen, therefore it is produced as a hydrochloride, which is stable.

We have proposed a method of obtaining Mc, which consists in 2-amino-4-imino-2-thiazoline hydrochloride fragment.



To a solution of sodium methanolate with stirring phthalonitrile was added without access to sunlight. After stirring reaction mass for 1,5 h, 2-amino-4 iminothiazoline hydrochloride was added, then the reaction mass was stirred at 45–50 °C for 5 h under a layer of argon. After cooling to room temperature, the mixture was poured onto water, the precipitate formed was filtered off, washed with water and dried in air. The obtained black powder was purified by multiple extraction of impurities in the Soxhlet apparatus with acetone. As a result, two products were identified.

The first is a black powder, soluble in DMF, poorly soluble in methanol, insoluble in water. The structure was confirmed on the basis of data of electronic, IR spectroscopy, mass spectrometry. The target Mc was isolated with 37 % yield.

The second product, which was extracted after distilling off acetone, is a brown powder. According to electronic, IR spectroscopy, mass spectrometry it was established that this is a non-cyclic three-link product. The yield was 4 %.

Thus, we have shown the possibility of using aromatic heterocyclic diamine hydrochloride in the synthesis of Mc and the intermediate products of this synthesis.

The financial support was got from RFBR (agreement 19-03-00888). The work was carried out using the resources of the Center for the collective use of scientific equipment "ISUCT".

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THE STUDY OF PHYSICAL AND CHEMICAL PROPERTIES OF COMPLEXES OF MAGNETIC NANOPARTICLES (MNPS) AND PHOTOSENSITIZERS (PS) OF BACTERIOCHLORIN RANGE

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This research work is devoted to the study of the interaction between bacteriochlorin derivatives and a protein coating of magnetic nanoparticles (MNPs) – human serum albumin (HSA). In the course of the study, it was founded that the complex of magnetic nanoparticles with photosensitizers of the bacteriochlorin range coated by protein is not stable enough and aggregates during prolonged storage. To increase the colloidal stability of the system, we used a stabilizing stealth coating, polyethylene glycol. Using the method of dynamic light scattering (DLS), it was proved that the MNP-PS complex additionally coated with PEG is much more stable than the MNP-PS complex covered only with HSA. We also studied the binding constant of HSA with various modified PS (4,6,8).

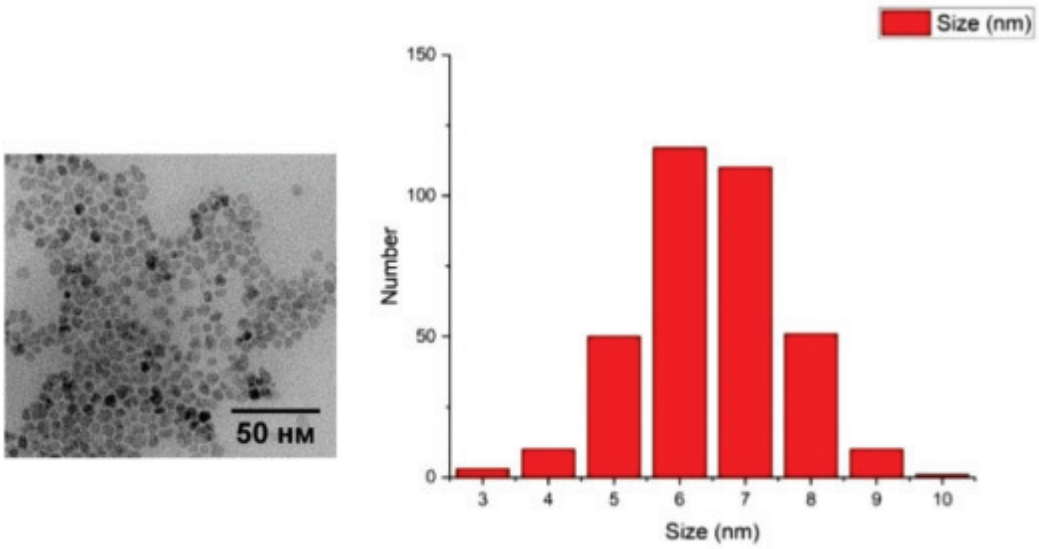

Fig. *Transmission Electron Microscopy and Size Distribution of MNP-HSA-PEG-PS complexes*

Besides, later we investigated the release of the photosensitizer from the complex with magnetic nanoparticles in two ways. According to the first: previously obtained complexes were incubated in solutions with natural and synthetic detergents (Twin 20, HSA, fetal serum). This should have contributed to the release of PS from the complex with the MNPs. Then the solutions were centrifuged to separate the fraction of the MNP from the detergent solution. The fractions obtained were studied by physicochemical methods of analysis, and it was shown that PS does not release under the described conditions. The second way was to study the behaviour of MNP@ PS in the culture medium of tumour cells using confocal microscopy, and a fluorescent label was pre-sewn to the MNP.

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TIN (II) COMPLEXES BASED ON BIOLOGICALLY ACTIVE LIGANDS

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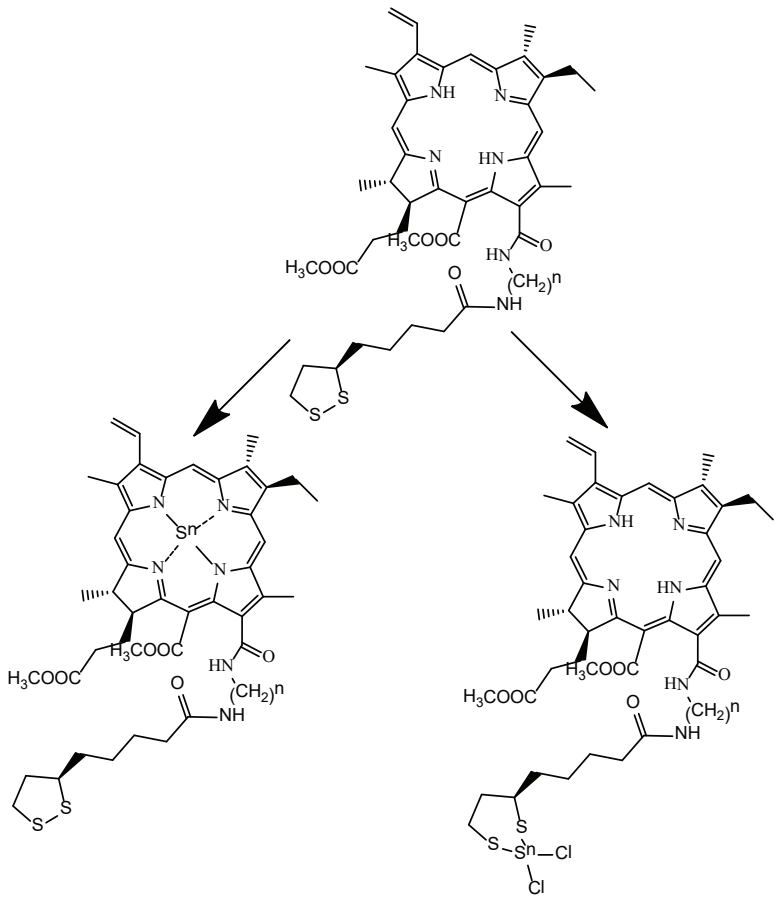
The combined treatment using both chemotherapy and photodynamic therapy has a number of advantages in contrast to monochemotherapy. One of the benefits is possibility to overcome multidrug-resistance. Thus, development and synthesis of new compounds with high efficiency in relation to chemotherapeutic-drug-resistant tumors are actual nowadays. Transition metal complexes can be used for these goals.

Tin (II) was chosen as a transition metal for combined antitumor agents development. Tin (II) complexes inhibit cell`s antioxidant system through reduction properties of metal.

During this work, two approaches to tin agents synthesis were reviewed and carried out. In the first case, we synthesized tin (II) complex with photosensitizer with an inclusion of metal in a macrocycle cavity. Another approach included synthesis of tin complexes with sulfur – containing photosensitizers on the periphery of a macrocycle.



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BIFUNCTIONAL SYSTEMS BASED ON DERIVATIVE DIPHENYLPHOSPHINE AND NATURAL

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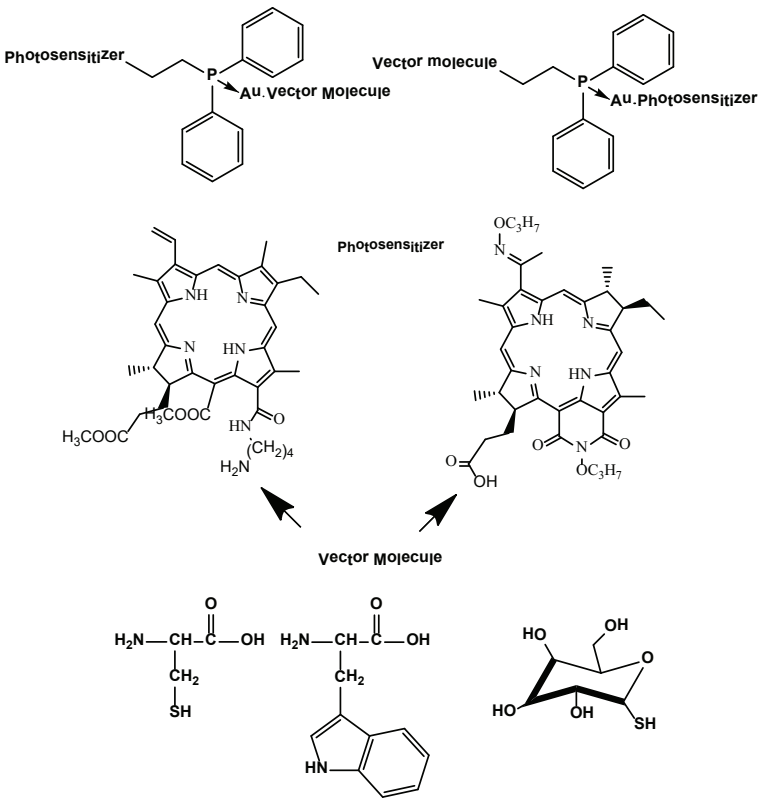
Reducing the resistance of cells to free radicals and oxidative stress can increase the effectiveness of photodynamic therapy (PDT), the main cytotoxic agent, which is singlet oxygen. As known thiolate and nitrogen-containing gold (I) complexes are able to inhibit thioredoxin reductase. This study includes the development of high-performance PS for combination therapy of cancer, based on dipropoxybacteriopurpurinimide (DPBPI).

Creation of bifunctional gold complexes is actual task for application in oncology such complexes can contain both PDT agent and fragments to improve the water-solubility or for targeted drug delivery.

For purposes of this study we developed strategy of synthesis bifunctional gold complexes. We used diphenylphosphine derivatives of acids and amines with different lengths of hydrocarbon radical.



The work was carried out with the financial support of the RFBR grant No 19-03-00302

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SYNTHESIS, STRUCTURE AND PROPERTIES OF SALTS BASED ON REDUCED TETRAPYRASINOPORPHYRAZINES

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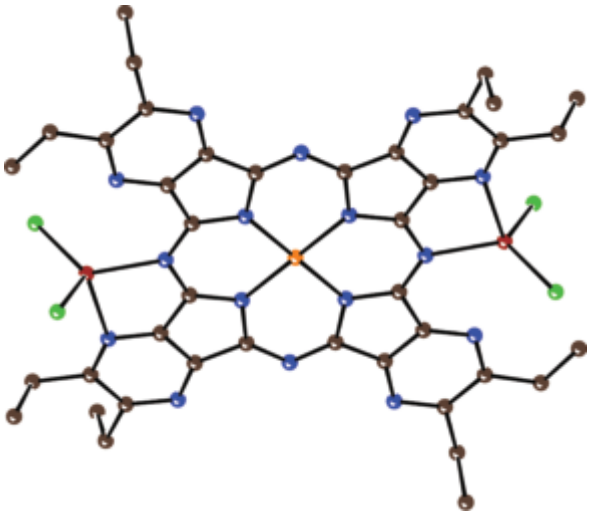
Porphines and their analogs represent an extensive class of macroheterocyclic compounds that are widely used in a number of high-tech areas – in the manufacture of light-emitting diodes, solar cells, transistors, storage devices, etc.

The reduction or oxidation of macrocycles leads to the appearance of an unpaired electron delocalized on a macrocycle. Such compounds can possess a number of interesting properties (for example, metallic conductivity, giant magnetoresistance, ferromagnetic interactions, and ferrimagnetic spin ordering).

The oxidation processes of macroheterocycles (in particular, the phthalocyanine cycle) are well studied. Recent studies have shown that compounds with reduced macroheterocycles, like oxidized macrocycles, can also have various physicochemical properties.

In this work, for the first time we have obtained a series of crystalline salts with reduced tetrapyrazinoporphyrazines.

At the reduction of free-base tetrapirazinoporphyrazine ($H_2TPyzPz$), a series of salts containing the anion radicals $H_2TPyzPz^{\bullet-}$ and dianions $H_2TPyzPz^{2-}$ was obtained. The effect of the degree of reduction of the tetrapyrazinoporphyrazine macrocycle on its molecular structure, optical and magnetic properties of salts has been investigated.



Reduction of iron (II) octaethyltetrapyrazinopo rphyrazine, $Fe^{II}TPyzPzEt_8$, by zinc dust allowed the preparation of crystalline salt $(PPN^+)_2\{Fe^{II}(TPyzPzEt_8)^{4-}(ZnCl_2)_2\}^{2-}$. Metallic zinc transfers two electrons to $Fe^{II}TPyzPzEt_8$ forming the $\{Fe^{II}(TPyzPzEt_8)^{4-}\}^{2-}$ dianions which coordinate two ZnCl2 units on the periphery of the TPyzPzEt8 macrocycle. Optical and EPR spectra show the formation of diamagnetic tetraanionic $\{TPyzPzEt_8\}^{4-}$ macrocycle**,** and as a result, two-electron reduction of $Fe^{II}TPyzPzEt_8$ is centered exclusively on the macrocycle.

A method for the synthesis of iron (II) tetra(2,3-quinoxalino)porphyrazine ($Fe^{II}T(2,3\text{-}Q)Pz$) was developed. At the reduction of $Fe^{II}T(2,3\text{-}Q)Pz$ in the presence of *N*-methylimidazole, the salt $\{cryptand[2.2.2](Na^+)\}_2\times[(N\text{-}MeIm)_2Fe^{I}(T(2,3\text{-}Q)Pz)^{3\bullet-}]^{2\bullet-}\times solv$ was obtained . Formation of the salt is accompanied by both the reduction of the central iron atom and the reduction of the macrocycle.

This work was supported by RSF Grant №. 17-73-10199.

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ABOUT THE ROLE OF METALPROPHIRINS IN THE SYNTHESIS OF HIGHLY SUBSTITUTE HYDROGELS BASED ON ACRYLAMIDE

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It is known that polymers of acrylamide with a volumetric-developed structure exhibit the properties of water-absorbing hydrogels. In the present work to obtain hydrogel wire whether the radical polymerization of acrylamide (AA) in the presence of an initiator $(NH_4)_2S_2O_8$ and metalloporphyrin additives (MP) in the form of chlorophyll, and of cobalt- and copper-containing metal complexes pheophytin. Samples of polyacrylamide, capable of absorbing 400 ÷ 1000 grams of water per 1 gram of hydrogel, were obtained. In our opinion, such high water absorption efficiency is connected with obtaining a supramolecular structure due to the large number of cross-links of the growing macrochains polyacrylamide. Metal porphyrins are capable of crosslinking growing macroradicals, but due to their low concentration compared to the initial acrylamide (approximately 4 orders of magnitude), this reaction route cannot ensure the formation of the required supramolecular structure. Therefore, we propose a hypothesis about the formation in the system under study of an intermediate with two reaction centers of AA with the participation of MP according to the following scheme:

$$CH_2{=}CH{-}C(O)NH_2 + MP \leftrightarrow \text{adduct} \quad (1)$$

$$\text{Adduct} \rightarrow \text{hydride MP} + CH_2{=}CH{-}C(O)N^{\bullet}H \quad (2)$$

$$CH_2{=}CH{-}C(O)N^{\bullet}H + CH_2{=}CH{-}C(O)NH_2 \rightarrow CH_2{=}CH{-}C(O){-}N(H){-}CH_2{-}C^{\bullet}H{-}C(O)NH_2 \quad (3)$$

$$\text{Hydride MP} + R^{\bullet} \rightarrow MP + RH \quad (4)$$

The equilibrium formation of the adduct is possible due to the coordination of the nitrogen atom of the amino group AA with the metal atom MP. The key is stage (2) with the formation of a two-center intermediate $CH_2{=}CH{-}C(O)N^{\bullet}H$ able to participate in the growth of a chain of macromolecules, and in cross-linking of these macromolecules. Regeneration of metalloporphyrinoccurs in the act of breaking a chain of a radical chain process in the interaction of the hydrogenated form of metalloporphyrin with any radical. Thus, MP participates in the catalytic cycle and ensures theformation of an intermediate necessary for the formation of a body-crosslinked supramolecular structure of polyacrylamide.

AUTHORS

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