УДК 535.355.4:546.881 doi: 10.33609/2708-129X.89.04.2023.73-89

LANTHANIDE-PORPHYRINS AND LANTHANIDE-PHTHALOCYANINES: DEVELOPMENT OF STABLE AND EFFECTIVE INFRARED 4F-EMITTIVE COMPOUNDS.

N.N. Semenishyn*, S.S. Smola, N.V. Rusakova

A.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine,
86 Lustdorfs'ka doroga, 65080 Odesa, Ukraine
Email: ssmbikola@yahoo.com

This review is devoted to different synthetic approaches for obtaining lanthanide complexes with porphyrins and phthalocyanines, studying their structure and emission features. Lanthanide-tetrapyrroles can be core-coordinated or/and coordinated by additional binding sites in polytopic derivatives. It is noteworthy that the polytopic tetrapyrroles allow obtaining polyheteronuclear compounds, which is quite interesting in terms of their particular *4f*-sensitization mechanism. A general structural difference between core-coordinated lanthanide-porphyrins and lanthanide-phthalocyanines is the ability of the latter to easily form poly-decker compounds, which leads to interesting changes in photochemical processes including *4f*-sensitization. The review also shows the main directions for the solution of the stability issue as well as different approaches for increasing the *4f*-luminescence effectiveness.

Keywords: lanthanides; porphyrins; phthalocyanines; *4f*-luminescence; sensitization.

INTRODUCTION. Extensive research on tetrapyrrole macroheterocycles (hereinafter just "tetrapyrroles") and their lanthanide complexes is driven by their high demand in various fields such as medicine [1–5], catalysis [6], luminescence spectroscopy [7] and solar energy conversion technologies [8]. It is noteworthy that a remarkable range of structures has been synthesized within a relatively short time. These structures range from basic alkyl- and arylporphyrins to derivatives that incorporate fragments capable of molecular recognition, polarity regulation, control of redox potentials, solubility, and other properties crucial for the practical application of nitrogen-containing macrocycles [9].

Among all lanthanides, only Nd(III), Er(III), and Yb(III) demonstrate *4f*-emission in the near-infrared (NIR) (Fig. 1) range when coordinated with macrocyclic tetrapyrroles. This limitation arises from the relatively low energy levels of the triplet states of tetrapyrroles in the phosphorescence region (approximately 800 nm), and only the mentioned lanthanide ions possess resonance levels that match the excitation energy transfer requirements.

The addition of organic molecule fragments capable of coordinating extra metal ions enhances the potential for self-organization in modified tetrapyrroles and it opens opportunities to form stable peripheral complexes. Tetrapyrroles that have been modified with flexible crown- and/or azacrown ether substituents, cyclic and acyclic aminopolycarbonic acids possess two distinct types of polydentate fragments. These modified tetrapyrroles serve as convenient building blocks for the construction of polynuclear metal complexes with exceptional spectral-luminescent properties. The stacking interaction between aromatic rings allows tetrapyrrole molecules to self-organize, while their unique spectroscopic, electrochemical, semiconductor, and catalytic properties, in combination with the distinctive spectral-luminescence properties of lanthanide ions, promote the exploration of new applications for polynuclear tetrapyrroles. The design of multicomponent systems holds great promise for achieving effective *4f*-luminescence in lanthanide ions (Ln(III)) due to the availability of multiple sources of excitation energy, excluding of quenching components from the inner coordination sphere, etc.

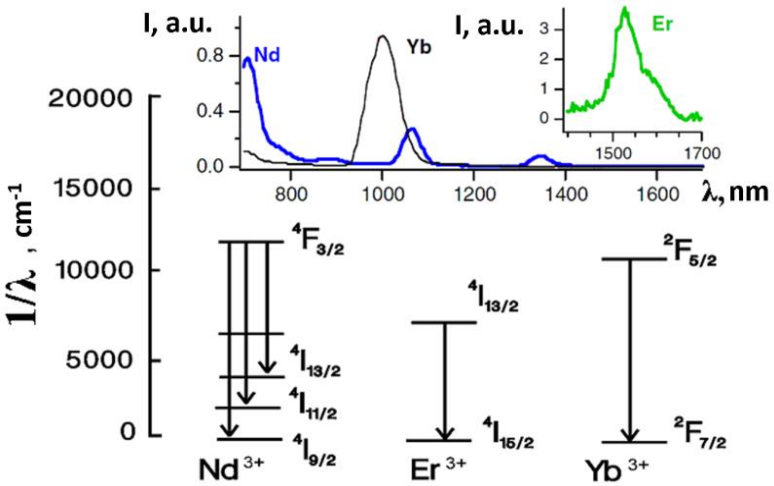

Fig. 1. Profiles of *4f*-luminescence spectra of Nd(III), Er (III), and Yb (III) ions and the corresponding electron transitions.

PORPHYRINS. Synthetic procedures for Ln-porphyrinates are generally based on the interaction of the corresponding porphyrin with an excess of lanthanide salt under the refluxing of a high-boiling solvent. In general, *e.g.* 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin (H_2tpp) and several equivalents of lanthanide *β*-diketonate are refluxed in 1,2,4-trichlorobenzene (or imidazole) for 3-4 hours and the crude product is then chromatographed to yield the desired complex. This method is still most commonly used nowadays [10].

It should be noted that all core-coordinated porphyrinates of lanthanides are relatively labile systems due to several factors. Firstly, lanthanides cannot undergo d^2sp^3 hybridization,

making it impossible to form strong covalent bonds with the ligand due to the shielding of d-orbitals. Secondly, the shielding of f-electrons by external electronic layers leads to the formation of π-bonds. Additionally, the large covalent radii of lanthanide ions strongly displace them from the plane of nitrogen atoms in the macrocycle. Lastly, the coordination with extra-ligands facilitates the dissociation of Ln-N bonds.

As a rule, the main reason of relatively low *4f*-quantum yields is a quenching effect of C-H and O-H bonds in coordination environment. For example energy dissipation in the Nd(III) ion occurs due to the overlapping of the $^4F_{3/2} \rightarrow {}^4I_{15/2}$ transition (5400 cm^{-1}) with the O–H bond vibrational quanta ν = 2 (6900 cm^{-1}) and such an excitation of vibration state leads to the effective quenching of the $^4F_{3/2}$-state [11].

Up to date, there were a lot of different techniques for improving the effectiveness of *4f*-luminescence in the IR range. Such approaches are based on the elimination of C-H and O-H bonds from the inner or outer coordination sphere of the lanthanide ion. Most effective methods are substitution of hydrogen by deuterium or fluorine [12] or using bulky groups [10]. Recently it was proposed to combine both mentioned approaches for one molecule [13]. The authors synthesized a molecule with both a bulky axial ligand and the totally deuterated (fluorinated) organic part of the molecule (Fig. 2). They achieved the unprecedented 69% quantum yield of Yb(III) ion luminescence in a deuterated solvent. This value should allow the use of such compounds as strong IR-emitters for different purposes, but three main problems hinder it. First of all it is model systems and the use of deuterated solvents in real practice (for example in medicine) is almost impossible. The second is the above-mentioned lability of these complexes [2], which severely limits their use. The third is a huge price for such kind of modification (*β*-fluorines, deuterium in any positions).

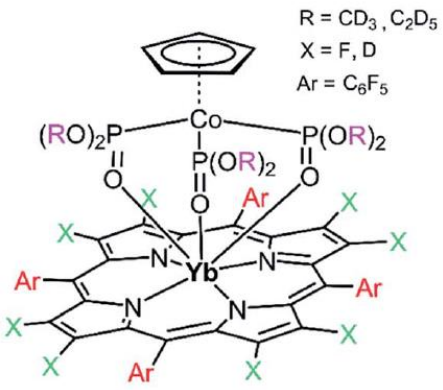

Fig. 2. Structure of fluorinated/deuterated Yb-porphyrins. Taken from [13].

So, there was proposed a simple approach to obtain stable Ln-porphyrins by the modification of starting porphyrin with aminopolycarboxylic (APC) acids, since their stability constants (lgβ) with lanthanides are >20 for H_5dtpa and >15 for H_4edta. Obtained polytopic porphyrins react with the ionic form of lanthanide at normal conditions (even at room temperature) by its APC site to form peripheral complexes (Fig. 3). Such modified porphyrins (particularly dtpa-derivatives) allow keeping the lanthanide ion saturated enough, hence preventing its interaction with the C-H or O-H bond containing components of the medium.

The coincidence between the absorption and excitation spectra of these complexes clearly shows that a ligand-to-lanthanide ion energy transfer from the triplet levels of porphyrins to the resonance levels of Ln(III) takes place [14]. It has been found that the values of *4f*-luminescence quantum yield for the

dtpa-complexes are higher than for the same edta-complexes [15], and that homobinuclear complexes (M=Ln, Fig. 3) have more effective *4f*-luminescence than mononuclear complexes [16]. The former can be explained by the greater saturation of the lanthanide ion in dtpa derivatives in comparison to edta ones, which results in the appearance of water (or other solvent) molecules in the inner coordination sphere of edta-derivatives (it was demonstrated for similar edta-compounds [17]).

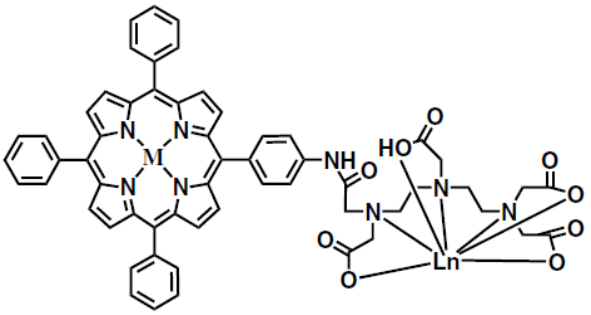

Fig. 3. Structure of peripheral Yb-porphyrins. Taken from [16].

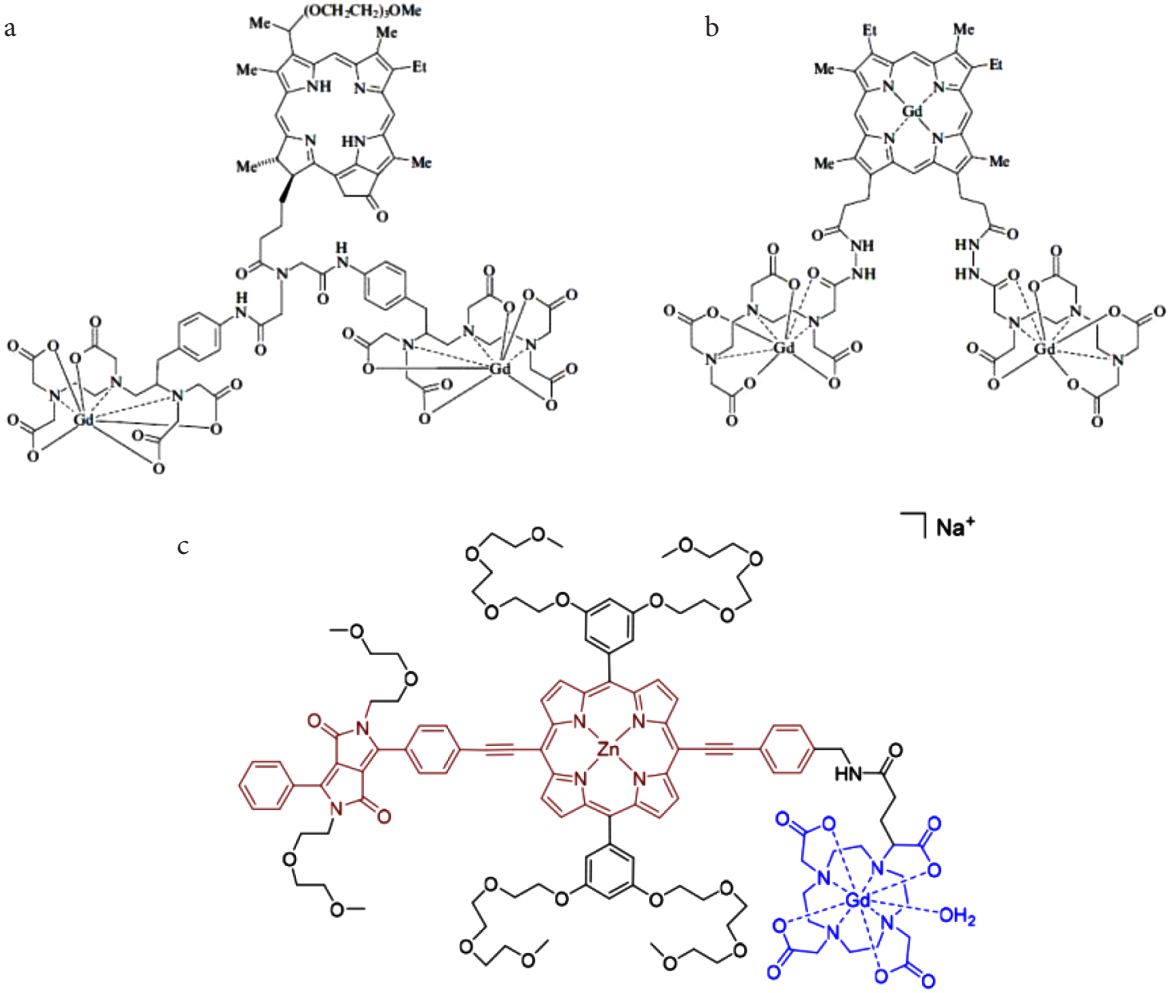

Fig. 4. Gd(III) complexes with synthetic porphyrins and Zn-porphyrins modified with dtpa and dota-fragments. Taken from [3, 18].

APC-based polytopic porphyrins allow obtaining homopolynuclear complexes. As a result it is possible to obtain modified Ln-porphyrins, which can act as MRI agents and photodynamic agents at the same time. Fig. 4 presents examples of polynuclear f-f and f-d complexes involving Gd(III) ions and porphyrins and Zn-porphyrins containing diethylenetriaminepentaacetate (dtpa) and tetraazacyclododecanetetraacetate (dota) fragments. These compounds have shown promising properties as contrast agents for the diagnosis of neoplasms [3, 18–19].

The synthesis of polynuclear complexes based on functionalized porphyrins typically occurs in a single step. Depending on the synthesis conditions, complexation can take place either at the peripheral substituents (Fig. 4, a), involve all ligand fragments including the porphyrin center (Fig. 4, b), or it is possible to obtain heteronuclear compounds by sequential synthesis (Fig. 4, c) based on different conditions of APC and porphyrin coordination with different metal ions. As a rule, in contrast to homonuclear complexes, the formation of heteronuclear complexes is more challenging as it requires step-by-step complexation of metals with polytopic ligands to avoid producing a mixture of products.

d-f-Heteropolynuclear complexes with erbium (III) ions were synthesized using a zinc-containing porphyrin block modified with fragments of 1,10-phenanthroline or 2,2'-dipyridyl [20]. Aromatic substituents were chosen for two reasons. Firstly, they offer the possibility of forming stable d-metal complexes. Secondly, the influence of the nature of aromatic spacers on the mutual arrangement of porphyrinate units was studied. The use of non-planar 2,2'-dipyridyl as a spacer led to a more flexible arrangement compared to the rigid binding provided by the condensed 1,10-phenanthroline linker (shown in Fig. 5).

The resulting compound exhibits sensitized *4f*-luminescence from the Er(III) ion in the NIR region at 1530 nm (transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$). This luminescence arises from resonant energy transfer from Pt(II) porphyrinate to the emitting levels of the Er(III) ion. This energy transfer mechanism is supported by the overlap of the luminescence spectra of d-metal porphyrinate and the f-f absorption spectra of erbium ions. Specifically, transitions from the ground level $^4I_{15/2}$ of the Er(III) ion occur to the levels $^4F_{9/2}$ and $^4I_{9/2}$, with absorption maxima at 652 nm and 801 nm, respectively.

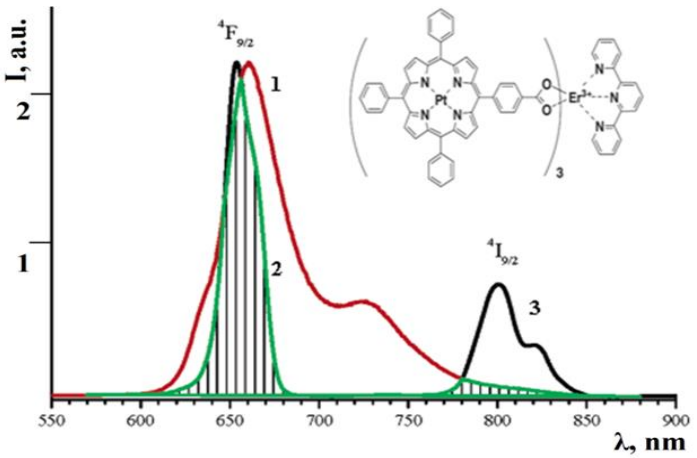

Fig. 5. The overlapping area (shaded) where the luminescence spectra of Pt-porphyrinate (1) and the absorption spectra of the Er(III) ion intersect (transitions $^4I_{15/2} \rightarrow {}^4F_{9/2}$ (2) and $^4I_{15/2} \rightarrow {}^4I_{9/2}$ (3). Taken from [20].

In a heteronuclear complex depicted in Fig. 6, the *4f*-luminescence of Nd(III) and Yb(III) ions was detected. The complex is based on a Pd(II) *β*-mono-aminotetraphenylporphyrinate, which has been modified with a dota derivative. Notably, in this study [21], the preparation of the d-metal porphyrinate occurs prior to the introduction of the lanthanide ion into the peripheral binding site.

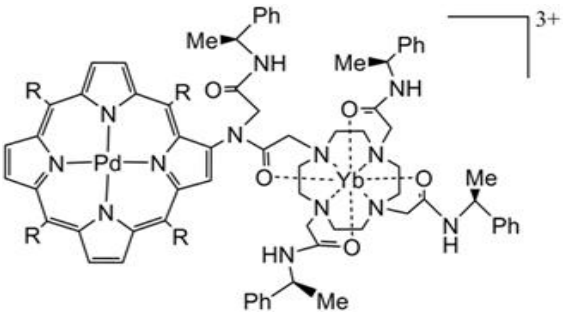

Fig. 6. Heteronuclear Yb-Pd complex with dota-functionalized porphyrin. Taken from [21].

Palladium complexes of porphyrins are known to possess long-lived triplet levels, which can be effectively quenched in the presence of oxygen in polar solvents. However, it has been demonstrated that modification with a dota fragment helps suppress oxygen quenching and significantly enhances the phosphorescence of palladium complexes by nearly an order of magnitude. The luminescence spectra of Nd(III) and Yb(III) ions were obtained in solutions of methanol (both deuterated and non-deuterated) under aerated and degassed conditions. It was found that the *4f*-luminescent signal in a deuterated solvent was increased by 4 times for Yb(III) and 2.5 times for Nd(III), indicating the sensitivity of the excited ion levels to quenching by OH vibrations. The excitation spectra of the samples in degassed solutions closely resembled the absorption spectra of the individual porphyrin complexes. This suggests a competitive energy transfer rate from the triplet levels of the porphyrin component to the levels of lanthanide ions, according to the authors. In neodymium-containing systems, energy transfer is more efficient compared to Yb(III)-Pd(II) complexes. This can be attributed to the larger overlap integrals between the absorption spectra of Nd(III) ions (with absorption maxima at 740 nm, 794 nm, and 865 nm corresponding to transitions from the ground level $^4I_{9/2}$ to $^4F_{7/2}$ + $^4S_{3/2}$, $^4F_{5/2}$ + $^4H_{9/2}$, and $^4F_{3/2}$, respectively) and the emission bands of porphyrinates.

Numerous heteronuclear complexes have been synthesized using bridging ligands [22–24]. However, the formation of d-d-heteronuclear complexes through this method is deemed impossible, likely due to the lower coordination numbers exhibited by d-metals compared to lanthanides. In contrast to previous studies, f-d-compounds are synthesized using lanthanide porphyrinates as the primary "building block" in the systems (as illustrated in Fig. 7).

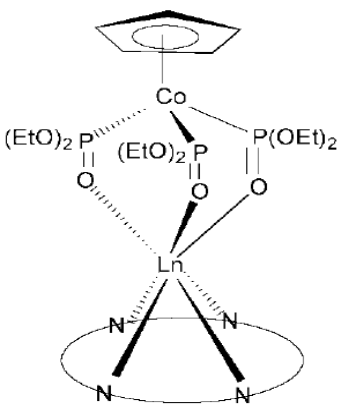

Fig. 7. Structure of lanthanide-cobalt heteronuclear compounds with bulky axial ligand Taken from [22].

Ln-Co complexes were successfully synthesized through the addition of (cyclopentadienyl)-tris-(diethylphosphinite)-cobaltate. These complexes feature effective shielding of the lanthanide ion by the cobalt-containing bulky fragment, resulting in the generation of relatively strong *4f*-luminescence signals from Yb(III), Nd(III), and Er(III) ions. One of the most significant and intriguing aspects of these compounds is their potential application as components in electroluminescent devices that emit in the NIR region. The desire to obtain homogeneous thin films for luminescent layers has prompted significant interest in the development of hybrid materials based on lanthanide porphyrinates [25–26].

Lanthanide-porphyrin complexes have emerged as highly promising materials for the development of emission layers for various applications [27–28]. The efficiency of electroluminescent devices has been significantly enhanced by carefully selecting appropriate extra ligands in complexes and matrix materials. Kango and colleagues proposed the replacement of acetylacetonate with a cobalt complex (as illustrated in Fig. 7). A device employing a similar structure exhibited distinct luminescence even at a low voltage of 4 V, with a radiation power ranging from approximately 0.2 μW cm^{-2} to 0.6 μW cm^{-2} at 10-15 V. Substituting polystyrene with poly(vinylcarbazole) did not noticeably affect the device characteristics, suggesting that charge carrier transport is primarily governed by the properties of the Yb(III) complexes. Interestingly, by substituting the cobalt complex with a pyrazolyl borate ligand, the power output of the device was increased by nearly an order of magnitude.

The formation of polynuclear porphyrin complexes is possible not only when additional complexing fragments are present in the ligand's structure, but also when multiple tetrapyrrole macrocycle rings are linked by spacer groups. While most studies focus on porphyrin complexes with d-metals, where the macrocycles are linked using various fragments to vary the distances between porphyrinates, the nature of the metal remains unchanged.

The dimerization of metalloporphyrins can also occur due to the presence of bridging extra ligands such as hydroxo groups, carboxylates and ethers [29]. However, these systems readily undergo substitution reactions. Porphyrins themselves can act as bridging ligands [30], resulting in equilibrium between mono- and bimolecular forms and changes in the absorption spectra of the resulting compounds. Homopolynuclear f-f complexes of porphyrins, in which the lanthanide ion is coordinated by four nitrogen atoms of the macrocycle and several extra ligands, exemplify this behavior. Particularly labile compounds are those with water, methanol, ethanol, dimethylformamide, halogen and hydroxide anions as extra ligands [31–32]. Such complexes have been isolated for the late-series lanthanides (Er, Yb, Lu), as the larger ionic radii of the early-series ions make effective binding to porphyrin difficult. These systems are highly labile, as the extra ligands can be substituted with molecules such as acetate, 8-hydroxyquinoline, diethoxyethane, tetrahydrofuran and 7-azabenzotriazole, etc. [33–34]. Moreover, they are prone to dimerization through the bridging function of the extra ligands. The structure shown in Fig. 8b was obtained through a two-phase synthesis involving the interaction of mono-complexes in dichloromethane at room temperature. A structural analysis revealed that the dimer possesses C_2 symmetry and consists of

two six-coordinate Yb(III) ions, with a distance of 3.581 Å between them, connected by two asymmetric bridging oxygen atoms from hydroxo- and 8-hydroxooxyquinoline extra ligands [22–24, 35].

The systems depicted in Fig. 8 exhibited a *4f*-luminescent signal, with a maximum wavelength (λ_{max}) ranging from 978 to 982 nm in the NIR region. This wavelength corresponds to the characteristic $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of the Yb(III) ion. Among these systems, the complex with water molecules as bridging ligands (complex 1) displayed the shortest lifetime of 1.02 μs, which is approximately 1.5 times shorter than the lifetime of the mononuclear counterpart. In contrast, complexes 2 and 3 showed an increase in τ_{4f}, with lifetimes of 3.17 μs and 2.27 μs, respectively. These lifetimes were considerably longer than the fluorescence lifetime, which was not entirely quenched in these systems, ranging from 4.3 to 4.8 ns. The authors attributed the decrease in IR luminescence intensity to an increase in the number of O-H oscillators in the complex molecules. More stable systems were obtained when *β*-diketones and tridentate ligands like hydridotris(pyrazol-1-yl)borate and cyclopentadienyl-tris-(dialkoxyphosphite)-cobaltate (I) were employed as extra ligands.

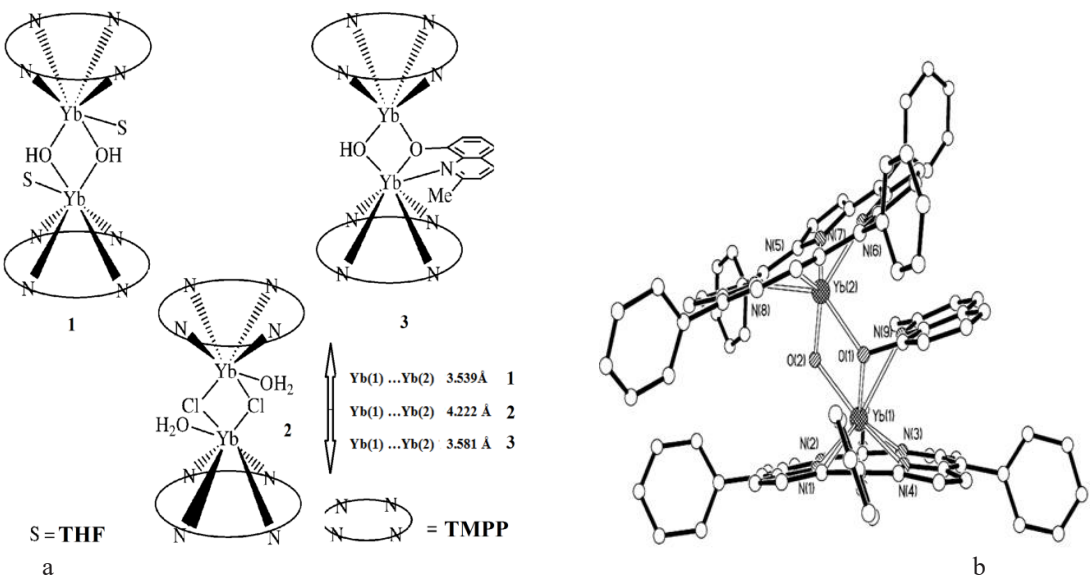

Fig. 8. Complexes of tetra(*p*-methoxyphenyl)-porphyrin (TMPP) (a) and the structure of the complex $[Yb(TMFP)(\mu\text{-}OH)]_2(THF)\cdot 2H_2O$ (b). Taken from [32].

PHTHALOCYANINES. Three main approaches for the synthesis of lanthanide-phthalocyanines can be described: template synthesis on phthalonitriles, metallation of free phthalocyanine, and axial substitution of the metal ion.

The template synthesis based on phthalonitriles is the simplest method for obtaining monophthalocyaninates of lanthanides [36]. Unsubstituted phthalocyaninates of Sm(III), Gd(III), Yb(III), Lu(III), as well as tetrachloro-, tetrabromo-, tetranitro-, and tetra-

crown-substituted complexes of lutetium have been synthesized using this method [37]. The compounds were obtained by melting the corresponding phthalonitriles with lanthanide salts in the temperature range of 200–300°C, followed by extraction with organic solvents. The synthesis conducted in alcohols in the presence of bases allows reduction at temperatures of 130–160°C. Both unsubstituted and cyclopropyl-substituted complexes of lutetium, as well as isopropylenedioxyphthalocyaninates of Sm(III), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), have been obtained using this method [38].

In contrast to monophthalocyaninates, the synthesis of sandwich complexes requires higher temperatures and increased synthesis duration. Double-decker phthalocyanines can be obtained with varying yields by heating a mixture of phthalonitrile and lanthanide acetate in molar ratios ranging from 1:4 to 1:8 at temperatures of 280–290°C. Conducting the synthesis at temperatures of 300-310°C, followed by vacuum sublimation of the products, allows the production of diphthalocyaninates with yields of up to 60%, depending on the nature of the central ion. As the lanthanide series progresses, the yields of diphthalocyaninates increase, while the yields of side products such as free phthalocyanines decrease. Diphthalocyaninates of practically the entire lanthanide series have been obtained using this method [38].

Triple-decker complexes are obtained by the interaction of phthalonitrile melts and lanthanide acetates at temperatures of 230-290°C for 1 hour. Thus, phthalocyanine complexes of lanthanide and yttrium ions have been obtained using this method [39].

A disadvantage of template synthesis is the low selectivity of the method, resulting in relatively low product yields, which necessitates additional purification of the products using chromatographic methods.

More advanced methods for the synthesis of phthalocyaninates are based on the interaction of the free ligand or its dianion with lanthanide salts. Planar complexes can be synthesized by reacting lanthanide chlorides or acetates with dianions obtained by the action of dibutyl lithium on the corresponding ligands. When using DBU or 1,10-phenanthroline as bases, tetra-crown-substituted and octa-alkyl-substituted monophthalocyaninates of lanthanides have been obtained with high yields.

The second variation of this reaction involves the interaction of alkaline metal phthalocyaninate (typically lithium) with various lanthanide derivatives. Unlike free ligands, lithium phthalocyaninate is highly soluble in methanol, tetrahydrofuran, acetone, and other organic solvents, allowing the reactions to be carried out under homogeneous conditions at relatively low temperatures. A series of monophthalocyaninate complexes with β-diketonates as external anions have been obtained using this approach [40–41]

Triple-decker phthalocyaninates of lanthanides are obtained by the interaction of lanthanide acetates or acetylacetonates with phthalocyanine. The reaction takes place in the presence of DBU at a temperature of 260°C. In the absence of a base and at a molar ratio of lanthanide to ligand of 3:1, complexes of La(III), Nd(III), and Tb(III) were synthesized under milder conditions (THF, 210°C) with yields exceeding 60%. The formed diphthalocyaninates, as side products, are separated by column chromatography on silica gel (eluent: $CHCl_3$) or on basic aluminum oxide (eluent: CH_2Cl_2 or $CHCl_3$-MeOH) [42].

Thus, the metallation of free ligands or their dianions with rare earth metal ions represents an efficient and selective method for synthesizing various mono-, di-, and triphthalocyaninate complexes of lanthanides and their analogues, exhibiting high yields and purity of the target products.

Axial substitution reactions in the metal ion are typically employed for obtaining monophthalocyaninate compounds. Currently, there are known methods for synthesizing monophthalocyaninates of indium, zirconium, hafnium, as well as lutetium. The use of this method is promising both for modifying the composition of metal complexes and for investigating their stability [43].

The composition of sandwich-type phthalocyanine complexes is characterized by the general formulas $[M(Pc)_2H]$, $[MPc_2\bullet]$ (the dot represents the Pc_2 group with a charge <4 due to the oxidation of one ligand to the Pc- state), $[M_2Pc_3]$, and $[MPc_4]$. The necessary conditions for the formation of sandwich phthalocyaninates are, firstly, that the covalent radius of the metal complexing agent should exceed 1.35 Å (the radius of the coordination cavity of phthalocyanine) and secondly, the oxidation state of the metal ion should be at least +3. The radii of lanthanide cations exceed the size of the cavities of phthalocyanine ligands, which is why, upon interaction, sandwich-type double- and triple-decker structures are predominantly formed. Depending on the synthesis conditions, different colored compounds are obtained - "green" or "blue" forms.

The question of the structure of the "blue" and "green" forms of lanthanide phthalocyaninates remained controversial for a long time until data from X-ray structural analysis of compounds were obtained. In particular, complexes of La(III), Gd(III), and Lu(III) with crown-substituted phthalocyanines in the "blue" form showed that lanthanide phthalocyaninates are neutral compounds [44].

For colored diphthalocyaninates, the absorption spectra are determined by the state of the chromophores of the two ligands and the presence or absence of interaction between them. Complexes in which the ligands are in an equivalent state, for example, $[Pc^{2-}M^{3+}Pc^{2-}]$, exhibit a *Q*-band in the absorption spectrum, which is split into two components: *Q*' and less intense *Q*''. This splitting is caused by the resonant dipole-dipole interaction between the chromophores of equivalent ligands and is manifested as a blue coloration of the compounds. The magnitude of the splitting and the relative positions of the *Q*' and *Q*'' bands depend on the nature of the complexing ion.

In the case of non-equivalence of chromophores resulting from ion association with a proton ($[MPc_2H]$), localization of the unpaired electron on one of the ligands ($[MPc_2^{\bullet}]$), or dimerization, a single intense Q-band is observed in the absorption spectrum. Its origin is attributed to the absence of resonant interaction between the ligands and leads to a green coloration of the compound. A characteristic feature of sandwich-like compounds is the presence of a weak absorption band in the range of 450–480 nm in the absorption spectrum, which corresponds to the ligand absorption with a non-equivalent chromophoric system of the phthalocyanine macrocycle.

Unlike porphyrins, free phthalocyanine ligands exhibit only fluorescence in the range of 680–720 nm, and the intensity can exceed that of porphyrins by up to 10 times [45]. These values allow for the estimation of the energy of the singlet levels of phthalocyanines, which falls within the range of 13800–14500 cm^{-1}. Therefore, only a limited number of Ln(III)

ions, such as Nd(III), Er(III), and Yb(III), whose excited levels lie below the ligand levels and whose spectra exhibit narrow bands in the infrared (IR) region, can exhibit *4f*-luminescence in complexes with phthalocyanines.

The practical use of phthalocyanine compounds is often hindered by their low solubility in organic solvents and water. To address this issue, various substituted derivatives of phthalocyanines have been synthesized. For example, the introduction of bulky substituents like naphthyl or crown ethers into the benzene rings of the phthalocyanine molecule can enhance its solubility in organic solvents [46–48]. Moreover, binding crown ether fragments as substituents to the benzene ring of the isoindole fragment allows the formation of heteronuclear supramolecular compounds with alkali and alkaline earth metal salts. These supramolecular crown-substituted phthalocyanines exhibit unique electrophysical and optical properties due to the presence of channels with ionic conductivity (crown ether fragments) and semiconductivity (phthalocyanine macrocycle). This has led to the development of supramolecular functional materials for applications in ionic and molecular electronics.

In the context of lanthanide complexes, semi-sandwich complexes of Er(III) with *tert*-butyl and pentyloxy-substituted phthalocyanines showed *4f*-luminescence under indirect excitation in the solid state and in DMSO-d_6. In contrast, bisphthalocyaninates did not exhibit intrinsic emission from Er(III) [46].

Binuclear lanthanide complexes based on hexa-*tert*-butyl-substituted phthalocyanines were also synthesized, where the macrocycles share one benzene ring as a linker. These complexes, involving Dy(III), Yb(III), and Lu(III) ions, display intense absorption in the NIR region, with the nature of lanthanide having minimal effect on the electronic spectrum and position of the *Q*-bands [47].

A series of lanthanide complexes with tetra(15-crown-5)phthalocyanine (H_2R_4Pc) of various types luminescent in the IR region were reported [49–51]. These include unsubstituted phthalocyaninates, monophthalocyaninates with different axial ligands, and di- and triphthalocyaninates (Fig. 9).

In all these complexes, the Ln(III) lanthanide ion is coordinated to four nitrogen atoms of the tetrapyrrole macroring. In the case of monophthalocyaninates, coordination also occurs to donor atoms of acetate ions, 1,10-phenanthroline or DBU. It was observed that the presence of a second ligand with respect to the tetrapyrrole ring influences the *4f*-luminescence of monophthalocyaninate complexes, with a nearly two-fold increase in luminescence observed in the presence of phenanthroline (or DBU). Yb(III) complexes of all types exhibit near-infrared *4f*-luminescence at 980 nm. The mechanism behind this luminescence is proposed to involve Dexter energy transfer or photoinduced electron transfer resulting in the reduction of Yb(III) to Yb(II) in the excited state of the complex.

Di- and triphthalocyaninates exhibit intense fluorescence in the range of 690-770 nm when excited in the UV region. The magnitude of the short-wavelength shift for the double- and triple-decker compounds depends on the nature of the complexing agent and decreases from Nd(III) to Lu(III). In sandwich-type phthalocyaninates, the *4f*-luminescence of Yb(III) is absent in the double -decker complex and is observed in the triple-decker complex. This is likely due to the resonance interaction between the complexing agents and a greater number of closely spaced macrocyclic chromophores.

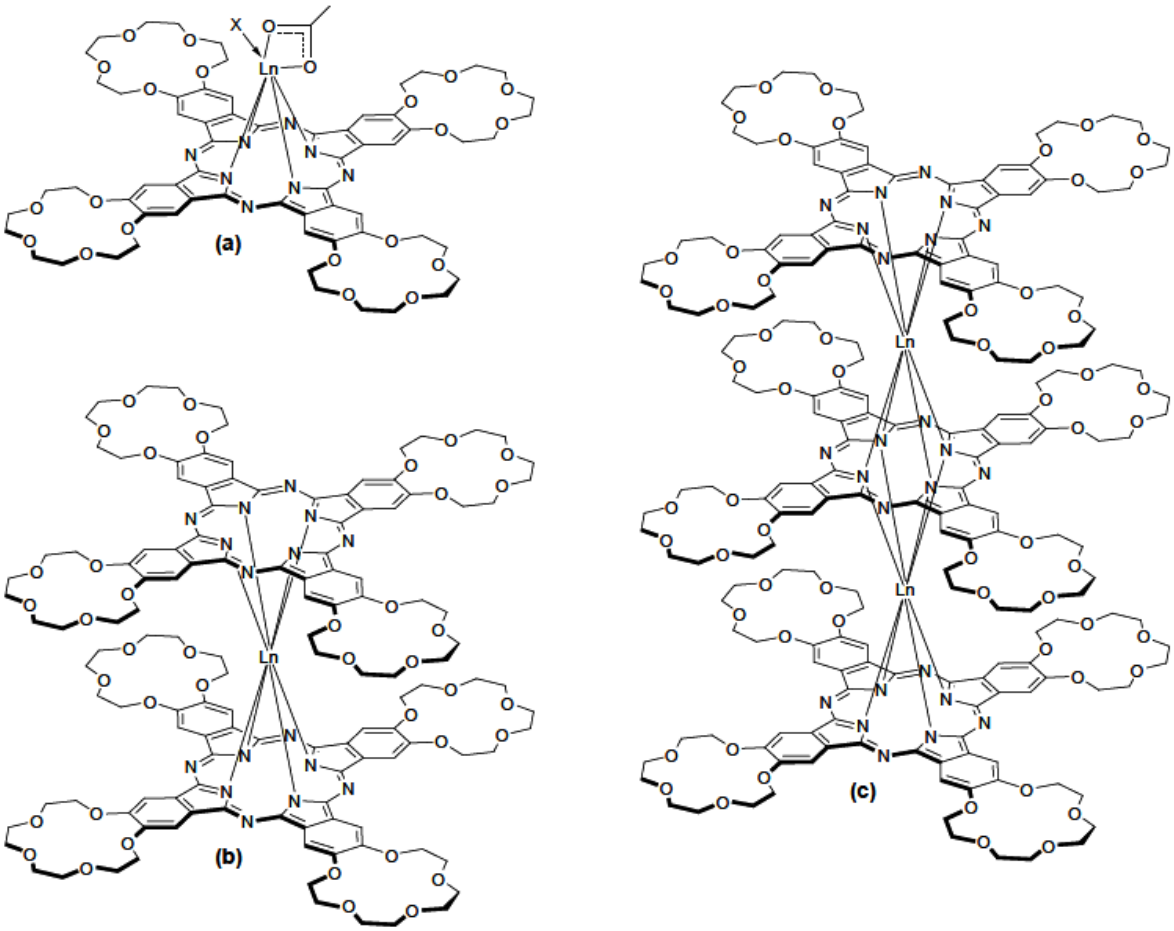

Fig. 9. Mono- (a), double- (b) and triple-decker Ln-phthalocyanines.

It was shown for the first time that *4f*-luminescence in the solid state can only be exhibited by Er(III) and Yb(III) ions in complexes with tetra(15-crown-5)phthalocyanine. Moreover, for erbium compounds, their intrinsic luminescence is also observed in solutions due to the low-lying resonance $^4I_{13/2}$ level of Er(III). The parameters of Er-centered emission at 1540 nm were found to be similar to those of known inorganic phosphors. This holds great promise for the development of new infrared emitters for telecommunication technologies, as well as applications in biology and medicine.

Analyzing the mentioned works on Ln(III) phthalocyaninates, two significant drawbacks cannot be overlooked. Firstly, the low solubility of phthalocyanine compounds in organic solvents and water complicates their practical use. Secondly, only a limited number of phthalocyanines with known composition and structure have been studied in complexes with lanthanide ions, and they do not exhibit high luminescence characteristics. This led to a little published research on the *4f*- luminescence of Ln(III) complexes with phthalocyanines. These limitations highlight the need for fur-

ther studies to overcome these drawbacks and explore new phthalocyanine complexes with lanthanide ions that possess improved solubility and enhanced fluorescence properties.

CONCLUSIONS. To conclude, the analysis of the mentioned works on Ln-tetrapyrroles suggests that the functionalization of macrocyclic ligands with chelating fragments holds promise for achieving high stability and good luminescence characteristics. Porphyrins and phthalocyanines are considered convenient molecular platforms for creating heteronuclear IR-luminescent complexes. However, there are two significant shortcomings in the aforementioned studies.

Firstly, the studies have focused on a limited number of tetrapyrroles, and their inherent structures may not initially lend themselves to high luminescent characteristics. This limitation particularly applies to natural porphyrins, which contain a significant number of C-H bonds. The vibrations of these bonds can lead to a reduction in the luminescence of Ln(III) ions. Exploring alternative or modified tetrapyrroles with improved structural features could be a fruitful direction for future research.

Secondly, the spectral-luminescent studies of Ln-tetrapyrroles have not been thoroughly analyzed in terms of the structural aspects of these compounds. Understanding the relationship between the structural features of tetrapyrroles and their luminescent properties is crucial for designing and optimizing highly luminescent complexes. Further investigations should involve comprehensive structural analysis alongside spectral and luminescent characterization to elucidate the structure-property relationships and develop guidelines for the design of efficient Ln-tetrapyrrole complexes.

The authors express their gratitude for the financial support of the National Academy of Sciences of Ukraine within the framework of the state budget theme «New luminescent near-infrared materials based on modified tetrapyrrole and complex oxide compounds of d- and f-elements: synthesis, design, properties» (0115U002223).

ЛАНТАНІД-ПОРФІРИНИ ТА ЛАНТАНІД-ФТАЛОЦІАНІНИ: РОЗРОБЛЕННЯ СТАБІЛЬНИХ ТА ЕФЕКТИВНИХ ІНФРАЧЕРВОНИХ 4F-ВИПРОМІНЮЮЧИХ СПОЛУК

М. М. Семенішин*, С. С. Смола, Н. В. Русакова

Фізико-хімічний інститут ім. О. В. Богатського НАН України,
Люстдорфська дорога, 86, Одеса 65080, Україна
**ssmbikola@yahoo.com*

Цей огляд присвячено різним синтетичним підходам щодо отримання комплексів лантанідів із порфіринами та фталоціанінами, вивченню їхньої структури та особливостей випромінювання. Лантанід-тетрапіроли можуть бути координованими ядром макроциклу та/або додатковими місцями зв'язування в політопних похідних. Слід зазначити, що політопні тетрапіроли дозволяють отримувати полігетероядерні сполуки, що є досить цікавим з точки зору їхнього особливого механізму 4f-сенсибілізації. Загальна структурна відмінність між

координованими лантанідами-порфіринами та лантанідами-фталоціанінами полягає в здатності останніх легко утворювати поліпалубні сполуки, що призводить до цікавих змін у фотохімічних процесах, включаючи 4f-сенсибілізацію. В огляді також показано основні напрямки вирішення проблеми стабільності, а також різні підходи до підвищення ефективності 4f-люмінесценції.

Ключові слова: лантаніди, порфірини, фталоціаніни, *4f*-люмінесценція, сенсибілізація.

REFERENCES

1. Pinar S., Rodah S., Sithi M., Mack J., Tebello N. Light-driven antimicrobial therapy of palladium porphyrins and their chitosan immobilization derivatives and their photophysical-chemical properties. *Dyes Pigm*. 2022. **203**: 110313. https://doi.org/10.1016/j.dyepig.2022.110313
2. Wai-Lun C., Chen X., Wai-Sum L., Bünzli J.-C.G., Wai-Kwok W., Ka-Leung W. Lanthanide-tetrapyrrole complexes: synthesis, redox chemistry, photophysical properties, and photonic applications. *Chem. Soc. Rev.* 2021. **50**: 12189. https://doi.org/10.1039/c9cs00828d
3. Jenni S., Bolze F., Bonnet C.S., Pallier A., Sour A., Tóth É., Ventura B., Heitz V. Synthesis and In Vitro Studies of a Gd(DOTA)–Porphyrin Conjugate for Combined MRI and Photodynamic Treatment. *Inorg. Chem.* 2020. **59** (19): 14389. https://doi.org/10.1021/acs.inorgchem.0c02189
4. Jin G.-Q., Chau C.V., Arambula J.F., Gao S., Sessler J.L., Zhang J.-L. Lanthanide porphyrinoids as molecular theranostics. *Chem. Soc. Rev.* 2022. **51**: 6177. https://doi.org/10.1039/d2cs00275b
5. Batinic-Haberle I., Tovmasyan A., Huang Zhiqing, Duan Weina, Du Li, Siamakpour-Reihani S., Cao Zhipeng, Sheng Huaxin, Spasojevic I., Alvarez Secord A. H_2O_2-Driven Anticancer Activity of Mn Porphyrins and the Underlying Molecular Pathways. *Oxid. Med. Cell. Longev.* 2021. **2021**: 6653790. https://doi.org/10.1155/2021/6653790
6. Piccirillo G., Maldonado-Carmona N., Marques D.L., Villandier N., Calliste C.A., Leroy-Lhez S., Ermelinda M., Eusébio S., Calvete M.J.F., Pereira M.M. Porphyrin@Lignin nanoparticles: Reusable photocatalysts for effective aqueous degradation of antibiotics. *Catal. Today.* 2022: 113903. https://doi.org/10.1016/j.cattod.2022.09.009
7. Teixeira R., Vaz Serra V., Botequim D., Paulo P.M.R., Andrade S.M., Costa S.M.B. Fluorescence Spectroscopy of Porphyrins and Phthalocyanines: Some Insights into Supramolecular Self-Assembly, Microencapsulation, and Imaging Microscopy. *Molecules.* 2021. **26** (14): 4264. https://doi.org/10.3390/molecules26144264
8. Gu J., Peng Y., Zhou T., Ma J., Pang H., Yamauchi Y. Porphyrin-based framework materials for energy conversion. *Nano Research Energy.* 2022. **1**: e9120009. https://doi.org/10.26599/nre.2022.9120009
9. Adeyemi O.O., Malinovskii V.L., Biner S.M., Calzaferri G., Haner R. Photon harvesting by excimer-forming multichromophores. *Chem. Commun.* 2012. **48**: 9589-9591. https://doi.org/10.1039/c2cc34183b
10. Van Raden J.M., Alexandropoulos D.I., Slota M., Sopp S., Matsuno T., Thompson A.L., Isobe H., Anderson H.L., Bogani L. Singly and Triply Linked Magnetic Porphyrin Lanthanide Arrays. *J. Am. Chem. Soc.* 2022. **144** (19): 8693. https://doi.org/10.1021/jacs.2c02084
11. Yanagida S., Hasegawa Y., Murakoshi K., Wada Y., Nakashima N., Yamanaka T. Strategies for enhancing photoluminescence of Nd^{3+} in liquid media. *Coord. Chem. Rev.* 1998. **171**: 461. https://doi.org/10.1016/S0010-8545(98)90069-8
12. Ning Y., Zhu M., Zhang J.-L. Near-infrared (NIR) lanthanide molecular probes for bio-

imaging and biosensing. *Coord. Chem. Rev.* 2019. **399**: 213028. https://doi.org/10.1016/j.ccr.2019.213028
13. Hu J.-Y., Ning Y., Meng Y.-S., Zhang J., Wu Z.-Y., Gao S., Zhang J.-L. Highly near-IR emissive ytterbium(iii) complexes with unprecedented quantum yields. *Chem. Sci.* 2017. **8**: 2702. https://doi.org/10.1039/c6sc05021b
14. Kuznetsova R.T., Ermolina E.G., Gadirov R.M., Mayer G.V., Semenishin N.N., Rusakova N.V., Korovin YuV. Luminescence of metal complexes of chelate-substituted tetraphenylporphyrin. *High Energy Chem.* 2010. **44**: 134. https://doi.org/10.1134/s0018143910020098
15. Rusakova N., Semenishyn N., Korovin Yu. Heteronuclear lanthanide-containing complexes on the base of modified porphyrins and their luminescent properties. *J. Porphyr. Phthalocyanines.* 2010. **14** (02): 166. https://doi.org/10.1142/S1088424610001817
16. Semenishyn N.N., Rusakova N.V., Mazepa A.V., Korovin Yu.V. Synthesis of Ditopic Porphyrins and Lanthanide Complexes on their Basis: Luminescent Features. *Macroheterocycles*. 2009. **2:** 57. https://doi.org/10.6060/mhc2009.1.57
17. Semenishyn N., Gross Z. Lanthanide-corrole conjugates. *Dalton Trans.* 2013. **42:** 3775. https://doi.org/10.1039/c2dt32842a
18. Li G., Slansky A., Dobhal M.P., Goswami L.N., Graham A., Chen Y., Kanter P., Alberico R.A., Spernyak J., Morgan J., Mazurchuk R., Oseroff A., Grossman Z., Pandey R.K. Chlorophyll-a Analogues Conjugated with Aminobenzyl-DTPA as Potential Bifunctional Agents for Magnetic Resonance Imaging and Photodynamic Therapy. *Bioconjug. Chem.* 2005. **16** (1): 32. https://doi.org/10.1021/bc049807x
19. Hindré F., Le Plouzennec M., De Certaines J.D., Foultier M. T., Patrice T., Simonneaux G. Tetra-p-aminophenylporphyrin conjugated with Gd-DTPA: Tumor-specific contrast agent for MR imaging. *J. Magn. Reson. Imaging.* 1993. **3** (1): 59. https://doi.org/10.1002/jmri.1880030111
20. Nah M.-K., Oh J.B., Kim H.K., Choi K.-H., Kim Y.-R., Kang J.-G. Photophysical Properties and Energy Transfer Pathway of Er(III) Complexes with Pt−Porphyrin and Terpyridine Ligands. *J. Phys. Chem. A*. 2007. **111** (28): 6157. https://doi.org/10.1021/jp0688512
21. Beeby A., Dickins R.S., Fitzgerald S., Govenlock L.J., Maupin C.L., Parker D., Riehl J.P., Siligardi G., Williams J.A.G. Porphyrin sensitization of circularly polarised near-IR lanthanide luminescence: enhanced emission with nucleic acid binding. *Chem. Commun.* 2000. **13**: 1183. https://doi.org/10.1039/b002452j
22. Wong W.-K., Hou A., Guo J., He H., Zhang L., Wong W.-Y., Li K.-F., Cheah K.-W., Xue F., Mak T.C.W. Synthesis, structure and near-infrared luminescence of neutral 3d–4f bi-metallic monoporphyrinate complexes. *J. Chem. Soc., Dalton Trans.* 2001. **20**: 3092. https://doi.org/10.1039/b104993n
23. Jiang F.-L., Wong W.-K., Zhu X.-J., Zhou G.-J., Wong W.-Y., Wu P.-L., Tam H.-L., Cheah K.-W., Ye C., Liu Y. Synthesis, Characterization, and Photophysical Properties of Some Heterodimetallic Bisporphyrins of Ytterbium and Transition Metals – Enhancement and Lifetime Extension of Yb^{3+} Emission by Transition-Metal Porphyrin Sensitization. *Eur. J. Inorg. Chem.* 2007. **2007** (21): 3365. https://doi.org/10.1002/ejic.200700153
24. Zhu X.-J., Zhang T., Zhao S., Wong W.-K., Wong W.-Y. Synthesis, Structure, and Photophysical Properties of Some Gadolinium(III) Porphyrinate Complexes. *Eur. J. Inorg. Chem.* 2011. **2011** (22): 3314. https://doi.org/10.1002/ejic.201100025
25. Kang T.-S., Harrison B.S., Foley T.J., Knefely A.S., Boncella J.M., Reynolds J.R., Schanze K.S. Near-Infrared Electroluminescence from Lanthanide Tetraphenylporphyrin: Polystyrene Blends. *Adv. Mater.* 2003. **15** (13): 1093. https://doi.org/10.1002/adma.200304692

26. Guo L., Yan B. Near-infrared luminescent hybrid materials using modified functional lanthanide (Nd^{3+}, Yb^{3+}) porphyrins complexes chemical bonded with silica. *Inorg. Chem. Commun.* 2011. **14** (11): 1833. https://doi.org/10.1016/j.inoche.2011.08.020
27. Zhu X., Wong W.-K., Wong W.-Y., Yang X. Design and Synthesis of Near-Infrared Emissive Lanthanide Complexes Based on Macrocyclic Ligands. *Eur. J. Inorg. Chem.* 2011. **2011** (30): 4651. https://doi.org/10.1002/ejic.201100481
28. Wang J., Xia M., Wei J., Jiao T., Chen Q., Chen Q., Chen X. Dual-signal amplified cathodic electrochemiluminescence aptsensor based on a europium-porphyrin coordination polymer for the ultrasensitive detection of zearalenone in maize. *Sens. Actuators B: Chem.* 2023. 382: 133532. https://doi.org/10.1016/j.snb.2023.133532
29. Miyazaki Y., Satake A., Kobuke Y. Oxidation of adamantane catalysed by imidazolylporphyrinatoiron(III) complexes and structural studies of 5-coordinating iron(III) porphyrin. *J. Mol. Catal. A Chem.* 2008. **283** (1-2): 129. https://doi.org/10.1016/j.molcata.2007.12.016
30. Ni Y., Marchal G., Jie Y., Lukito G., Petré C., Wevers M., Baert A.L., Ebert W., Hilger C.-S., Maier F.-K., Semmler W. Localization of metalloporphyrin-induced "specific" enhancement in experimental liver tumors: Comparison of magnetic resonance imaging, microangiographic, and histologic findings. *Acad. Radiol.* 1995. **2** (8): 687. https://doi.org/10.1016/s1076-6332(05)80437-4
31. He H.S., Wong W.-K., Li K.-F., Cheah K.-W. Synthesis, characterization and photoluminescence properties of monoporphyrinate lanthanide complexes. *Synth. Met.* 2004. **143** (1): 81. http://dx.doi.org/10.1016/j.synthmet.2003.10.011
32. He H., Zhu X., Hou A., Guo J., Wong W.-K., Wong W.-Y., Li K.-F., Cheah K.-W. Reactivity of aqua coordinated monoporphyrinate lanthanide complexes: synthetic, structural and photoluminescent studies of lanthanide porphyrinate dimer. *Dalton Tran.* 2004. **23:** 4064. https://doi.org/10.1039/b410600h
33. Foley T.J., Harrison B.S., Knefely A.S., Abboud K.A., Reynolds J.R., Schanze K.S., Boncella J.M. Facile Preparation and Photophysics of Near-Infrared Luminescent Lanthanide(III) Monoporphyrinate Complexes. *Inorg. Chem.* 2003. **42** (16): 5023. https://doi.org/10.1021/ic034217g
34. He H., Sykes A.G., May P. S., He G. Structure and photophysics of near-infrared emissive ytterbium(iii) monoporphyrinate acetate complexes having neutral bidentate ligands. *Dalton Trans.* 2009. **36:** 7454. https://doi.org/10.1039/b909243a
35. Li D.-M., Zhao Z.-X., Liu S.-Q., Liu G.-F., Shi T.-S., Liu X.-X. Synthesis of Unsymmetrical Schiff-Base Porphyrin with O-Nitrobenzaldehyde and its Lanthanide Complexes. *Synth. Commun.* 2000. **30** (22): 4017. https://doi.org/10.1080/00397910008087017
36. Botnar A.A., Bychkova A.N., Domareva N.P., Tikhomirova T.V., Vashurin A.S. Directed synthesis and study of their spectroscopic behavior in solution of rare-earth phthalocyaninates substituted by benzyloxy- and methylphenylethylphenoxy-groups. *J. Incl. Phenom. Macrocycl. Chem.* 2022. **102**: 303. https://doi.org/10.1007/s10847-021-01120-3
37. Kasuga K., Ando M., Morimoto H. The Radical Formation of Diphthalocyanine Complexes of Lanthanum(III), Neodymium(III) and Yttrium(III) with p-Benzoquinone. *Inorg. Chim. Acta.* 1986. **112** (1): 99. https://doi.org/10.1016/S0020-1693(00)85667-4
38. Tomilova L.G., Ivanov A.V., Kostyuchenko I.V., Shulishov E.V., Nefedov O.M. Synthesis of metal phthalocyanines with cyclopropyl substituents. *Mendeleev Commun.* 2002. **12** (4): 149. https://doi.org/10.1070/MC2002v012n04ABEH001614
39. Li R., Ma P., Dong S., Zhang X., Chen Y., Li X., Jiang J. Synthesis, Characterization, and

OFET Properties of Amphiphilic Heteroleptic Tris(phthalocyaninato) Europium(III) Complexes with Hydrophilic Poly(oxyethylene) Substituents. *Inorg. Chem.* 2007. **46** (26): 11397. https://doi.org/10.1021/ic7016825

40. Bo S., Tang D., Liu X., Zhen Z. Synthesis, spectroscopic properties and electrochemistry of (2,9,16,23-tetrasubstituted phthalocyaninato) erbium complexes. *Dyes Pigm.* 2008. **76** (1): 35. https://doi.org/10.1016/j.dyepig.2006.08.030
41. Černý J., Dokládalová L., Horáková P., Lyčka A., Mikysek T., Bureš F. Preparation and characterization of novel double-decker rare-earth phthalocyanines substituted with 5-bromo-2-thienyl groups. *Chem. Cent. J.* 2017. **11**: 31. https://doi.org/10.1186/s13065-017-0260-x
42. Iwase A., Tanaka K. Synthesis and electrochemistry of acetylacetonatolanthanide(III)-phthalocyaninates. *Electrochim. Acta.* 1990. **35** (11-12): 1707. https://doi.org/10.1016/0013-4686(90)87069-E
43. Tomachynski L.A., Chernii V.Ya., Volkov S.V. Synthesis and spectral characterization of bis(β-diketonato)zirconium(IV) and -hafnium(IV) phthalocyaninates. *J. Porphyr. Phthalocyanines.* 2002. **06** (02): 114. https://doi.org/10.1142/s1088424602000154
44. Voloshin Y.Z., Varzatskii O.A., Korobko S.V., Chernii V.Y., Volkov S.V., Tomachynski L.A., Pehn'o V.I., Antipin M.Yu., Starikova Z.A. Ditopic Macropolycyclic Complexes: Synthesis of Hybrid Phthalocyaninoclathrochelates. *Inorg. Chem.* 2005. **44** (4): 822. https://doi.org/10.1021/ic048189t
45. Toupance T., Ahsen V., Simon J. Ionoelectronics. Cation-Induced Nonlinear Complexation: Crown Ether- and Poly(ethylene oxide)-Substituted Lutetium Bisphthalocyanines. *J. Amer. Chem. Soc.* 1994. **116** (12): 5352. https://doi.org/10.1021/ja00091a046
46. Bo S., Hu J., Wang Q., Liu X., Zhen Z. Near-infrared luminescence properties of erbium complexes with the substituted phthalocyaninato ligands. *Photochem. Photobiol. Sci.* 2008. **7:** 474. https://doi.org/10.1039/b715809b
47. Tolbin A.Yu., Pushkarev V.E., Tomilova L.G. New phthalocyanine complexes with rare-earth elements. *Mendeleev Commun.* 2008. **18** (2): 94. https://doi.org/10.1016/j.mencom.2008.03.015
48. Kasuga K., Tsutsuo M. Some new developments in the chemistry of metallophthalocyanine. *Coord. Chem. Rev.* 1980. **32** (1): 67. https://doi.org/10.1016/S0010-8545(00)80370-7
49. Smola S.S., Semenishyn N.N., Rusakova N.V., Martynov A.G., Birin K.P., Gorbunova Yu.G., Tsivadze A.Yu. Infrared 4f-Luminescence of Erbium(III) Complexes with Tetrapyrrole Ligands. *Macroheterocycles*. 2018. **11** (3): 262. http://dx.doi.org/10.6060/mhc180691r
50. Semenishyn N.N., Smola S.S., Rusakova N.V., Kamalov G.L., Gorbunova Yu.G., Tsivadze A.Yu. Luminescence Features of Neodymium(III) Compounds with Various Tetrapyrrole Macrocycles. *Macroheterocycles*. 2017. **10** (3): 268. http://dx.doi.org/10.6060/mhc170621r
51. Snurnikova O.V. Smola S.S., Fadeyev E.N., Sinelshchikova A.A., Gorbunova Yu.G., Lapkina L.A., Tsivadze A.Yu., Rusakova N.V.The First Example of Near-Infrared 4f Luminescence of Sandwich-Type Lanthanide Phthalocyaninates. *Macroheterocycles*. 2012. **5** (4-5): 343. https://doi.org/10.6060/mhc2012.121193r

Стаття надійшла 16.05.2023.