

HOMO- AND HETERONUCLEAR Yb(III) AND Lu(III) COMPLEXES WITH CALIX[4]ARENE MODIFIED WITH PORPHYRIN SUBSTITUENTS.

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In this work we describe the approaches for the synthesis of lanthanide-containing homo- and heteronuclear complexes using 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(*N-meso*-(*p*-aminophenyl)-*meso*-triphenylporphyrincarbonyl)methoxy]-calix[4]arene (**1**). Such spatially preorganized calix[4]arene macrocycle facilitates lanthanide cation coordination, impacting the structure and analytical signal of porphyrin substituents. The study employs two synthesis strategies resulting in mononuclear and homobinuclear complexes, influenced by steric effects and changes in hydrogen bonding. The complexes exhibit changes in fluorescence spectra due to intramolecular dimerization and hydrogen bonding during complex formation. Mononuclear complexes (**Ln-1**) are synthesized under mild conditions, while homobinuclear complexes (**Ln₂-1**) require high-boiling solvents and specific reaction conditions, detailed synthesis procedures are described. The structural changes during complex formation were analyzed with the use of NMR analysis. The absorption spectra of lanthanide complexes demonstrate shifts in maxima, reflecting coordination changes, with notable variations between mononuclear and homobinuclear complexes. Additionally, heteronuclear compounds with copper(II), zinc(II), and palladium(II) exhibit distinctive absorption patterns, emphasizing the role of d-metal ions. Luminescence studies reveal the sensitization of 4f-luminescence by both calix[4]arene and porphyrin fragments. The use of deuterated solvents enhances 4f-luminescence intensity, highlighting solvent effects. Furthermore, 4f-luminescence characteristics were investigated in both solid and solution states for heterometallic compounds, emphasizing differences between copper-containing and zinc/palladium-containing complexes. The results offer valuable insights into the design, synthesis, and spectral properties of these complexes, showcasing their potential applications in various fields, and the findings contribute to the understanding of lanthanide-porphyrin systems and their coordination behavior.

Key words: lanthanide, complexes, calix[4]arene, porphyrin, synthesis, luminescence.

INTRODUCTION. One of the most important incentives for research in the field of lanthanide chemistry is their ability to form luminescent compounds with various organic chromophore ligands. The luminescent properties of such compounds depend on the nature of the f-metal chromophore and ligand, the environment, and other factors. 4f-luminescence in the near infrared (IR) range is highly demanded in medicine (biomarker technology) for a number of important reasons: the complete absence of absorption and luminescence overlap of biological objects in certain wavelength regions of this range [1, 2]. The IR range is safe for humans compared to the UV / visible range; IR photons scatter much less than UV/visible light.

Infrared research is also being stimulated by the defense sector's demand for all military night vision equipment: binoculars, drones, armored vehicles, infrared goggles, etc. Lanthanide compounds are now widely used for security purposes, in fiber optic telecommunications networks.

Heteronuclear lanthanide-containing complexes have recently attracted increasing attention not only due to their optical, but also magnetic and catalytic properties. In most works devoted to such complexes, as a rule, acyclic ligands containing chromophore fragments were studied [3–5].

Functionalization of macrocyclic ligands by chelating fragments is one of the most promising directions in the design of heteronuclear lanthanide complexes. At the same time, such classes of compounds as calix[4]arenes and porphyrins, due to the presence of extended π -electron system, can be considered as convenient molecular platforms for creating heteronuclear complexes that luminesce in the

visible (calix[4]arenes) and near-IR region (porphyrins).

Calix[4]arenes are used as molecular scaffolds for constructing three-dimensional receptors in combination with porphyrin fragments via covalent bonds [6, 7]. Functionalization of phenolic hydroxyl groups in porphyrin-calix[4]arenes conjugates leads to a multiple increase in their receptor ability [8] as well as makes it possible to successfully apply a wide range of spectral methods to study intermolecular interactions.

Tetrapyrroles are one of the optimal compounds for obtaining objects emitting in the IR range (macrocycles themselves are characterized by intense absorption in the UV and visible regions of the spectrum). Low-energy donor triplet T-levels provide efficient intramolecular energy transfer to resonant levels of lanthanide ions emitting in the IR range, among which Nd(III), Er(III), Yb(III) have the most intensive signal [9]. The synthesis and study of complex compounds with tetrapyrroles having several donor centers are of interest in connection with the possibility of their use as primary molecular blocks for constructing more complex polynuclear systems with a given structure and predictable properties. The presence of metal centers of different nature in such complexes makes it possible to control the possibility of effective luminescence of both the ligand itself and the lanthanide ion. In this case, the choice of a strategy for the synthesis of such compounds is of particular importance.

The purpose of this work is to develop approaches to the synthesis of new lanthanide-containing homo- and heteronuclear complexes based on *5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis[(N-meso-(p-aminophenyl)-meso-triphenylporphyrincarbonyl)methoxy]-*

calix[4]arene (**1**) and establishing the influence of the structure of the obtained complexes on their spectral characteristics.

EXPERIMENT AND RESULTS DISCUSSION. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(*N-meso*-(*p*-aminophenyl)-*meso*-triphenylporphyrincarbonyl)methoxy]calix[4]arene (**1**) was carried out with the use carboxymethoxycalix[4]arene(**2**) and *p*-monoamino-*meso*-tetraphenylporphyrin (**3**) as starting reagents according to [10]. The difference of the proposed technique is the use of low temperature (-10–(-15)°C) to exclude the formation of by-products, which lead to the increase of the yield of the ligand up to 75–80%.

5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(*N-meso*-(*p*-aminophenyl)-*meso*-triphenylporphyrincarbonyl)methoxy]calix[4]arene, ESI-MS: 1988 (11%) [M+2], 670 (82%), 628 (100%). NMR ¹H: (300 MHz, CDCl₃): 2.81 (s, 4H, NH_{pyr.}), 1.18 (s, 18H, (CH₃)₃C), 1.31 (s, 18 H, (CH₃)₃C), 3.69 (d, 4H, ArCH₂Ar), 4.48 (d, 4H, ArCH₂Ar), 4.94 (s, 4H, OCH₂CO), 7.15 (s, 4H, ArH), 7.22 (s, 4H, ArH), 7.65–7.76 (m, 20 H, CH_{porf.}), 8.12–8.18 (m, 10H, CH_{porf.}), 8.27 (d, 8H, CH_{porf.}), 8.78 (s, 8H, ArH_{porf.}), 8.83 (s, 2H, 2OH), 8.88 (d, 4H, CH_{porf.}), 9.17 (d, 4H, CH_{porf.}), 11.11 (s, 2H, NHCO).

The main idea behind the design of calix[4]arene-porphyrin systems is that a spatially pre-organized calix[4]arene macrocycle accepts a lanthanide cation consequently changing the structure and the analytical signal of porphyrin substituents. The interaction of the orbitals of the porphyrin rings (intramolecular dimerization) and the intramolecular hydrogen bonds between the amide groups keep these substituents close to each other, whereas, during complex formation along the lower rim of

the calixarene, the distance between the porphyrin fragments increases. These changes are observed in the fluorescence spectra.

Depending on the synthesis strategy with calix[4]arene-diporphyrin (**1**), two types of complexes were obtained. The first type, a mononuclear complex **Ln-1** was synthesized using lanthanide hexachlorides (LnCl₃×6H₂O), with the participation of donor groups of the lower rim of calixarene (Fig. 1a, Ln = Yb(III), Lu(III)). The second type, a homobinuclear complex **Ln₂-1** was synthesized by the interaction of lanthanide porphyrinates **Ln-3** with dicarboxymethoxy-calix[4]arene (**2**) – (Fig. 1b). In contrast to the previously described methods [11], the complexation reaction with porphyrin-calix[4]arenes was carried out in the presence of equimolar amounts of triethylamine. Higher temperature conditions and an increase in reaction time are probably caused by the steric effects of bulky substituents, as well as changes in the system of hydrogen bonds between them. The yield of complexes is 60–65%.

Lanthanide chloride (0.15 mmol) LnCl₃×6H₂O was dissolved under heating in 15 ml of acetonitrile and boiled in the presence of triethyl orthoformate (TEOF, 0.5 ml) for 30 min. Then an equimolar amount of ligand **1** (0.15 mmol) was added. The reaction mixture was stirred until the ligand was completely dissolved, and then triethylamine (0.1 ml) was added and boiled for 4.5–5 hours. After the end of the synthesis, the solvent was removed. The obtained solid product was dissolved in chloroform (15–20 ml) and washed with water (3×20 ml). The organic fraction was evaporated, the complex was dried at 110–120°C for 3.5–4 hours. The yield of complexes is 70–72%.

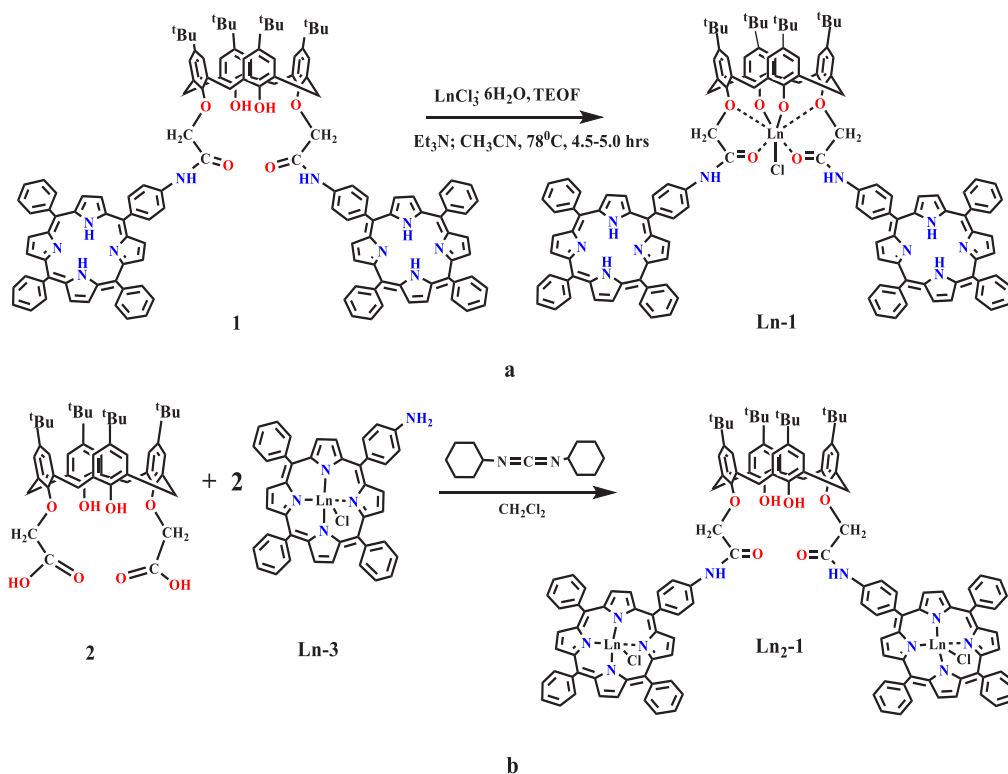


Fig. 1 – Scheme of synthesis of mono- (a) and binuclear (b) complexes based on calix[4]arene-diporphyrin.

Yb-1, $[\text{Yb}(\mathbf{1})(\text{CH}_3\text{CN})\text{Cl}]$, Elemental analysis for $\text{C}_{138}\text{H}_{119}\text{N}_{11}\text{ClO}_6\text{Yb}$: Calculated %: C, 74.1, H, 5.4, Ln, 7.7; Cl, 1.6; Found, %: C, 74.2, H, 5.7, Ln, 7.9; Cl, 1.4. MS (MALDI), m/z : 2235 $[(\text{M}+\text{H})^+]$.

Lu-1, $[\text{Lu}(\mathbf{1})(\text{CH}_3\text{CN})\text{Cl}]$, Elemental analysis for $\text{C}_{138}\text{H}_{119}\text{N}_{11}\text{ClO}_6\text{Lu}$: Calculated %: C, 74.1, H, 5.4, Ln, 7.8; Cl, 1.6; Found, %: C, 73.9, H, 5.3, Ln, 8.0; Cl, 1.5. MS (MALDI), m/z : 2237 $[(\text{M}+\text{H})^+]$.

Synthesis of **Ln₂-1** homobinuclear complexes was carried out from the corresponding **Ln-3** lanthanide porphyrinates [9]. A sample (0.17 mmol) of **2** was dissolved in 10 ml of methylene chloride, cooled to 0 – $(-3)^\circ\text{C}$, and dicyclohexylcarbodiimide (6.82 mmol) was added. The resulting mixture was stirred

while cooling for 10–15 minutes, then the required amount of lanthanide porphyrinate **Ln-3** (0.34 mmol) was added, and stirring was continued for more than three hours. The reaction progress was monitored by thin-layer chromatography in chloroform-hexane-acetonitrile (10:10:1). To remove cyclohexylurea, the reaction mixture was kept at a temperature of -10 – $(-15)^\circ\text{C}$ for 10–12 hours, the resulting precipitate was filtered off. The mother liquor was evaporated and the dry residue was dissolved in a minimal amount of a mixture of chloroform-hexane-acetonitrile (10:10:1). The resulting solution was passed through a column packed with silica gel using the above mentioned mixture as eluent. Yield 50–56%.

Yb₂-1, [Yb₂(**1**)(CH₃CN)₂Cl₂], Elemental analysis for C₁₄₀H₁₂₀N₁₂Cl₂O₆Yb₂: Calculated, %: C, 67.7, H, 4.9, Ln, 13.9; Cl, 2.9; Found, %: C, 67.6, H, 5.1, Ln, 14.1; Cl, 2.7. MS (MALDI), m/z: 2483 [(M+H)⁺].

Lu₂-1, [Lu₂(**1**)(CH₃CN)₂Cl₂], Elemental analysis for C₁₄₀H₁₂₀N₁₂Cl₂O₆Lu₂: Calculated, %: C, 67.6, H, 4.9, Ln, 14.1; Cl, 2.9; Found, %: C, 67.5, H, 4.7, Ln, 14.3; Cl, 3.1. MS (MALDI), m/z: 2485 [(M+H)⁺].

Elemental analysis data of the homonuclear compounds were confirmed by ¹H NMR spectra of complexes with diamagnetic lutetium ion and make it possible to identify some structural changes that occur during complex formation. The disappearance of the signals of the protons of the phenolic groups of **Lu-1** is a consequence of their replacement by a lanthanide ion, and the shift of the signals of the protons of the O-CH₂-CO groups of the complex to the low field ($\Delta\delta = 0.37$ ppm) indicates the participation of oxygen atoms of ether groups in the formation metal ion coordination site. The signals from protons of methylene bridges at 3.40 and 3.75 ppm for **Lu-1**, (3.69 and 4.48 ppm for **1**) with the values of the difference between them ($\Delta\delta = 0.35$ and 0.79 ppm, respectively), indicates a decrease in the distortion of the calix[4]arene macrocycle in the complex compared to the ligand. As for the complex **Lu₂-1**, in which the lanthanide ion is coordinated by the pyrrole nitrogen atoms, in the NMR spectrum there are no significant changes in the bands of the calix[4]arene component compared to the ligand. At the same time, the signals of the NH protons of the pyrrole fragments disappear, which indicates their substitution during complex formation, and the signals of the protons located in the β -positions of the porphyrins shift to the low field, which is a consequence of a redistribution of the electron density in the porphyrinate fragments.

Heteronuclear compounds were synthesized with the use of mononuclear complexes of copper (II), zinc (II) and palladium (II) with vacant donor groups. The choice of d-metals was determined both by the specifics of their complexation with the porphyrin macrocycle and by the spectral features of the metal ions. Selective introduction of the lanthanide ion into the lower rim of the calix[4]arene or into the cavity of the porphyrinate substituent was realized due to significant differences in the conditions of complex formation. The formation of complexes of Ln(III) with calix[4]arenes takes place under relatively mild conditions, and the preparation of lanthanide-porphyrins requires the use of high-boiling solvents [9, 12, 13].

The synthesis was carried out according to the scheme presented in Fig. 2. The reaction mixture was boiled for 5–6 hours and left overnight at room temperature. The complex was precipitated with ethanol (50 ml), the precipitate was filtered, washed with ethanol (3×50 ml). They were dried at room temperature for a day in a vacuum desiccator. The yields of target products were 48–54%.

Yb-Cu₂-1, [YbCu₂(**1**)(CH₃CN)Cl]. Elemental analysis for C₁₃₈H₁₁₅N₁₁ClO₆YbCu₂: Calculated, %: C, 70.3; H, 4.9; Yb, 7.3; Cu, 5.4; Cl, 1.5; Found, %: C, 70.5; H, 5.1; Yb, 7.4; Cu, 5.5; Cl, 1.3. MS (MALDI), m/z: 2357 [(M+H)⁺].

Lu-Cu₂-1, [LuCu₂(**1**)(CH₃CN)Cl]. Elemental analysis for C₁₃₈H₁₁₅N₁₁ClO₆LuCu₂: Calculated, %: C, 70.2; H, 4.9; Lu, 7.4; Cu, 5.4; Cl, 1.5; Found, %: C, 70.0; H, 5.1; Lu, 7.6; Cu, 5.2; Cl, 1.6. MS (MALDI), m/z: 2358 [(M+H)⁺].

Yb-Zn₂-1, [YbZn₂(**1**)(CH₃CN)Cl]. Elemental analysis for C₁₃₆H₁₁₂N₁₀ClO₆YbZn₂: Calculated, %: C, 70.2; H, 4.9; Yb, 7.3; Zn, 5.5; Cl, 1.5; Found, %: C, 70.3; H, 5.1; Yb, 7.5; Zn, 5.6; Cl, 1.7. MS (MALDI), m/z: 2359 [(M+H)⁺].

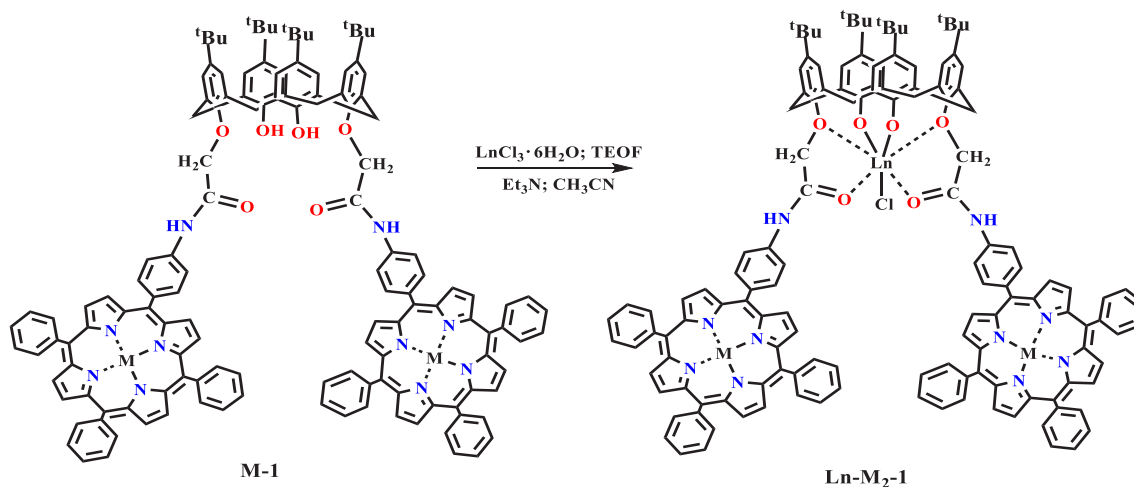


Fig. 2 – Scheme of synthesis of heteronuclear complexes.
 M = Cu(II), Zn(II), Pd(II); Ln = Yb(III), Lu(III)

Lu-Zn₂-1, [LuZn₂(1)(CH₃CN)Cl]. Elemental analysis for C₁₃₆H₁₁₂N₁₀ClO₆LuZn₂: calculated, %: C, 70.1; H, 4.9; Lu, 7.4; Zn, 5.5; Cl, 1.5; Found, %: C, 70.3; H, 5.0; Lu, 7.5; Zn, 5.7; Cl, 1.7. MS (MALDI), m/z: 2360 [(M+H)⁺]. NMR ¹H (CDCl₃), ppm: 1.18 (s, 18H, (CH₃)₃C), 1.32 (s, 18H, (CH₃)₃C), 3.49 (d, 4H, ArCH₂Ar), 4.20 (d, 4H, ArCH₂Ar), 4.92 (s, 4H, OCH₂CO), 7.15 (s, 4H, ArH), 7.23 (s, 4H, ArH), 7.51–7.70 (m, 20H, CH_{porph.}), 8.12–8.18 (m, 10H, CH_{porph.}), 8.27 (d, 8H, CH_{porph.}), 8.70 (s, 8H, CH_{porph.}), 8.85–8.88 (m, 4H, CH_{porph.}), 8.93 (d, 2H, NHCO), 9.27 (d, 4H, CH_{porph.}).

Yb-Pd₂-1, [LuPd₂(1)(CH₃CN)Cl]. Elemental analysis for C₁₃₈H₁₁₅N₁₁ClO₆YbPd₂: Calculated, %: C, 67.8; H, 4.7; Yb, 7.1; Pd, 8.7; Cl, 1.5; Found, %: C, 67.7; H, 4.7; Yb, 7.1; Pd, 8.9; Cl, 1.6. MS (MALDI), m/z: 2443 [(M+H)⁺].

Lu-Pd₂-1, [LuPd₂(1)(CH₃CN)Cl]. Elemental analysis for C₁₃₈H₁₁₅N₁₁ClO₆LuPd₂: Calculated, %: C, 67.8; H, 4.7; Lu, 7.1; Pd, 8.7; Cl, 1.5; Found, %: C, 67.7; H, 4.9; Lu, 7.3; Pd, 8.9; Cl, 1.6. MS (MALDI), m/z: 2444 [(M+H)⁺].

The formation of lanthanide complexes

with **1** leads to changes in the shape, intensity, and position of the absorption spectra maxima (Table 1). When the Lu(III) ion is coordinated at the lower rim of the calix[4]arene component of **1**, the absorption spectra of the **Lu-1** complex change significantly, both in comparison with the ligand and the lutetium-containing complex of the initial calixarene **Lu-2**. In the UV region for the **Lu-1** complex, a broadened but not split band with a maximum at 280 nm and a second band at 312 nm are detected, which confirms the coordination of the lanthanide ion by phenolic groups. In this case, a bathochromic shift (5 nm) of the first band and a hypsochromic (8 nm) shift of the second band relative to the spectrum of the dicarboxy-calix[4]arene complex are observed.

Porphyrin-originated bands maxima and intensity in the spectrum of **Lu-1** (410–650 nm region) practically do not change compared to the ligand, which indicates a slight change in the position of the porphyrin substituents relative to each other in the complex compared to the free ligand. It should be noted that the

absorption spectra of complexes with ytterbium and lutetium ions coincide, which indicates their identical structure.

In the absorption spectrum of the **Lu₂-1** complex some characteristic changes during the formation of metal porphyrinates were observed such as a bathochromic shift of the Soret band ($\Delta\lambda = 7$ nm) compared to **1** as well as the presence of only two bands in the visible region instead of four in **1**. The absorption of the calix[4]arene component, in comparison with the ligand, does not undergo changes in complexes of this type.

4f-Luminescence excitation spectra of Yb(III) complexes appear to be similar to the absorption spectra of the corresponding compounds. The observed similarity indicates an intramolecular excitation energy transfer from the organic part of the complex molecule to the resonance levels of Yb(III) ions. However, in these objects it was interesting to trace changes not only in the 4f-luminescent characteristics of ytterbium-containing compounds, but also in the fluorescence and phosphorescence spectra of complexes with diamagnetic lutetium ions.

Table 1.

Spectral-luminescent characteristics of homo- and heteronuclear complexes of Lu(III) (C=1·10⁻⁵M, DMF).

Compound	λ_{\max} , nm / (lge)	λ_{fl} , nm	E_s , cm ⁻¹	λ_{phos} , nm	E_p , cm ⁻¹
1	274 (3.8), 410/417 (4.2/4.8), 515 (3.6), 550 (3.3), 590 (3.1), 644 (2.9)	650, 718	15 390	845	11830
Lu-1	280(3.4), 312 (2.5), 418 (5.1), 516 (4.2), 552 (3.8), 591 (3.5) 648 (3.4)	652 710	15 500	845	11 800
Lu₂-1	278 (3.8), 425 (4.9), 557 (3.5), 595 (3.1)	648 715	15 400	852	11 700
Lu-Cu₂-1	279 (3.6), 312 (2.6), 416 (5.28), 541(4.23), 576 (3.53)	610	16 390	820	12 200
Lu-Zn₂-1	280 (3.3), 314 (2.5), 423 (5.24), 560 (4.26), 602 (3.90)	602 656	16 600	780	12 800
Lu-Pd₂-1	280 (3.3), 312 (2.6), 415 (5.53), 517 (4.75), 563 (sh)	562, 605	17 800	685	14 600
Lu-2	273 (3.6), 276 (3.5), 320 (2.6)	406	24 600	420	23 800
Lu-3	425 (4.8), 557 (3.3), 597 (3.0)	624 682	16 000	858	11 700

It should be noted that the ligand-centered luminescence from the calix[4]arene component is not observed in the spectrum of **Lu-1** complex. At the same time, fluorescence bands with maxima at 652 and 710 nm and low-temperature phosphorescence bands with a maxi-

mum at 845 nm, characteristic for the porphyrin macrocycle, were recorded. This fact is probably associated with the additional energy transfer from the triplet levels of the calix[4]arene component to the corresponding levels of porphyrinate substituents.

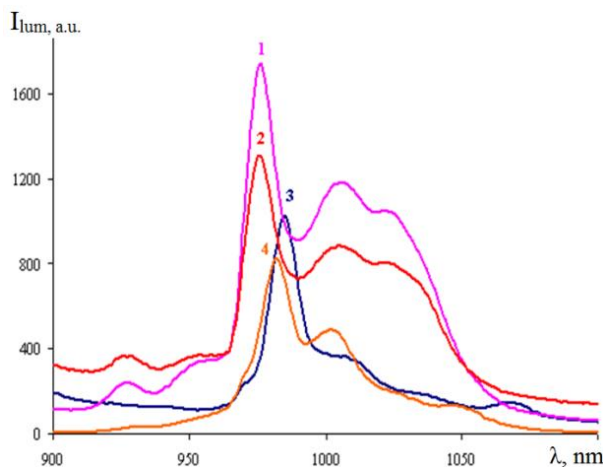


Fig. 3 – 4f-Luminescence spectra of **Yb₂-1** (1), **Yb-3** (2), **Yb-1**(3) and **Yb-2** (4) ($C_{Yb} = 1 \times 10^{-5} M$, DMF, 278K).

The 4f-luminescence of the mononuclear complex **Yb-1** is 1.3 times more intense than that of a similar complex with calixarene. The maximum of the 4f-emission varies from 976 to 985 nm. When the complex is excited in Soret band (417–425 nm), a 4f-luminescent signal is detected, the intensity of which is very low.

Insignificant changes in the energies of singlet and triplet levels compared to **1** are revealed in the fluorescence and phosphorescence spectra of the binuclear complex **Lu₂-1** (Table 1). However, it should be noted that the energies of the the excited singlet and triplet levels differ from the original “block” **Lu-3**. The values of the energy of the triplet levels of calix[4]arene ($\sim 23800 \text{ cm}^{-1}$) and porphyrin ($\sim 11700 \text{ cm}^{-1}$) are higher than the emitting level of ytterbium Yb(III) (${}^2F_{5/2}$, 10300 cm^{-1}), which makes intramolecular energy transfer possible from the macrocyclic components of the complex to the lanthanide ion. In the IR region, due to the 4f-luminescence of Yb(III) ions, the energy transfer occurs in both mono-

nuclear and binuclear complexes (Table 2). When excited in Soret band, they lead to luminescence of **Yb₂-1** almost twice as high as that of the original “block” **Yb-3** under similar conditions. Moreover, 4f-luminescence of the binuclear complex **Yb₂-1** is observed upon 320 nm excitation, which is the band of the calix[4]arene “block”, and its intensity is almost the same as the signal excited in Soret band. Thus, it can be assumed that in this complex 4f-luminescence is sensitized not only by porphyrin, but also by calix[4]arene fragments.

Table 2.

4f-Luminescent parameters of the homonuclear Yb(III) complexes ($C=1 \cdot 10^{-5} M$, DMF).

Complex	λ_{\max} , nm	ϕ
Yb-1	985, 1008, 1036	0.0032
Yb₂-1	978, 1007, 1026	0.0047
Yb-2	982, 1003, 1027	0.0028
Yb-3	976, 1005, 1024	0.0042

In order to minimize the influence of OH- and CH-vibrations of solvent molecules, a series of solutions with different contents of deuterated solvent were studied. It was shown that with increasing of the concentration of DMSO- d_6 and DMF- d_6 , the luminescence intensity continuously grows up: more smoothly for the **Yb-1** complex (Fig. 4, a), while for **Yb₂-1** a sharp increase in intensity is observed at DMSO- d_6 concentrations above 60 vol.%. (Fig. 4, b). The use of deuterated solvents leads to an increase in the intensity of ytterbium 4f-luminescence by 5.5 and 2.3 times in DMSO- d_6 or by 3.6 and 2.0 times in DMF- d_6 for **Yb₂-1** and **Yb-1**, respectively.

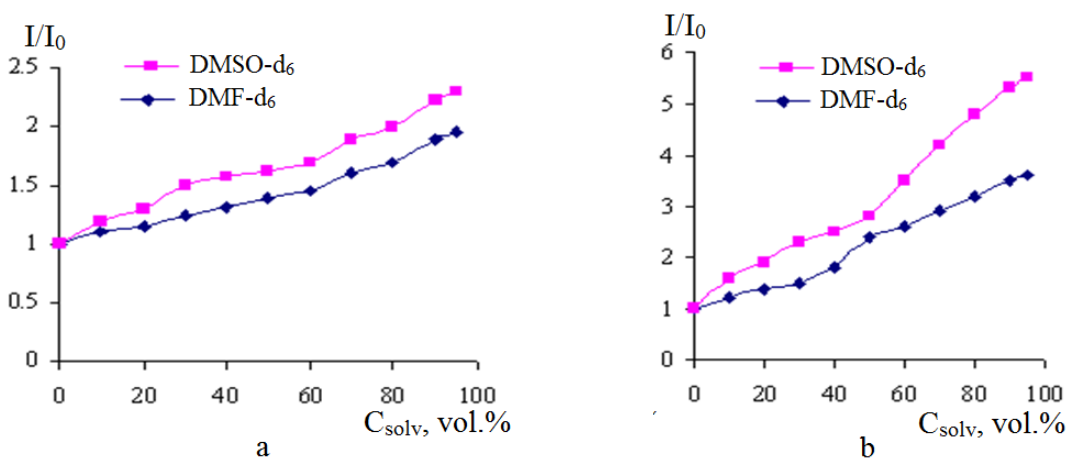


Fig. 4 – Plot of the intensity of 4f-luminescence of the complexes Yb-1 (a) and Yb₂-1 (b) vs the content of deuterated solvents.

The formation of heteronuclear complexes with lanthanides and d-elements coordinated in porphyrin fragments was monitored by changes in the characteristic bands in the absorption spectrum. The parameters of the absorption spectrum (Table 1) of heteronuclear complexes strongly depends on the nature of the d-metal ion, which is caused by the formation of molecular orbitals from the coplanar ligand chromophore and a metal ion.

The absorption spectra of f-d-heteronuclear complexes and the spectra of corresponding d-porphyrinates are very similar. The intensity of the Soret band increases, when d-metal ions are coordinated (Table 1). This fact indicates that the singlet levels in the molecule are highly populated and, as a consequence, more efficient molecular fluorescence and phosphorescence, as well as sensitized luminescence of lanthanide ions, are possible.

In the molecular fluorescence spectra of f-d complexes, bands were found in the region of 550–610 nm and 600–660 nm, corresponding to the 0–0 and 0–1 transitions. Due to the low

fluorescence intensity for copper (II) porphyrinates, only the first transition was detected. The energy values of the triplet levels, as follows from the phosphorescence spectra, decrease from Lu-Cu₂-1 to Lu-Pd₂-1.

4f-Luminescent properties have been studied for heterometallic compounds both in solid state and in solutions. For Yb(III)-Cu(II) complexes, it was not possible to detect 4f-luminescence in solution. Its absence is explained by the fact that the intersystem crossing conversion $T_1 \rightarrow S_0$ in copper (II) porphyrinate has a very high probability (about 10^{12} s^{-1}), and the probability of transitions $T_1 \rightarrow {}^2F_{5/2}$ for Yb(III) is in the range of 10^8 – 10^{10} s^{-1} [14]. Thus, the process of luminescence sensitization becomes non-competitive: its probability is 2–4 orders of magnitude lower than the probability of the intercombination transition $T_1 \rightarrow S_0$.

In contrast to the copper-containing complex, in heteronuclear compounds of zinc and palladium it was possible to detect 4f-luminescence of Yb(III) in 975–985 nm region. In heteronuclear complexes with zinc, an increase

in 4f-luminescence of ytterbium is observed compared to mononuclear by 1.8 times, both in the solid sample and in solution ($\varphi_{4f} = 0.0058$), for palladium complexes the increase is slightly less by 1.4 times ($\varphi_{4f} = 0.0045$), which can be explained by the competition of two processes $T_1 \rightarrow S_0$ ($\approx 10^4 \text{ s}^{-1}$) and $T_1 \rightarrow {}^2F_{7/2}$ ($\approx 10^8 - 10^{10} \text{ s}^{-1}$).

CONCLUSIONS. Calix[4]arenes covalently modified with porphyrin fragments are convenient polytopic molecular platforms for the preparation and study of homo- and heteronuclear f-d-complexes. In mononuclear complexes **Ln-1**, the lanthanide ion coordinates four oxygen atoms of the lower rim of calixarene and two oxygen atoms of the carbonyl groups of the substituents to form two five-membered metallocycles. In binuclear complexes **Ln₂-1** lanthanide ions are coordinated along the macro ring of porphyrin fragments and are located on the periphery of the molecule. The coordination polyhedron of lanthanide ion in heteronuclear f-d complexes **Ln-M₂-1** is formed by oxygen atoms: two from the phenolic groups of the lower rim of calix[4]arene and four from carboxymethoxy groups. The d-metal ions (Zn(II), Cu(II), Pd(II)) are coordinated along the periphery of the complex molecule in the porphyrinate rings. It has been shown that the coordination of the lanthanide ion along the lower rim of calix[4]arene has virtually no effect on porphyrin fluorescence, but sensitization of 4f luminescence occurs both with the participation of the calix[4]arene matrix and porphyrin fragments. It has been established that in heteronuclear complexes based on calix[4]arene-diporphyrin, the determining factor in the efficiency of 4f-luminescence sensitization is the nature of the d-metal. The maximum 4f-luminescence characteristics were found for Ln(III)–Zn(II) complexes.



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ГОМО- ТА ГЕТЕРОЯДЕРНІ КОМПЛЕКСИ УЬ(III) ТА Lu(III) З КАЛІКС[4]АРЕНОМ, МОДИФІКОВАНИМ ПОРФІРИНОВИМИ ЗАМІСНИКАМИ

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У цій роботі описано підходи до синтезу лантанідвмісних гомо- та гетероядерних комплексів із використанням 5,11,17,23-тетра-*трет*-бутил-25,27-дигідрокси-26,28-біс[(*N*-*мезо*-(*n*-амінофеніл)-*мезо*-трифенілпорфіринкарбоніл)метокси]-калікс[4]арену (1). Такий просторово задалегідь

організований калікс[4]ареновий макроцикл полегшує координацію катіонів лантанідів, впливаючи на структуру та аналітичний сигнал порфіринових замісників. У дослідженні використано дві стратегії синтезу, що призводять до одноядерних і гомобіядерних комплексів під впливом стеричних ефектів і змін у водневих зв'язках. У комплексах виявлено зміни в спектрах флуоресценції внаслідок внутрішньомолекулярної димеризації та водневих зв'язків під час утворення комплексу. Моноядерні комплекси (**Ln-1**) синтезовано в м'яких умовах, тоді як гомоядерні комплекси (**Ln₂-1**) вимагають висококиплячих розчинників і специфічних умов реакції. Процедури синтезу детально описано. Структурні зміни під час комплексоутворення аналізували за допомогою ЯМР-спектрів. Спектри поглинання комплексів лантанідів демонструють зміщення максимумів, що відображають зміни координації з помітними варіаціями між моноядерними та гомобіядерними комплексами. Крім цього, гетероядерні сполуки з міддю (II), цинком (II) і паладієм (II) демонструють характерні моделі поглинання, що підкреслює роль іонів d-металів. Дослідження люмінесценції виявляють сенсibiлізацію 4f-люмінесценції як калікс[4]ареновими, так і порфіриновими фрагментами. Використання дейтерованих розчинників посилює інтенсивність 4f-люмінесценції, що вказує на вплив розчинника. Крім цього, досліджено характеристики 4f-люмінесценції як у твердому стані, так і в розчині для гетерометалевих сполук, та виявлено відмінності між комплексами, що містять мідь, і комплексами, що містять цинк/паладій. Результати дають достатньо повне уявлення про дизайн, синтез і спект-

ральні властивості цих комплексів, демонструючи їхнє потенційне застосування в різних галузях, а результати сприяють розумінню лантанід-порфіринових систем та їхніх координаційних властивостей.

Ключові слова: лантаніди, комплекси, калікс[4]арен, порфірин, синтез, люмінесценція.

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