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Lower rim-modified calix[4]arenes with fragments of EDTA (DTPA) and their Ln(III) complexes (Ln = Yb, Lu): synthesis and NIR-luminescent properties

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Derivatives of *p-tert*-butylcalix[4]arene substituted on the lower rim with fragments of aminopolycarboxylic acids (EDTA, DTPA) were obtained. Mono and binuclear complexes with lanthanide (III) ions were synthesized using these compounds. The effect of the number and type of aminopolycarboxylic acid fragments on the luminescence of ligands and complexes was studied. The influence of the distance between the emitting ion and the calixarene macrocycle on the intensity of 4f-luminescence was analyzed.

K e y w o r d s: calix[4]arenes, EDTA, DTPA, lanthanides, luminescence.

INTRODUCTION. Coordination compounds of lanthanides with calix[n]arenes are of great interest as the building blocks for supramolecular ensembles, such as calix-porphyrin ionic associates, calix-crown ethers, complex compounds with neutral molecules, systems for the selective recognition of components of biologically active substances (amino acids, ribonucleic acids) [1]. The possibility of the functionalization of lower and upper rims with various substituents determines the prospects for the use of lanthanide-calix[n]arenes in many fields of material science (luminescent coatings, materials for lasers, fiber-optic transmission lines), medicine (contrast agents), analytical and bioanalytical chemistry (various luminescent sensors and markers), in the formation of enzyme-like systems and membranes [2].

The introduction of nitrogen-containing groups at the lower rim of calixarene through the modification of amido and amino groups allows one to obtain a series of nitrogen-containing receptors with different binding ability to metal cations [3]. Among widely used chelating agents aminopolycarboxylic (APC) acids are the convenient compounds in terms of high stability of their metal complexes. Therefore, the study of the properties of such compounds is relevant and promising.

EXPERIMENT AND DISCUSSION OF THE RESULTS. All reagents and solvents in spectroscopic studies purchased from commercial suppliers had the analytical grade and used without further purification. The compounds L^1H_3, L^2H_2 and L^7H_5 were synthesized according to methods described earlier [4, 5]. Synthesis of mononuclear complexes L^1H_3 and L^2H_2 with lanthanide ions was described previously (Fig. 1) [6]. Mononuclear (for L^3H_6, L^4H_7 and L^7H_5) and homobinuclear (for L^5H_8 and L^6H_{10}) complexes with ytterbium (III) and lutetium (III) were obtained with the use of calix[4]arenes containing aminopolycarboxylic acid fragments, which chelate the lanthanide ion.

All ligands and complexes were obtained in solid state and characterized by means of elemental analysis, mass spectrometry (MALDI), thin-layer chromatography (TLC), and NMR spectroscopy. The lanthanide content in the complexes was determined with the use of the complexometric method with an arsenazo I indicator. Mass spectra of the compounds by the MALDI method were recorded on a Varian Autoflex II spectrometer. 1 H NMR spectra were obtained on a Bruker Avance-300 spectrometer (300 MHz) in DMSO-d6 solutions with an internal TMS standard at 25°C. IR spectra were recorded on a Shimadzu FT-IR 8400S spectrophotometer in KBr pellets.

Absorption spectra in the UV and visible regions were recorded using Specord M40 UV/VIS spectrophotometer. The luminescence excitation and emission spectra were recorded on a Fluorolog FL 3-22 spectrofluorimeter, Horiba JobinYvon (Xe lamp 450 W), equipped for measurements both at room temperature and at 77 K (PMT R928P for the visible region and InGaAs photo-resistance cooled for 77 K for the IR region).

Modification of *p-tert*-calix[4]arene. The general approach for the modification of a calix[4]arene molecule with EDTA or DTPA fragments was in the acylation of the appropriate dianhydride with aminoethoxy groups located at the lower rim of *p-tert*-butylcalix[4]arene. The reaction was held in DMF at 80°C in presence of triethylamine (Fig. 1). Compounds L^3H_6 and L^4H_7 were obtained from monoaminoethoxy calix[4]arene L^1H_3. The synthesis of the diaminoethoxy derivative (L^2H_2), with two amino and anhydride fragments in the macrocycle molecule at the opposite ends, suggests the possibility of the formation of several reaction products. Using one equivalent of DTPA dianhydride, according to [5], the compound L^7H_5 was obtained, in which the chelating fragment acts as a bridge connecting two opposite phenolic rings of the macrocycle. With the gradual addition of the nucleophilic agent (L^2H_2) dropwise to the solution of APC dianhydride taken in a 6-fold excess, it was possible to add two acid fragments to the calix[4]arene matrix (compounds L^5H_8 and L^6H_{10}).

L^3H_6: Yield: 83%. Mp>320°C. Calc. for $C_{56}H_{75}N_3O_{11}$, %: C 69.61, H 7.82; found, %: C 69.48, H 7.51. MS (MALDI): 965 (M^+). IR (KBr), ν, cm^{-1}: 3346 (NH, OH), 2961 (C-H), 2868 (C-H), 1758 (C=O), 1483 (C-C). NMR ^{1}H (DMSO-d_6), δ, ppm.: 1.11 s (9H, t-Bu), 1.14 s (18H, t-Bu), 1.16 s (9H, t-Bu), 2.72-2.90 m (4H, N-$(CH_2)_2$-N), 3.05 s (6H, N-CH_2-CO), 3.34 s (2H, N-CH_2-CO), 3.39 d (4H, Ar-CH_2-Ar), 4.06 d (2H, Ar-CH_2-Ar), 4.27 d (2H, Ar-CH_2-Ar), 6.88 d

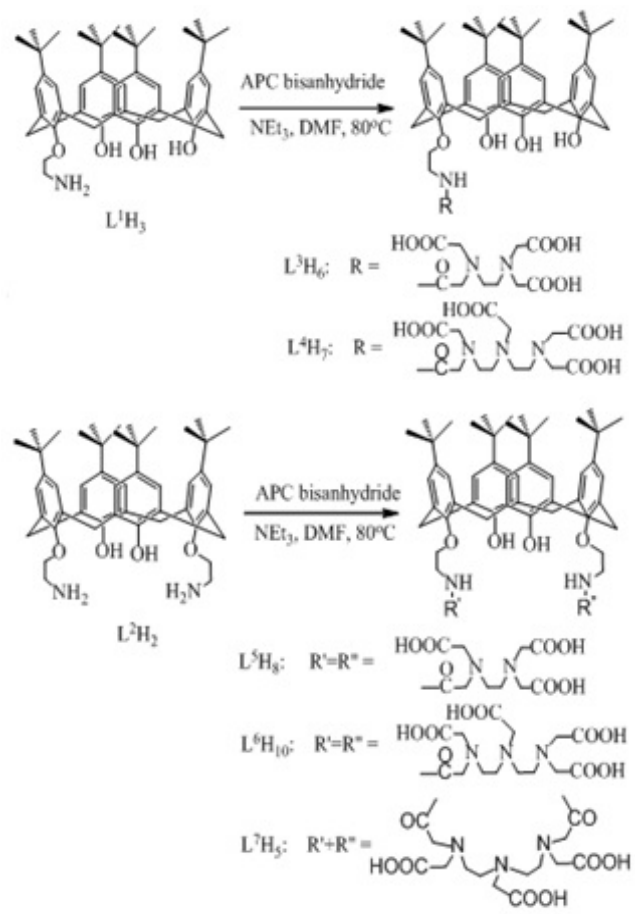

Fig. 1. Scheme of the lower rim modification of calix[4]arenes with APC fragments

(2H, Ar-H), 7.02 s (2H, Ar-H), 7.05 d (2H,Ar-H), 7.18 s (2H, Ar-H), 11.88 s (3H, COOH).

L^4H_7: Yield: 81%. Mp>320°C. Calc. for $C_{60}H_{82}N_4O_{13}$, %: C 67.52, H 7.74, found, %: C 67.22, H 7.95.MS (MALDI): 1066 (M^+). IR (KBr), ν, cm^{-1}: 3348 (NH+OH), 2964 (C-H), 2868 (C-H), 1760 (C=O), 1483 (C-C). NMR^{1}H (DMSO-d_6), δ, ppm: 1.12 s (9H, t-Bu), 1.14 s (18H, t-Bu), 1.16 s (9H, t-Bu), 2.72-2.90 m (8H, N-$(CH_2)_2$-N), 3.07 s (8H, N-CH_2-CO), 3.34 s (2H, N-CH_2-CO), 3.39 d (4H, Ar-CH_2-Ar), 4.06 d (2H, Ar-CH_2-Ar), 4.27 d (2H, Ar-CH_2-Ar), 6.87 d (2H, Ar-H), 7.00 s (2H, Ar-H), 7.04 d (2H, Ar-H), 7.14 s (2H, Ar-H), 11.88 s (4H, COOH).

L^5H_8: Yield: 74%. Mp>320°C. Calc. for $C_{56}H_{75}N_3O_{11}$, %: C 69.61, H 7.82; found, %: C 69.48, H 7.51. MS (MALDI): 1282 (M^+). IR (KBr), ν, cm^{-1}: 3364 (NH, OH), 2961 (C-H), 2866 (C-H), 1754 (C=O), 1476 (C-C). NMR^{1}H (DMSO-d_6), δ, ppm: 1.10 s (18H, t-Bu), 1.24 s (18H, t-Bu), 2.72-2.90 m (8H, N-$(CH_2)_2$-N), 3.06 s(12H, N-CH_2-CO), 3.35 s (4H, N-CH_2-CO), 3.43 d (4H, Ar-CH_2-Ar), 4.40 d (4H, Ar-CH_2-Ar), 6.92 s (4H, Ar-H), 7.05 s (4H, Ar-H), 11.68 s (6H, COOH).

L^6H_{10}: Yield: 75%. Mp>320°C. Calc. for $C_{56}H_{75}N_3O_{11}$, %: C 69.61, H 7.82; found, %: C 69.48, H 7.51. MS (MALDI): 1484 (M^+). IR (KBr), ν, cm^{-1}: 3367 (NH, OH), 2962 (C-H), 2867 (C-H), 1756 (C=O), 1476 (C-C).NMR^{1}H (DMSO-d_6), δ, ppm: 1.10 s (18H, t-Bu), 1.24 s (18H, t-Bu), 2.72-2.90 m (16H, N-$(CH_2)_2$-N), 3.07 s (16H, N-CH_2-CO), 3.35 s (4H, N-CH_2-CO), 3.40 d (4H, Ar-CH_2-Ar), 4.41 d (4H, Ar-CH_2-Ar), 6.93 s (4H, Ar-H), 7.05 s (4H, Ar-H), 11.68 s (8H, COOH).

L^7H_5: Yield: 72%. Mp>320°C. Calc. for $C_{62}H_{85}N_5O_{12}$, %: C 68.17, H 7.84, found, %: C 68.54, H 7.32.MS (MALDI): 1091 (M^+). IR (KBr), ν, cm^{-1}: 3365 (NH, OH), 2961 (C-H), 2866 (C-H), 1755 (C=O), 1476 (C-C).NMR^{1}H (DMSO-d_6), δ, ppm: 0.99 s (18H, t-Bu), 1.03 s (18H, t-Bu), 2.33 t (4H, N-$(CH_2)_2$-N), 2.79 t (4H, N-$(CH_2)_2$-N), 3.05 s (6H, N-CH_2-CO), 3.32 s (4H, N-CH_2-CO), 3.43 d (4H, Ar-CH_2-Ar), 4.40 d (4H, Ar-CH_2-Ar), 6.92 s (4H, Ar-H), 7.04 s (4H, Ar-H), 11.88 s (3H, COOH).

To identify the obtained compounds by mass spectrometry, the MALDI method was used, since the FAB method did not give unambiguous results. This is probably due to the high affinity of APC fragments to the polar matrix (*m*-nitrobenzyl alcohol), which leads to increased fragmentation of molecules. Peaks of molecular ions were recorded in MALDI mass spectra recorded under conditions of determination of negative ions. In addition to them, peaks were observed in the spectrum, indicating fragmentation, in which the hydroxy groups of APC fragments were sequentially separated.

In PMR spectra of modified calix[4]arenes, insignificant changes in the position of the signals of protons of *tert*-butyl groups, protons of methylene bridges of the calixarene macrocycle and phenolic rings are observed in comparison with the spectra of aminoethoxy derivatives, which indicates the cone conformation of the macrocycle molecules [6]. In the 2.4–3.5 ppm region, a series of signals appear relative to the protons of methylene groups of aminopolycarboxylate. Signals of protons of carboxy groups appear at δ = 11.9 ppm. Instead of two proton signals of amino and hydroxy groups, which are observed in the spectrum of the initial amino derivatives, a wide singlet appears at δ = 7.9 ppm, which is associated with the participation of amide protons in the formation of a hydrogen bond with phenolic protons.

The assignment of bands in the IR spectra of free ligands was carried out in accordance with published data for substituted calix [4] arenes.The IR spectra of the obtained compounds contain vibrational absorption bands from groups of both the macrocyclic platform and the APC fragment. In the 3200–3600 cm^{-1} region a broad band with maxima at 3346–3373 cm^{-1} is observed, which is likely due to the overlap of vibration bands of OH bonds of the lower rim of the calix[4]arene and unassociated NH bonds of the amide group. In the region of 2850–3000 cm^{-1}, a group of bands is observed, which was assigned to a superposition of stretching and deformation vibrations of CH-bonds from both calix[4]arene and acid fragments. The IR spectra of the L^3H_6-L^7H_5 compounds are characterized by the presence of an intense band in the region of 1754–1760 cm^{-1}, which remains almost at the sameposition when the number and type of acid fragments change. This band was assigned to the stretching vibrations of carboxyl groups. As for the bands in the region of 1470–1490 cm^{-1}, they can be attributed to the deformation vibrations of the CH_2-groups superimposed on the frequency of asymmetric vibrations of the carboxyl group. In addition, in the range of 1440–1460 cm^{-1}, there is a band of skeletal vibrations of the aromatic component of the macrocycle, which also complicates the interpretation of IR spectra.

Synthesis of Yb(III) and Lu(III) complexes. The synthesis of lanthanide-containing complexes based on modified calix[4]arenes was carried out by the interaction of the ligand with lanthanide chlorides hexahydrates at the rate of 0.9 mol of $LnCl_3$ for each APC fragment. Significantly greater stability constants of rare earth aminopolycarboxylates (logK = 15 – 19) compared with complexes in which the ion is coordinated by phenolic oxygen atoms (logK = 3 – 8) suggests that the calixarene

T a b l e 1

Data of elemental analysis and mass spectrometric measurements of lanthanides complexes with calix[4]arenes

Complex	m/z (MALDI), (%)	(calculated / found), %		
		C	H	Ln
$YbL^3(DMF)_2$	1135[M^+]	58.1/58.3	6.8/6.5	13.5/13.7
$YbL^4(DMF)$	1236[M^+]	57.7/57.8	6.6/6.3	13.2/12.9
$Yb_2L^5(DMF)_4$	1622[M^+]	50.2/50.4	6.1/6.2	18.1/18.4
$Yb_2L^6(DMF)_2$	1824[M^+]	49.9/49.5	5.9/5.6	17.6/17.4
$YbL^7(DMF)$	1261[M^+]	58.5/58.2	6.7/6.5	13.0/13.2
$LuL^3(DMF)_2$	1137[M^+]	60.0/60.2	6.8/6.6	13.6/13.3
$LuL^4(DMF)$	1238[M^+]	58.2/58.6	6.4/6.1	14.1/14.4
$Lu_2L^5(DMF)_4$	1626[M^+]	50.1/50.4	6.1/6.3	18.2/18.0
$Lu_2L^6(DMF)_2$	1828[M^+]	49.9/49.7	5.9/5.7	17.7/17.4
$LuL^7(DMF)$	1263[M^+]	58.4/58.2	6.7/6.5	13.1/13.2

fragment is not involved in coordination. The data of elemental analysis and mass spectrometric measurements of complexes of lanthanides with calix[4]arenes are given in Table 1. In the MALDI mass spectra mono- and binuclear complexes of calix[4]arene derivatives, peaks of the corresponding molecular ions are observed.

LuL^3H_3: IR (KBr), ν, cm^{-1}: 3328 (NH, OH), 2961 (C-H), 2868 (C-H), 1654 (C=O), 1479 (C-C). NMR^1H (DMSO-d_6), δ, ppm:1.12 s (9H, t-Bu), 1.15 s (18H, t-Bu), 1.17 s (9H, t-Bu), 2.95-3.13 t (4H, N-$(CH_2)_2$-N), 3.26-3.54 m (8H, N-CH_2-CO), 3.36 d (4H, Ar-CH_2-Ar), 4.02 d (2H, Ar-CH_2-Ar), 4.28 d (2H, Ar-CH_2-Ar), 6.90 d (2H, Ar-H), 7.04 s (2H, Ar-H), 7.09 d (2H, Ar-H), 7.15 s (2H, Ar-H).

LuL^4H_4: IR (KBr), ν, cm^{-1}: 3346 (NH, OH), 2961 (C-H), 2868 (C-H), 1653 (C=O), 1482 (C-C). NMR^1H (DMSO-d_6), δ, ppm:1.10 s (9H, t-Bu), 1.14 s (18H, t-Bu), 1.17 s (9H, t-Bu), 2.95-3.13 m (8H, N-$(CH_2)_2$-N), 3.22-3.45 m (10H, N-CH_2-CO), 3.42 d (4H, Ar-CH_2-Ar), 4.09 d (2H, Ar-CH_2-Ar), 4.29 d (2H, Ar-CH_2-Ar),6.88 d (2H, Ar-H), 7.01 s (2H, Ar-H), 7.05 d (2H, Ar-H), 7.16 s (2H, Ar-H), 11.88 s (1H, COOH).

$Lu_2L^5H_2$: IR (KBr), ν, cm^{-1}: 3343 (NH, OH), 2963 (C-H), 2867 (C-H), 1649 (C=O), 1478 (C-C). NMR^1H (DMSO-d_6), δ, ppm: 1.08 s (18H, t-Bu), 1.21 s (18H, t-Bu), 2.93-3.09 m (8H, N-$(CH_2)_2$-N), 3.24-3.54 m (16H, N-CH_2-CO), 3.43 d (4H, Ar-CH_2-Ar), 4.40 d (4H, Ar-CH_2-Ar), 6.92 s (4H, Ar-H), 7.05 s (4H, Ar-H).

$Lu_2L^6H_4$: IR (KBr), ν, cm^{-1}: 3336 (NH, OH), 2961 (C-H), 2866 (C-H), 1652 (C=O), 1476 (C-C). NMR^1H (DMSO-d_6), δ,

ppm: 1.08 s (18H, t-Bu), 1.22 s (18H, t-Bu), 2.94-3.11 m (16H, N-$(CH_2)_2$-N), 3.24-3.54 m (20H, N-CH_2-CO), 3.48 d (4H, Ar-CH_2-Ar), 4.35 d (4H, Ar-CH_2-Ar), 6.93 s (4H, Ar-H), 7.03 s (4H,Ar-H), 11.68 s (2H, COOH).

LuL^7H_2: IR (KBr), ν, cm^{-1}: 3340 (NH, OH), 2962 (C-H), 2868 (C-H), 1648 (C=O), 1479 (C-C). NMR ^1H (DMSO-d_6), δ, ppm:1.00 s (18H, t-Bu), 1.03 s (18H, t-Bu), 2.95-3.13 m (8H, N-$(CH_2)_2$-N), 3.22-3.45 m (10H, N-CH_2-CO), 3.46 d (4H, Ar-CH_2-Ar), 4.44 d (4H, Ar-CH_2-Ar), 6.91 s (4H, Ar-H), 7.05 s(4H, Ar-H).

NMR spectra of Lu(III) complexes were compared with the data obtained for free ligands. A shift of the proton signals of methylene groups from APC fragments to the low field region by 0.20–0.25 ppm was found. At the same time, the signals of the phenyl, *tert*-butyl and methylene protons remains practically unchanged, which is probably due to the absence of the coordination of calix[4]arene phenolic fragments by Lu(III) ion. In the spectra of the complexes LuL^3H_3, $Lu_2L^5H_2$, and LuL^7H_2, the signals of the protons of the carboxyl groups disappear, and for LuL^4H_4 and $Lu_2L^6H_4$ the signal intensity decreases by 4 times indicating the coordination of Lu(III) ions by the chelating APC fragment.

In all IR spectra of the complexes, the conservation of the broadened intense band is observed at 3200-3600 cm^{-1}. In this area, vibrational bands of both amide NH-bonds and phenolic hydroxy groups are superimposed, as well as the remaining hydroxy groups of APC fragments, which complicates their analysis. However, the absence of a significant shift in the maximum of this band may indicate the preservation of the hydrogen bond system and the absence of ionization of phenolic hydroxy groups. It was not possible to define the bands corresponding to the symmetric vibrations of the carboxy groups, which is probably due to the overlap of a large number of calyx[4]arene macrocycle bands in this region (1350 – 1450 cm^{-1}). The coordination of the lanthanide ion is confirmed because of the appearance of ν(Ln-O) bands at 455-460 cm^{-1}.

According to the results of physicochemical methods, it can be assumed that the coordination polyhedron of lanthanide in synthesized complexes is formed due to tertiary nitrogen atoms and oxygen atoms of APC fragments. Solvent molecules (DMF) also are present in the coordination sphere, which is typical for lanthanide aminopolycarboxylates [7] (Fig. 2). The lanthanide ions is not coordinated by the donor atoms of the lower rime phenolic groups, probably, because of the steric factors and the length of linkers linking calix[4]arenes to an acid fragment. This was previously proved for the mononuclear complex L^7H_5 with europium (III) [5]. Figure 2 shows the structure of the homonuclear complexes LnL^3H_3, $Ln_2L^5H_2$ and LnL^7H_2, where Ln = Yb(III), Lu(III).

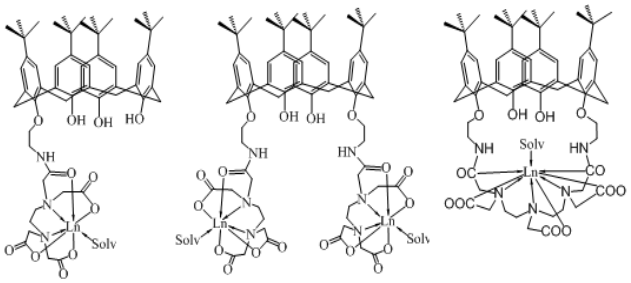

Fig. 2. Structure of lanthanide-containing complexes of calix[4]arenes

T a b l e 2

Spectral and luminescent properties of ligands and their complexes with lutetium (III) (C = 1×10^{-4} M; DMF)

Compound	Absorption λ, nm, (lgε)	Molecular fluorescence			
		λ_{fl}, nm	λ_{ph}, nm	E_S,cm^{-1}	E_T,cm^{-1}
L^3H_6	278 (4.01) 286 (4.03)	418	444	23920	22520
L^4H_7	279 (4.04) 286 (4.06)	416	440	24040	22730
L^5H_8	282 (4.03) 290 (4.02)	423	449	23640	22270
L^6H_{10}	283 (4.04) 290 (4.03)	421	443	23750	22570
L^7H_5	280 (4.04) 288 (4.03)	420	455	23810	21980
LuL^3H_3	274 (3.94) 281 (3.95)	432	468	23150	21370
LuL^4H_4	276 (3.96) 284 (3.97)	430	465	23250	21500
$Lu_2L^5H_2$	275 (3.95) 283 (3.96)	434	470	23040	21270
$Lu_2L^6H_4$	276 (3.97) 283 (3.99)	433	467	23090	21410
LuL^7H_2	278 (3.96) 285 (3.93)	437	474	22880	21100

Spectral-luminescent properties. The absorption spectra of the compounds L^3H_6 - L^7H_5 contain two characteristic bands of calixarenes in the region of 270–290 nm (ε = 7000–10000). An increase of intensity and a bathochromic shift of 3-12 nm are observed comparing to the spectra of the initial aminoethoxy derivatives L^1H_3 and L^2H_2. It is known that ionization of phenolic hydroxy groups, upon their dissociation or complex formation, leads to the appearance of bands in the absorption spectra in the range 300–320 nm. The absence of these bands in the spectra of the complexes confirms that the hydroxy groups of calix[4]arene do not participate in the coordination of lanthanide ions (Table 2).

Fluorescence is observed in the region of 410–420 nm for all solutions of calix[4]arenes at 295 K (Fig. 3a). Moreover, in comparison with the initial aminoethoxy derivatives, a bathochromic shift of these bands is observed (by 700–1000 cm^{-1}). The phosphorescence spectra determining the lower triplet state of the ligand were recorded when the samples were cooled to 77 K. The phosphorescence spectra of ligands also undergo significant changes: a bathochromic

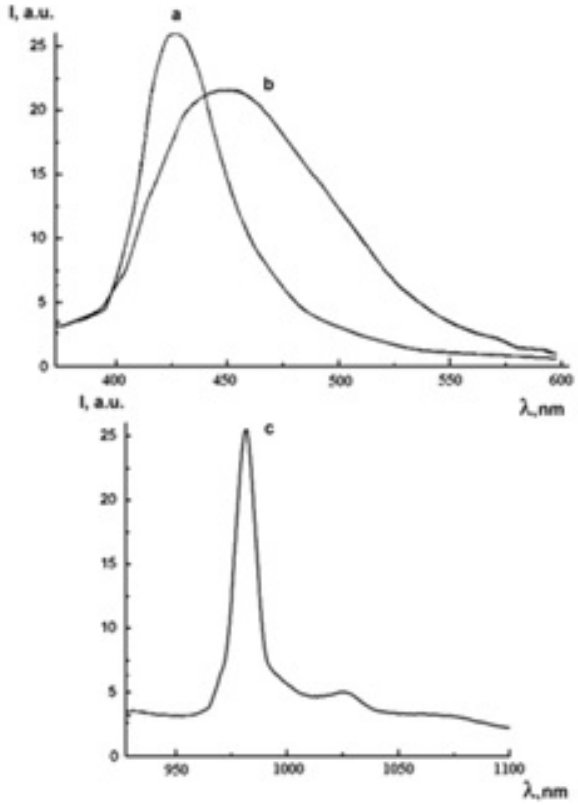

Fig. 3. Spectra of molecular fluorescence (a), phosphorescence (b) $Lu_2L^6H_4$ and 4f-luminescence $Yb_2L^6H_4$ (c) ($C=10^{-3}$M; DMF).

shift of 1000-1700 cm^{-1} is observed. It is associated with a decrease in the energy of triplet levels (E_{T1} = 21980-22730 cm^{-1}) (Fig. 3b) (Table 2). Positions of singlet levels in complexes decrease by 500-1500 cm^{-1} and triplet levels by 600-1000 cm^{-1}. The intensity of the bands remains virtually unchanged as compared to ligands.

The data in Table 2 indicate that since the triplet levels are higher than the resonance level of the Yb(III) ion (10200-10300 cm^{-1}), 4f-luminescence is possible for all compounds through the intramolecular energy transfer mechanism. When all the Yb(III) complexes are excited at the absorption maxima, a band in the region of 975–985 nm is observed in the luminescence spectra (Fig. 3), which corresponds to the transition from the excited $^2F_{5/2}$ level of the lanthanide ion to the ground level $^2F_{7/2}$. Due to the excitation energy transfer to ytterbium ion, the molecular fluorescence of the complexes is significantly quenched in comparison with ligands (more than 80%). It was found that the quantum yields of *4f*-luminescence of ytterbium complexes with L^3H_6 and L^4H_7 are lower than for compounds with the initial aminoethoxy derivatives (Table 3).

T a b l e 3

Spectral-luminescent characteristics of Yb(III)-calix[4]arenes complexes

Complex	λ_{max}, nm	$\varphi\times10^3$
YbL^1*	981	1.9
YbL^2(Cl)*	982	1.6
YbL^3H_3	981	1.1
YbL^4H_4	981	1.3
YbL^5H_3	981	2.3
$Yb_2L^6H_2$	981	2.4
$Yb_2L^7H_4$	982	2.1

Two main factors that influence the 4f-luminescence intensity of complexes of modified calix[4]arenes as compared to complexes of the initial aminoethoxy derivatives should be taken into account. First, the coordination of the ion with the APC fragment leaves a minimum space for solvent molecules (which have luminescence quenching effect) in the internal coordination sphere of the complex. Secondly, the emitting ion is removed from the calixarene photoantenna, which affects the decrease in luminescence intensity.

As a result of structural optimization

by means of the molecular mechanics method (HyperChem 8.0.6 program), it was shown that Yb(III) ion is 4 times (about 8.6Å) more distant from phenolic oxygen atoms in comparison with the complexes of the initial L^1H_3 and L^2H_2. The largest quantum yield among mononuclear complexes was found for the complex with L^7H_5, in which this distance decreases to 5.9Å.

In binuclear complexes $Yb_2L^5H_2$ and $Yb_2L^6H_4$, in spite of the removal of emitting ions from the calix[4]arene, the intensity of 4f-luminescence increases by 1.7-2 times in comparison with mononuclear complexes. Since molecular fluorescence is completely quenched in both mononuclear and binuclear complexes, an increase of intensity and quantum yield of Yb-centered emission is the evidence of the more efficient excitation energy transfer due to a decrease in non-radiative losses.

Less intense signal in the case of both mono- and binuclear EDTA-substituted complexes are likely due to the fact that the ytterbium ion coordinated by the EDTA fragment forms donor-acceptor bonds with only six donor atoms. Thus, the coordination sphere of the lanthanide ion is less saturated, and extra-coordination of larger number of solvent molecules is possible. Latter leads to an additional possibility of dissipating the excitation energy. The estimated number of donor atoms (for DTPA-derivatives) provided by one acid fragment is 8, which is typical for diethylenetriaminepentaacetates of lanthanides [7].

It was also found that Lu(III) complexes reveal biological activity. The antibacterial activity of the L^4H_7 derivative and its lutetium complex were studied against various species of Gram positive, such as *Staphylococcus aureus*, as well as *Escherichia coli* (Gram negative) bacteria. L^4H_7 was characterized by a rather high level of antibacterial action on *S. aureus* cells, practically without affecting the Gram negative microorganism development, while its lutetium complex had an inhibitory effect on both species of test microorganisms.

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CONCLUSIONS. Calix[4]arenes substituted at the lower rim with fragments of aminopolycarboxylic acids (EDTA, DTPA) were synthesized. Mono and binuclear complexes with lanthanide (III) ions were synthesized using these compounds. All compounds were characterized by means of various physico-chemical methods, and structures of complexes were proposed. *4f*-Luminescence of the lanthanide ion is realized in the mononuclear complexes of calix[4]arenes, and when an additional ion is introduced into the macrocycle, its intensity is approximately doubled. The data obtained allow us to conclude that the structure of functionalized ligands significantly affects the differences in the luminescent properties of complexes based on them. In this case, the effect of the structure of additional ligands, their amount, and the method of combining with the macrocycle is manifested. This is confirmed by the fact that the complexes of lanthanides with calix[4]arenes, which are the basic compounds for the production of APC-modified ligands (*p-tert*-butylcalix[4]arenes, L^1H_3 and L^2H_2), have approximately equal values of the quantum yields of 4f-luminescence.

КАЛІКС[4]АРЕНИ, МОДИФІКОВАНІ ПО НИЖНЬОМУ ОБОДУ ФРАГМЕНТАМИ ЕДТА (ДТПА), ТА ЇХ Ln(III) КОМПЛЕКСИ (Ln = Yb, Lu): СИНТЕЗ ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ У БЛИЖНІЙ ІЧ ОБЛАСТІ

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Отримані похідні *п-трет*-бутілкалікс[4]арену, заміщені по нижньоик ободу фрагментами амінополікарбонових кислот (ЕДТА, ДТПА). Моно та біядерні комплекси з іонами лантанідів (III) були синтезовані за допомогою цих сполук. Вивчено вплив кількості та типу фрагментів амінополікарбонових кислот на люмінесценцію лігандів та комплексів. Проаналізовано вплив відстані між випромінюючим іоном і макроциклом каліксарену на інтенсивність 4f-люмінесценції.

Ключові слова: калікс[4]арени, ЕДТА, ДТПА, лантаніди, люмінесценція.

КАЛИКС[4]АРЕНЫ, МОДИФИЦИРОВАННЫЕ ПО НИЖНЕМУ ОБОДУ ФРАГМЕНТАМИ ЭДТА (ДТПА), И ИХ Ln(III) КОМПЛЕКСЫ (Ln = Yb, Lu): СИНТЕЗ И ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА В БЛИЖНЕЙ ИК ОБЛАСТИ

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Получены производные *п-трет*-бутилкаликс[4]арена, замещенные по нижнему ободу фрагментами аминополикарбоновых кислот (ЭДТА, ДТПА). С помощью этих соединений были синтезированы моно- и биядерные комплексы с ионами лантанидов (III). Изучено влияние количества и типа фрагментов аминополикарбоновых кислот на люминесценцию лигандов и комплексов. Проанализировано влияние расстояния между излучающим ионом и макроциклом каликсарена на интенсивность 4f-люминесценции.

Ключевые слова: каликс[4]арены, ЭДТА, ДТПА, лантаниды, люминесценция

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