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Synthesis of Mesomorphic Derivatives of Methyl 2,4-Dihydroxybenzoate and Spectral and Luminescence Properties of Their Lanthanide Complexes

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Abstract—The derivatives of methyl 2,4-dihydroxybenzoate containing fragments of different organic acids in position 4 have been synthesized. Their mesomorphic properties have been investigated. Lanthanide complexes of the prepared compounds have been obtained. Their spectral properties have been studied.

Keywords: methyl 2,4-dihydroxybenzoate derivatives, mesomorphism, lanthanide complexes, luminescence

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Previously we have obtained a series of derivatives of 2-hydroxybenzoic acid with different structure and studied the conditions of complex formation Tb(III) ion [1]. It has been shown that the intensity of their luminescence increases in following series: esters of 2-acyloxybenzoic acid < esters of 2-methoxybenzoic acid < esters of 2-hydroxybenzoic acid. Further, we have prepared the derivatives of 2,4-dihydroxybenzoic acid and its aldehyde acylated at position 4 as well as their luminescing complexes with Eu(III) (for aldehydes) and Tb(III) (for acids), but the intensity of luminescence of these complexes has been moderate [3]. Most of the prepared ligands has exhibited mesomorphic properties. The studies devoted to the preparation of liquid-crystalline lanthanide complexes based on mesogenic and non-mesogenic ligands are known [3–5].

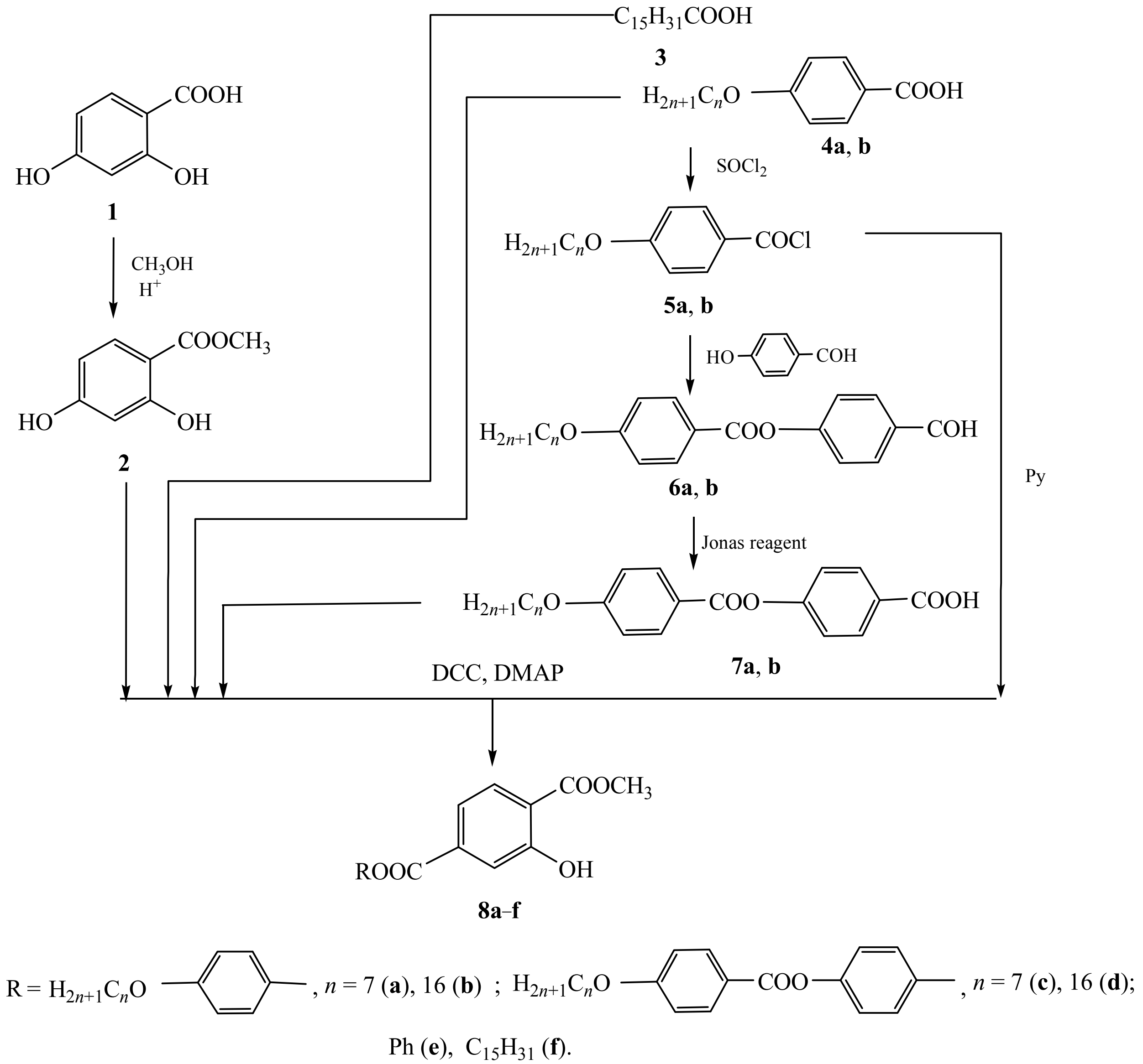
Basing on the earlier reports, we can conclude that the combination of ester and hydroxyl fragments in the coordination site of lanthanide complexes is optimal to achieve strong photoluminescence, owing to the formation of stable six-membered chelate cycle. Moreover, the ligand molecule should contain other functional groups to modulate other important properties of the lanthanide complexes (thermal stability and solubility in organic solvents). Such structure is characteristic of derivatives of methyl 2,4-dihydroxybenzoate. The preparation and investigation of some of such compounds is reported herein.

Synthesis of methyl 2,4-dihydroxybenzoate derivatives is represented at Scheme 1. The starting methyl 2,4-dihydroxybenzoate **2** was prepared via refluxing 2,4-dihydroxybenzoic acid **1** in methanol in the presence of catalytic amount of sulfuric acid as described in [6]. Then, [4-(2-hydroxymethoxycarbonyl)phenyl]4-alkoxybenzoates **8a**, **8b** and [4-(2-hydroxymethoxycarbonyl)phenyl]4-(4-alkoxybenzoyloxy)benzoates **8c**, **8d** were prepared via the interaction of ester **2** with 4-alkoxybenzoic acids **4a**, **4b** and 4-(4-alkoxybenzoyloxy)benzoic acids **7** (synthesized as described in [7, 8]) via the carbodiimide mechanism. The reaction was carried out at molar ratio of methyl 2,4-dihydroxybezoate : acid = 2 : 1.

The structures of the final compounds **8a**–**8d** were confirmed by means of ^{1}H NMR spectroscopy.

The investigation of the prepared derivatives of 2,4-dihydroxybenzoic acid using polarization microscopy revealed the formation of liquid-crystalline phases. The types of mesophase and temperatures of phase transitions are given in the Table 1. According to the obtained data, [4-(2-hydroxymethoxycarbonyl)phenyl]-

Scheme 1.



4-alkoxybenzoates **8a**, **8b** formed monotropic nematic and smectic phases at in a narrow temperature range, at relatively low temperature. In the case of compound **8b** with longer terminal group, polymorphism was observed. Incorporation of an additional aromatic cycle (compounds **8c**, **8d**) resulted in significant increase and broadening of the temperature range of the mesophase existence. Moreover, both mesophases became enantiotropic; polymorphism was observed for the compound containing terminal heptyloxy group.

[4-(2-Hydroxymethoxycarbonyl)phenyl]benzoate **8e** containing a non-substituted benzoic acid moiety at position 4 and [4-(2-hydroxymethoxycarbonyl)phenyl]hexadecanoate **8f** containing long alkyl group at position 4 were prepared for comparative investigation of the mesomorphic properties. The synthesis of compound **8e** via carbodiimide mechanism failed: only the side product (*N*-acylurea) was isolated. Therefore, synthetic approach involving acyl chlorides was used instead. Benzoyl chloride **5** was obtained using the reaction with thionyl chloride [9]. The acylation of methyl 2,4-dihydroxybenzoate was carried out in anhydrous ether medium at cooling with ice and using Py to bind the evolving HCl (Scheme 1). The structure of [4-(2-hydroxymethoxycarbonyl)phenyl]benzoate **8e** was confirmed by means of ^{1}H NMR spectroscopy. In detail, the proton of the hydroxy group was registered

Table 1. Types of mesomorphism and temperatures of phase transitions for derivatives of methyl 2,4-dihydroxybenzoate **8a**–**8f**

Comp. no.	*n*	Temperatures of phase transitions, °C[a]
8a	7	Cr 67 I 59.3 N 42.3 Cr
8b	16	Cr 76.4 I 65.4 N 60.3 Sm 56.0 Cr
8c	7	Cr 117 Sm 126 N >200 I
8d	16	Cr 98.07 SmA 156.I N 171.2 I
8e	Ph	Cr 90.0 I
8f	$C_{15}H_{31}$	Cr 43.0 I

[a] (Cr) solid crystal, (N) nematic phase, (SmA and Sm) smectic phases, (I) isotropic liquid.

Table 2. Spectral and luminescence parameters of derivatives of methyl 2,4-dihydroxybenzoate **8a**–**8f**

Comp. no.	ε, L cm^{-1} mol^{-1}	λ_{abs}, nm	λ_{ex}, nm	$E(T_1)$, cm^{-1}
8a	41700	265.6	340	21100
8b	23200	266.1	273 345	21186
8c	44000	265.0	340	20700
8e	34700, 9500	241.2, 300	365	20790
8f	17100, 6700	242.6, 300.8	340	20705

as singlet at 10.94 ppm, protons of the aromatic cycle in the *ortho*-position to carbonyl group were registered as doublet at 8.20 ppm, protons at *meta*- and *para*-positions of the ring resonated as multiplet signals at 7.72–7.6 and 7.58–7.44 ppm ranges, respectively.

Compounds **8e** and **8f** did not possess mesomorphism. The significance decrease in the melting point was observed for the derivative of hexadecenoic acid **8f**.

The possibility of the formation as well as spectral and luminescence properties of Tb(III) complexes with derivatives of methyl 2,4-dihydroxybenzoate have been studied (Table 2). The data on compound **8d** were extracted from [10]. The preparation of lanthanide complexes with 2,4-dimethoxybenzoic acid and observation of strong emission bands of Tb(III) have been reported [11], but the authors did not provide the luminescence spectra.

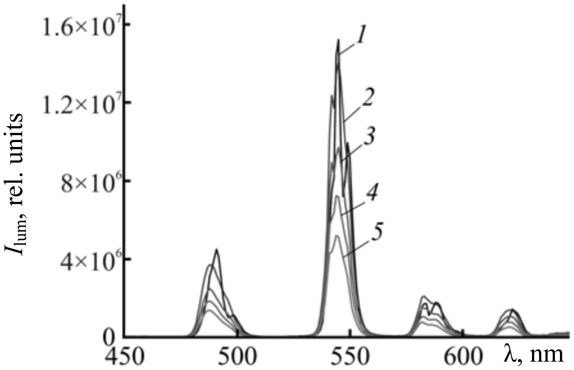


Fig. 1. Excitation and luminescence spectra of Tb(III) complexes with ligands **8a** (*1*) (λ_{ex} = 340 nm), **8e** (*2*), **8f** (*3*) (λ_{ex} = 340 nm), **8b** (*4*) (λ_{ex} = 345 nm), and **8c** (*5*) (λ_{ex} = 340 nm). $c_{Tb} = 1\times10^{-4}$ M, $c_L = 5\times10^{-4}$ M.

According to the data given in the Table 2, ligands **8b** and **8c** absorbed short-wave light with λ_{max} = 265–266 nm and showed high energies of the triplet states $E(T_1)$ = 20700–21186 cm^{-1} and $E(T_1)$ = 23480–23980 cm^{-1}, indicating the possibility of intramolecular excitation transfer to Ln(III) ion. The values of molar absorptivity (23200 and 44000 L cm^{-1} mol^{-1} for compounds **8b** and **8c**, respectively) indicated strong absorption of UV radiation by those compounds.

It was shown that the derivatives of methyl 2,4-dihydroxybenzoate presented in Table 2 formed complexes with Tb(III) ion exhibiting strong luminescence. The band corresponding to electric dipole transition $^5D_4 \rightarrow {}^7F_5$, hypersensitive to the influence of the ligand field, was the strongest in the luminescence spectrum of Tb(III) complex, revealing the transitions from $^5D_4$ excited state to sublevels of the ground state: $^7F_6$ (λ = 490 nm), $^7F_5$ (λ = 544 nm), $^7F_4$ (λ = 584 and 592 nm), and $^7F_3$ (λ = 620 nm) (Fig. 1). The energy of triplet excited states of the ligands was higher than that of the $^5D_4$ excited state of Tb(III) ion (20500 cm^{-1}). As a result, efficient excitation energy transfer to resonance state of Tb(III) occurred.

The investigation of the solution pH influence on luminescence of Tb(III) complexes with the studied ligands showed that the complexes were formed in weakly acidic and neutral media (pH = 6.6–7.0, Table 3). In acidic solutions, the degree of the complexes formation was low; in alkali solutions, the complexes were decomposed into the lanthanide hydroxides. The highest value of I_{lum} was achieved in the case of complexing in aqueous solutions. Molecules of DMSO and DMF could substitute the ligands from inner coordination sphere of Tb(III) ion because of the presence of donor oxygen and nitrogen atoms, respectively. As a result, in those cases I_{lum} value was decreased.

Components ratio in complexes determined using the limited logarithm was Ln : L^1 = 1 : 2. The dependence of I_{lum} value of the complexes on the concentrations of terbium and ligands was studied. The optimal Tb concentration was found to be of 1×10^{-4} mol/L, and that of the ligands was of 5×10^{-4} mol/L. The highest I_{lum} values were observed immediately after the components mixing and remained stable for 72 h.

The influence of additional ligands (L^2) on the I_{lum} value of complexes was investigated in view of the formation of coordination-unsaturated compounds. Insignificant increase in the Tb(III) luminescence in the complexes with compound **8b** was observed in the presence of organic bases: trioctylphosphine oxide, triphenylphosphine oxide, and α,α'-dipyridyl (by 1.2, 1.3, and 1.6 times, respectively). The same effect was observed for the complexes with ligand **8e** in the presence of triphenylphosphine oxide and α,α'-dipyridyl (by 1.2 and 1.3 times, respectively, Table 4).

The formation of hetero-ligand complexes was confirmed by spectrophotometry and luminescence spectroscopy: the shift and splitting of the band corresponding to the Ln(III) transition hypersensitive to the introduction of the second ligand were observed. For example, the change in the excitation spectrum pattern was observed in the case of the formation of hetero-ligand complexes Tb(**8b**)$_2$ with α,α'-dipyridyl (Fig. 2). The luminescence excitation spectra of Tb(III) complex with ligand **8a** contained a broad band in the 250–300 nm range. In the case of the formation of Tb(III) hetero-ligand complexes with ligand **8a** and α,α'-dipyridyl, the band in the 250–300 nm range was not observed, only the band in the 300–380 nm range with maximum at 340 nm was present (Fig. 3). Using the limited logarithm method, it was shown that inner coordination sphere of the complexes contained one molecule of the organic base, and the components ratio in the hetero-ligand complexes was Tb(III) : L^1 : L^2 = 1 : 2 : 1.

Table 3. Conditions of complexing and spectral and luminescence parameters of solutions of Tb(III) complexes with derivatives of methyl 2,4-dihydroxybenzoate ($c_{\text{Ln}} = 1\times10^{-4}$ M, $c_{\text{L}} = 5\times10^{-4}$ M)

Complex	pH	I_{lum}, rel. units		
		544 nm	582 nm	622 nm
Tb(**8a**)$_2$	6.6	1526	173	143
Tb(**8b**)$_2$	6.9	521	72	41
Tb(**8c**)$_2$	7.1	723	105	63
Tb(**8e**)$_2$	6.8	1407	209	139
Tb(**8f**)$_2$	7.0	972	148	135

Table 4. Influence of additional ligands (L^2) on luminescence intensity of Tb(III) complexes with derivatives of methyl ester of 2,4-dihydroxybenzoic acid[a]

Complex	I_0, rel. units	I, rel. units			I/I_0		
		trioctylphosphine oxide	triphenylphosphine oxide	α,α'-dipyridyl	trioctylphosphine oxide	triphenylphosphine oxide	α,α'-dipyridyl
Tb(**8a**)$_2$	1600	714	1012	1745	0.4	0.6	1.1
Tb(**8b**)$_2$	502	590	645	781	1.2	1.3	1.6
Tb(**8c**)$_2$	723	721	925	715	1.0	1.3	0.9
Tb(**8e**)$_2$	1407	631	1609	1830	0.4	1.2	1.3
Tb(**8f**)$_2$	972	644	799	680	0.6	0.8	0.7

[a] I_0 and I are intensities of luminescence in the absence and in the presence of L^2; $c_{\text{Tb}} = 1\times10^{-4}$ M, $c(\text{L}^1) = 5\times10^{-4}$ M, $c(\text{L}^2) = 4\times10^{-4}$ M, λ_{lum} = 544 nm.

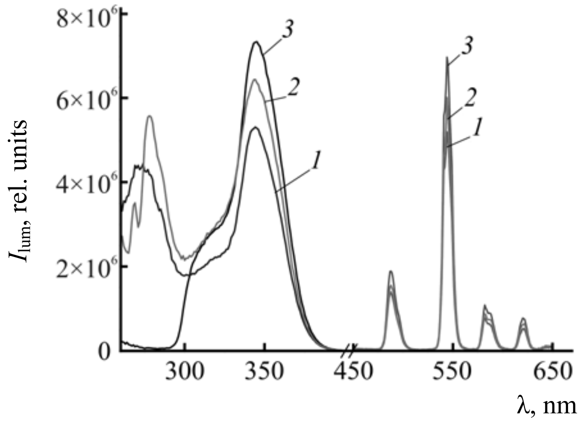


Fig. 2. Excitation and luminescence spectra of Tb(III) complexes with ligand **8b** (*1*) and hetero-ligand complexes in the presence of triphenylphosphine oxide (*2*) and α,α'-dipyridyl (*3*). $c_{Tb} = 1\times10^{-4}$ M, $c(L^1) = 5\times10^{-4}$ M, $c(L^2) = 4\times10^{-4}$ M.

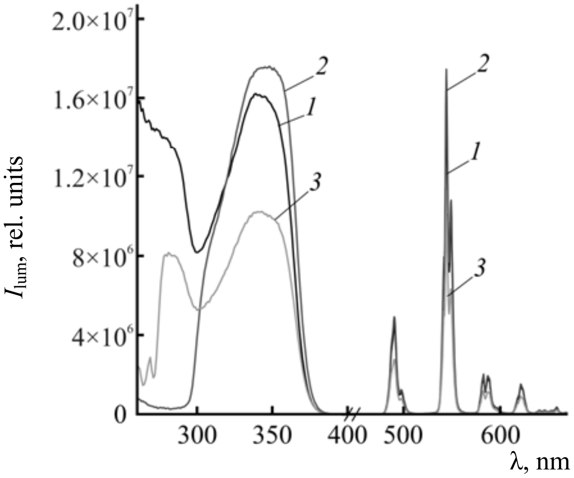


Fig. 3. Excitation and luminescence spectra of Tb(III) complexes with ligand **8a** (*1*) and hetero-ligand complexes in the presence of triphenylphosphine oxide (*2*) and α,α'-dipyridyl (*3*). $c_{Tb} = 1\times10^{-4}$ M, $c(L^1) = 5\times10^{-4}$ M, $c(L^2) = 4\times10^{-4}$ M.

[4-(2-Hydroxymethoxycarbonyl)phenyl]benzoate **8e** was the only of the studied compounds which formed luminescing complex with Eu(III). Probably, in that case excitation transfer from triplet state of the ligand (20790 cm^{-1}) to the $^5D_1$ level (19000 cm^{-1}) of europium ion took place, followed by non-radiative transition to the first excited state $^5D_0$ (17 cm^{-1}), from which irradiation occurred. Wide energy gap between the metal and ligand levels enhanced the non-radiative energy losses, and the complex exhibited weak luminescence. The strongest band of the luminescence spectra of the europium complex corresponded to the $^5D_0\rightarrow{}^7F_2$ transition, with maximum at 612 nm. For the rest of methyl 2,4-dihydroxybenzoate derivatives, energy of the triplet states was significantly higher than that of excited state of Eu(III) ion, and the major part of energy was lost without emission.

It was shown using the limited logarithm method that the composition of Eu(III) complexes with compound **8e** formed at low concentrations of the ligand (about equal to the lanthanide content) corres-ponded to Eu : **8e** = 1 : 1. The components ratio was changed to Eu : **8e** = 1 : 2 at higher ligand concentration.

The study of the effect of additional ligands on luminescence of the formed hetero-ligand complexes showed that the most prominent increase in the I_{lum} value of Eu(III) in complex with ligand **8e** was observed in the presence of triphenylphosphine oxide and 1,10-phenantroline as organic bases (by 55 and 35 times, respectively, Fig. 4).

Tb(III) complex with [4-(2-hydroxymethoxycarbonyl)phenyl]4-hexadecyloxybenzoate **8b** soluble in $CHCl_3$, CCl_4, and chlorobenzene and exhibiting strong luminescence with λ_{max} = 545 nm was obtained and isolated for the preliminary assessment of its practical application. Excitation and luminescence spectra of that complex are given at Fig. 5. The investigation of structure of the prepared complex will be reported separately.

In summary, the derivatives of methyl 2,4-dihydroxybenzoate containing fragment of mesogenic 4-*n*-alkoxybenzoic or 4-(4-alkoxybenzoyloxy)benzoic acids in position 4 were found to be optimal for the preparation of lanthanide complexes. The presence of long terminal hydrocarbon substituents hindering crystallization allowed the preparation of the low-defective films and achieve maximal radiation efficiency. The luminescence intensity of the prepared coordination compounds with Tb(III) ions in solution as well as in solid state exceeded that of known carboxylate complexes. That fact, along with good solubility in organic solvents, makes those compounds promising for their application as emission elements.

EXPERIMENTAL

^{1}H NMR spectra of solutions in $CDCl_3$ or DMSO-d_6 were recorded using a Bruker AVANCE DRX 500 spectrometer (operating frequency 500 MHz, internal reference – TMS). Excitation and luminescence spectra of the ligands and complexes were registered

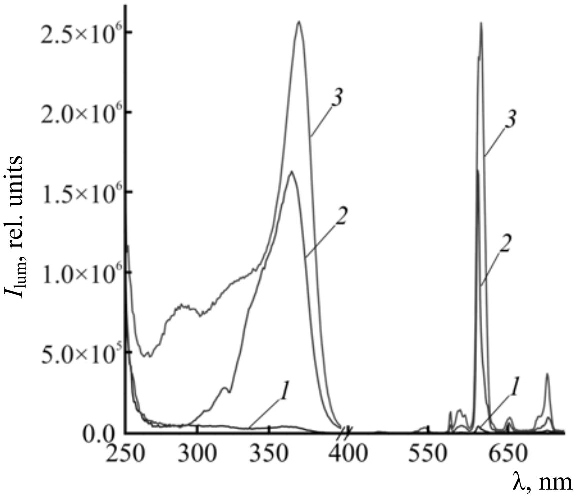


Fig. 4. Excitation and luminescence spectra of Eu(III) complexes with ligand **8e** (*1*) and hetero-ligand complexes in the presence of triphenylphosphine oxide (*2*) and α,α'-dipyridyl (*3*). $c_{Eu} = 1\times10^{-4}$ M, $c(L^1) = 5\times10^{-4}$ M, $c(L^2) = 4\times10^{-4}$ M.

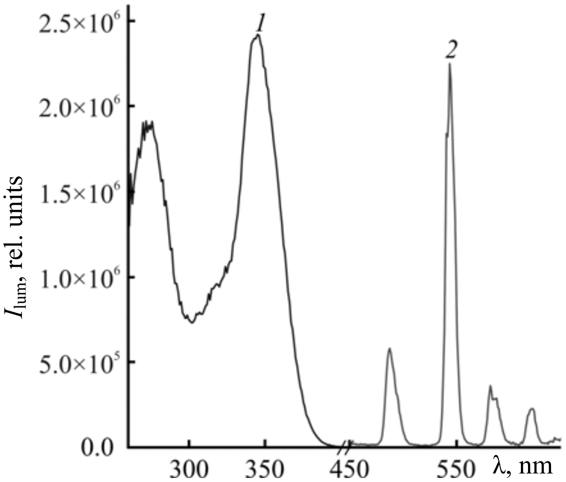


Fig. 5. Excitation and luminescence spectra of Tb(III) complexes with ligand **8b**.

using a Fluorolog FL 3-22 spectrofluorometer (HORIBA Jobin-Yvon Inc., France). Temperatures of phase transitions were studied via polarization microscopy using a POLAM R-312 microscope and a DSC Q2000 differential scanning calorimeter (USA) (heating rate 1 deg/min). Energies of the triplet states of organic ligands were calculated from the phosphorescence spectra of their complexes with gadolinium and yttrium at 77 K. pH values of the solutions were measured using a OP-211/1 pH-meter (Radelkis, Hungary) (glass electrode calibrated using standard buffer solutions).

Methyl-2,4-dihydroxybenzoate (2) was prepared as described in [6]. Yield 50%, mp 116°C (mp 117–118°C [6]).

4-*n*-Heptyloxybenzoyl chloride (5a) was prepared as described in [9]. Yield 93.2%, colorless liquid, bp 208°C (4 mmHg).

4-Hexadecyloxybenzoyl chloride (5b) was prepared using the same method. Yield 95.2%, mp 50°C.

4-(4-Heptyloxybenzoyloxy)benzaldehyde (6a) was prepared as described in [7]. Yield 66.7%, white crystals, mp 56°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.89 t (3H, CH_3, ^3J = 7.2), 1.20–1.55 m (8H, CH_2), 1.76–1.90 m (2H, $\underline{CH_2}CH_2O$), 4.05 t (2H, CH_2O, ^3J = 6.5), 6.98 d (2H, Ar, ^3J = 8.7), 7.40 d (2H, ArCOH, ^3J = 8.4), 7.97 d (2H, ArCOH, ^3J = 8.4), 8.14 d (2H, Ar, ^3J = 9.0), 10.02 s (1H, COH). Found, %: C 74.29; H 7.04. $C_{21}H_{24}O_4$. Calculated, %: C 74.09; H 7.10.

4-(4-Hexadecyloxybenzoyloxy)benzaldehyde (6b). The preparation procedure and constants are given in [8].

4-(4-Heptyloxybenzoyloxy)benzoic acid (7a) was prepared using a method similar to the one described in [8]. Yield 4.0 g (72.3%), white solid substance. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.90 t (3H, CH_3, ^3J = 6.9), 1.26–1.49 m (8H, CH_2), 1.73–1.81 m (2H, $\underline{CH_2}CH_2O$), 4.11 t (2H, CH_2O, ^3J = 6.5), 7.14 d (1H, Ar, ^3J = 8.8), 7.42 d (2H, ArCOOH, ^3J = 8.6), 8.05–8.14 m (2H, Ar, 2H, ArCOOH). Found, %: C 71.02; H 6.64. $C_{23}H_{28}O_5$. Calculated, %: C 70.77; H 6.80.

4-(4-Hexadecyloxybenzoyloxy)benzoic acid (7b). The preparation procedure and constants are given in [8].

[4-(2-Hydroxymethoxycarbonyl)phenyl]-4-heptyloxybenzoate (8a). 0.59 g (0.48 mmol) of 4-dimethylaminopyridine (DMAP) was added to a solution of 1.3 g (6 mmol) of ester **2** and 1.4 g (6 mmol) of 4-(4-heptyloxybenzoyloxy)benzoic acid in 20 mL of anhydrous chloroform under stirring. After 10 min, 1.24 g (6 mmol) of *N*,*N'*-dicyclohexylcarbodiimide (DCC) was added. The reaction mixture was stirred for 10 h at room temperature. The precipitate was filtered off and washed with methylene chloride (15 mL); the residue of dicyclohexylurea precipitate was filtered off, and the solvent was removed under reduced pressure. The final product was recrystallized from an ethanol–

benzene mixture (5 : 1), then from 95 mL of hexane and 35 mL of benzene. The final product was purified using by column chromatography (Al_2O_3, L = 40/250 eluent—chloroform). Yield 1.2 g (46%), white solid substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.91 t (3H, CH_3, ^3J = 6.9), 1.20–1.51 m (7H, CH_2), 1.75–1.90 m (2H, $\underline{CH_2}CH_2O$), 3.97 s (3H, $COOCH_3$), 4.05 t (2H, CH_2O, ^3J = 6.6), 6.77–6.79 d. d (1H, H^5, ^3J = 8.8, ^4J = 2.2), 6.87 d (1H, H^3, ^4J = 2.2), 6.97 d (2H, $H^{10,12}$, ^3J = 8.8), 7.90 d (1H, H^6, ^3J = 8.6), 8.12 d (2H, $H^{9,13}$, ^3J = 8.6), 10.91 s (1H, OH). Found, %: C 68.56; H 6.61. $C_{22}H_{26}O_6$. Calculated, %: C 68.38; H 6.78.

[4-(2-Hydroxymethoxycarbonyl)phenyl]-4-hexadecyloxybenzoate (8b) was prepared similarly. Yield 81.2%, white solid substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.90 t (3H, CH_3, ^3J = 6.9), 1.21–1.52 m (26H, CH_2), 1.78–1.90 m (2H, $\underline{CH_2}CH_2O$), 3.98 s (3H, $COOCH_3$), 4.06 t (2H, CH_2O, ^3J = 6.6), 6.79–6.81 d. d (1H, H^5, ^3J = 8.8, ^4J = 2.2), 6.89 d (1H, H^3, ^4J = 2.2), 6.98 d (2H, $H^{10,12}$, ^3J = 8.8), 7.91 d (1H, H^6, ^3J = 8.6), 8.13 d (2H, $H^{9,13}$, ^3J = 8.6), 10.92 s (1H, OH). Found, %: C 72.80; H 8.43. $C_{31}H_{26}O_6$. Calculated, %: C 72.63; H 8.65.

[4-(2-Hydroxymethoxycarbonyl)phenyl]-4-(4-heptyloxybenzoyloxy)benzoate (8c) was prepared similarly. Yield 63.5%, white solid substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.92 t (3H, CH_3, ^3J = 6.5), 1.22–1.64 m (10H, CH_2), 1.75–1.96 m (2H, $\underline{CH_2}CH_2O$), 3.99 s (3H, $COOCH_3$), 4.07 t (2H, CH_2O, ^3J = 6.5), 6.79–6.82 d. d (1H, H^5, ^3J = 10.6, ^4J = 2.2), 6.90 d (1H, H^3, ^4J = 2.2), 7.00 d (2H, $H^{17,19}$, ^3J = 8.8), 7.39 d (2H, $H^{10,12}$, ^3J = 8.6), 7.93 d (1H, H^6, ^3J = 8.6), 8.17 d (2H, $H^{16,20}$, ^3J = 8.6), 8.27 d (2H, $H^{9,13}$, ^3J = 8.6), 10.95 s (1H, OH). Found, %: C 68.91; H 5.87. $C_{29}H_{30}O_8$. Calculated, %: C 68.76; H 5.97.

[4-(2-Hydroxymethoxycarbonyl)phenyl]-4-(4-hexadecylozybenzoyloxy)benzoate (8d) was prepared similarly. Yield 52%, white solid substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 t (3H, CH_3, ^3J = 6.9), 1.21–1.53 m (26H, CH_2), 1.77–1.89 m (2H, $\underline{CH_2}CH_2O$), 3.97 s (3H, $COOCH_3$), 4.05 t (2H, CH_2O, ^3J = 6.6), 6.79–6.82 d. d (1H, H^5, ^3J = 8.8, ^4J = 2.2), 6.89 d (1H, H^3, ^4J = 2.2), 6.98 d (2H, $H^{17,19}$, ^3J = 8.8), 7.38 d (2H, $H^{10,12}$, ^3J = 8.8), 7.92 d (1H, H^6, ^3J = 8.8), 8.16 d (2H, $H^{16,20}$, ^3J = 8.8), 8.26 d (2H, $H^{9,13}$, ^3J = 8.8), 10.93 s (1H, OH). Found, %: C 72.25; H 7.53. $C_{38}H_{48}O_8$. Calculated, %: C 72.13; H 7.65.

[4-(2-Hydroxymethoxycarbonyl)phenyl]benzoate (8e). 0.68 g (0.0086 mol) of anhydrous pyridine was added to a solution of 2.22 g (0.01 mmol) of compound **2** in 15 mL of anhydrous diethyl ether. A solution of 1 mL (0.0086 mol) of benzoyl chloride in 5 mL of anhydrous benzene was slowly added to the cooled (0°C) reaction mixture. The mixture was kept overnight, stirred at room temperature for 10 h, and then poured onto crushed ice. The precipitate was filtered off. The filtrate was extracted with benzene (3 × 35 mL) and dried over $MgSO_4$. After the removal of benzene, the precipitate was twice recrystallized from ethanol with activated carbon. Yield 0.75 g (32%), white solid substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.97 s (3H, $COOCH_3$), 6.81–6.79 d. d (1H, ArOH, ^3J = 8.8, ^4J = 1.0), 6.89 d (1H, ArOH, ^4J = 1.0), 7.42–7.59 m (2H, Ar), 7.60–7.72 m (1H, Ar), 7.91 d (1H, ArOH, ^3J = 8.5), 8.19 d (2H, Ar, ^3J = 7.1), 10.94 s (1H, OH). Found, %: C 66.30; H 4.20. $C_{15}H_{12}O_5$. Calculated, %: C 66.18; H 4.44.

[4-(2-Hydroxymethoxycarbonyl)phenyl]hexadecanoate (8f). 40.3 mg (0.33 mmol) of DMAP was added to a solution of 0.74 g (3.3 mmol) of ester **2** and 0.845 g (3.3 mmol) of anhydrous *n*-decanoic acid in 25 mL of anhydrous chloroform under stirring. After 10 min, 0.681 g (3.3 mmol) of DCC was added. The obtained reaction mixture was stirred for 23 h at room temperature. Then the precipitate was filtered off. After removal of solvent, the precipitate was recrystallized from ethanol. Yield 3.5 g (26.3%), white crystalline substance, mp 43°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 10.88 s (1H, OH), 7.85 d (1H, Ar, ^3J = 8.8), 6.8–6.65 m (2H, Ar), 3.95 s (3H, OCH_3), 2.75–2.40 m [2H, $CH_2C(O)$], 1.90–1.60 m [2H, $CH_2CH_2C(O)$], 1.6–1.1 m (24H, CH_2), 0.88 t (3H, CH_3, ^3J = 6.9). Found, %: C 70.89; H 9.40. $C_{24}H_{37}O_5$. Calculated, %: C 71.08; H 9.19.

Procedure of preparation of complexes. 0.1 M stock solutions of Tb(III) or Eu(III) chlorides for the investigation of complex formation were prepared via following procedure. High-pure terbium (99.988%) and europium oxides (99.99%) were dissolved in hydrochloric acid (1 : 1), and the excess of acid was evaporated off. The solid residue was dissolved in methanol and diluted in a measuring flask to the required volume. The concentration of lanthanide ions was determined using complexometric titration. Initial solutions of reagents with concentration 0.1 mol/L were prepared via dissolution of the weighed portions in ethanol. The calculated volume of 0.01 M solution of $TbCl_3$ or $EuCl_3$ was put in a test tube, and 0.01 M ligand solution was added to the components ratio

Ln : L = 1 : 5. Solvents were added to the final volume (5 or 10 mL). Then the mixture was kept during 30 min for the complex formation. For the preparation of hetero-ligand complexes, 0.4–0.5 mL (10^{-2} M) of ethanolic solution of trioctylphosphine oxide or 0.3–0.4 mL of aqueous solution of 1,10-phenantroline was added to the complex solution. The pH value was adjusted by the addition of 40% aqueous solution of urotropine.

Tb(III) complex with [4-(2-hydroxymethoxycarbonyl)phenyl]4-hexadecylbenzoate. 0.1 mmol of aqueous solution of $Tb(ClO_4)_3$ and several drops of NH_4OH were added to a solution of 154 mg (0.3 mmol) of compound **8b** in 20 mL of ethanol obtained at heating to ~35°C. The formed white precipitate was filtered off, washed with cold ethanol, and dried. Yield 115 mg (66%).

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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