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Synthesis of New Derivatives of 2,4-Dihydroxybenzoic Acid and Aldehyde and the Study of the Spectral-Luminescent Properties of Their Lanthanide Complexes

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Abstract—4-Acylated derivatives of 2,4-dihydroxybenzoic acid and aldehyde were synthesized. It was found that 2-hydroxy-4-[(4-decyloxy)benzoyloxy]benzaldehyde coordinates to Eu(III) ion, and when the aldehyde group is replaced by the carboxy group, a complex with Tb(III) ions is formed. The photoluminescent properties of the resulting complexes in solution were studied.

Keywords: coordination compounds of lanthanides, 2,4-dihydroxybenzoic acid, benzaldehyde, luminescence

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Coordination compounds possessing luminescent properties attract interest for both theoretical and practical reasons. From theoretical viewpoint, directed synthesis of new coordination compounds that effectively absorb light in the desired spectral region and are capable of intense luminescence requires establishing the relationship between the structure of the ligands and the photoluminescent properties of complexes thereof. As to practical reasons, luminescent coordination compounds find application as luminescent labels in analytical chemistry and biology and as materials for organic electroluminescent devices (organic light-emitting diodes, OLEDs) [1].

Two main classes of coordination compounds that are applied in OLEDs are those of *s, p*, and *d* elements exhibiting broad-band luminescence and those of lanthanides, whose narrow-band luminescence is associated with *f*–*f* transitions in the lanthanide ion [2]. Coordination compounds of *s, p*, and *d* metals (Mg, Be, Al, and Zn) show resistance to moisture, oxygen, and light and are thermally stable; also, a high degree of purification is possible for them. Coordination compounds of lanthanides are characterized by high luminescence quantum yields and narrow emission bands, and these properties make them suitable for extensive applications in optoelectronics [3–5].

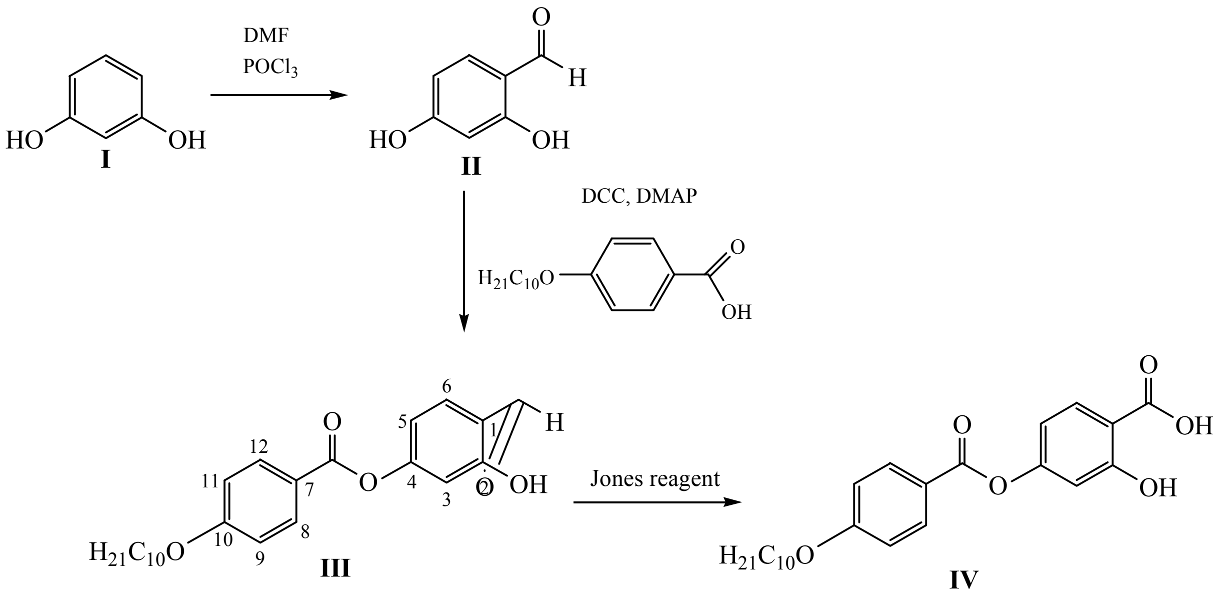
New materials are actively sought now for OLEDs. An increasing number of relevant studies carried out abroad demonstrate the promise of the use of electroluminescent devices based on lanthanide complexes. The reason is that up to 100% power conversion efficiencies can be achieved with triplet emitters. For application of lanthanide complexes as emitters in electroluminescent devices, see [6–14].

Luminescence studies on rare-earth complexes are mostly dedicated to those with β-diketones as organic ligands. However, a significant drawback of lanthanide β-diketonates is their low photostability and low thermal stability. In this respect, noticeable benefits are offered by coordination compounds of lanthanides with carboxylic acids, which not only possess good UV-absorption properties and high luminescence intensity but also outperform β-diketonates in photostability and thermal stability [9, 10].

Lanthanide complexes with aldehydes have received little research attention [15, 16].

Here, we synthesized 2-hydroxy-4-[(4-decyloxy)-benzoyloxy]benzaldehyde (**III**) and 2-hydroxy-4-[(4-decyloxy)benzoyloxy]benzoic acid (**IV**) (Scheme 1) and examined how their functional groups influenced the complexing with lanthanide ions and the photoluminescent properties of these complexes.

Scheme 1.



By formylation of resorcinol **I** according to the known procedure from [17], 2,4-dihydroxybenzaldehyde **II** was prepared. Using the carbodiimide method with an excess of aldehyde **II**, 2-hydroxy-4-[(4-decyloxy)benzoyloxy]benzaldehyde **III** was synthesized and further oxidized to 2-hydroxy-4-[(4-decyloxy)benzoyloxy]benzoic acid **IV** by Jones reagent [18].

The structure of the compounds synthesized was proved by ^{1}H NMR spectroscopy and mass spectrometry.

Spectral luminescent properties of 2,4-dihydroxybenzoic acid derivatives and their complexes with Ln(III) ions. To assess the complexing ability of compounds **III** and **IV** as potential ligands for complexing with lanthanide ions, their essential spectral characteristics were determined. The UV spectra of these compounds exhibit absorption bands with maxima at λ_1 = 269.2, λ_2 = 319 (**III**), and λ = 263 nm (**IV**) (Fig. 1) and high molar extinction of 42400 (**III**) and 30000 L cm^{-1} mol^{-1} (**IV**).

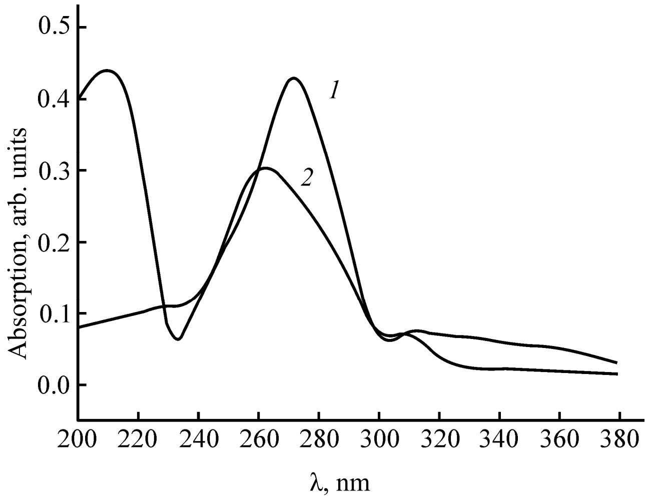


Fig. 1. Absorption spectra of (*1*) aldehyde **III** and (*2*) acid **IV** ($c = 1 \times 10^{-5}$ M).

The triplet-state energy level of aldehyde **III** (19880 cm^{-1}) is higher that that of the excited state of the Eu(**III**) ion (17300 cm^{-1}). The triplet state of acid **IV** (20580 cm^{-1}) is higher in energy than the excited states of the Eu(III) (17300 cm^{-1}) and Tb(III) ions (20500 cm^{-1}), and their complexing may involve an efficient transfer of excitation energy from the ligand to the resonance levels of the lanthanide ions.

Aldehyde **III** forms an intensely luminescent complex with Eu(III). In this case, the excitation energy is likely to be transferred from the triplet level of the ligand to the $^5D_1$ energy level of the europium ion (19000 cm^{-1}), followed by nonradiative deactivation to the first excited state $^5D_0$ (17300 cm^{-1}) from which emission occurs. The most intense band in the luminescence spectra of europium complexes is that with the maximum at 612 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition. In the case of the Tb(III) ion, the sensitized luminescence is not observed, since the triplet state of com-pound **III** lies in lower energy level than the $^5D_4$ excited state of the Tb(III) ion (20500 cm^{-1}), and an energy transfer from the ligand to the resonance level of the lanthanide is impossible.

Acid **IV** forms a complex with Tb(III) exhibiting intense luminescence with the maximum at 545 nm due to the $^5D_4 \rightarrow {}^7F_5$ transition. The triplet-state energy level of acid **IV** is higher than that of the $^5D_4$ excited state of the Tb(III) ion, so an efficient transfer of the excitation energy to the resonance level of Tb(III) is possible in principle. A significant energy gap between the triplet level of the ligand and the emitting level of the Eu(III) ion leads to a large nonradiative loss of excitation energy, resulting in virtually zero intensity of sensitized luminescence (I_{lum}).

Conditions of Eu(III) and Tb(III) complexing with compounds III, IV. Complexing of lanthanides with compounds **III, IV** is observed over a broad pH range (4–9) with the luminescence intensity I_{lum} being at a maximum in neutral medium at pH 6.9 for compound **III** and 7.1 for compound **IV**. The medium is brought to optimum pH by adding a 40% solution of hexamine. At lower pH (acidic solutions) the degree of complex formation is low, and in alkaline solutions (pH > 9) the complexes decompose to give lanthanide hydroxides.

The luminescence intensity I_{lum} of the compounds depends on the nature of the solvent, being the highest in water-ethanol (Eu–aldehyde **III**) and water-acetone (Tb–acid **IV**) media containing 5 vol % of ethanol (acetone). The introduction of organic solvents (acetonitrile, dimethylformamide, and dimethyl sulfoxide) causes a significant decrease in the analytical signal. Due to the presence of donor oxygen (in DMSO) and nitrogen (in DMF) atoms with which the lanthanide ions are coordinated, these solvents exhibit ligand properties and displace the molecules of the 2,4-dihydroxybenzoic acid derivatives from the inner coordination sphere of the Tb(III) ion, leading to a decrease in I_{lum}.

The examination of I_{lum} of the complexes as a function of Ln(III) and ligand concentrations showed that the optimum concentration was 1×10^{-4} M for Ln(III) and of 4×10^{-4} M for the ligands. The luminescence intensity I_{lum} is at a maximum immediately after the components are mixed and remains constant for 72 h.

Using the limiting logarithmic method, the ratio of the components in the Ln–ligand compounds was determined. Complexing of Eu(III) with aldehyde **III** at low ligand concentrations (close to the lanthanide concentration) leads to formation of 1 : 1 Eu–aldehyde **III** complexes. With ligand concentration increasing to the optimum level, the ratio of the components in the Eu–aldehyde **III** complex reaches 1 : 2. The Tb–acid **IV** complex has the same composition.

Considering formation of coordinatively unsaturated compounds in the present case, it seemed appropriate to examine how I_{lum} of the complexes is affected by surfactants and donor-active additives. Our experiments with cationic, anionic, and nonionic surfactants, as well as with additives containing nitrogen and oxygen donor atoms showed that in the presence of surfactants and additives I_{lum} of the Tb–acid **IV** complex remains unchanged. In the case of the complex of Eu(III) with aldehyde **III**, the largest increase in I_{lum} is observed in the presence of organic bases trioctylphosphine oxide and 1,10-phenanthroline (30- and 100-fold, respectively) (Fig. 2). These significant increases in the analytical signal are associated with the displacement of water molecules from the inner coordination sphere of the metal and the formation of mixed-ligand complexes, leading to decreased nonradiative loss of excitation energy. These processes make it possible to increase the luminescence intensity and quantum yield [12].

As determined by the limiting logarithmic method, there is one 1,10-phenanthroline (trioctylphosphine oxide) molecule in the inner coordination sphere of the complexes, and the component ratio in the Eu(III)–aldehyde–1,10-phenanthroline (trioctylphosphine oxide) mixed-ligand complexes is 1 : 2 : 1. In the formation of mixed-ligand complexes, an additional efficient transfer of the excitation energy from the molecules of the organic bases to the metal ion is also possible. The triplet-state energy level of trioctylphosphine oxide lies at 21980 cm^{-1}, which enables an efficient transfer of the excitation energy to the $^5D_2$ energy level of europium (21500 cm^{-1}). In the case of 1,10-phenanthroline (with the triplet energy level of 20650 cm^{-1}) the energy is transferred to the $^5D_1$ level of the Eu(III) ion (19000 cm^{-1}), and this is followed by nonradiative deactivation to the first excited state $^5D_0$ (17300 cm^{-1}).

In the presence of 1,10-phenanthroline, certain changes in the nature of the luminescence spectrum of the Eu(III) complex with aldehyde **III** were observed (Fig. 2). The splitting of the band due to the $^5D_0 \rightarrow {}^7F_2$ transition is indicative of a change in the symmetry of the coordination polyhedron. In the case of trioctylphosphine oxide this effect is not observed.

The luminescence excitation spectrum of the complex of Eu(III) with aldehyde **III** exhibits a band in

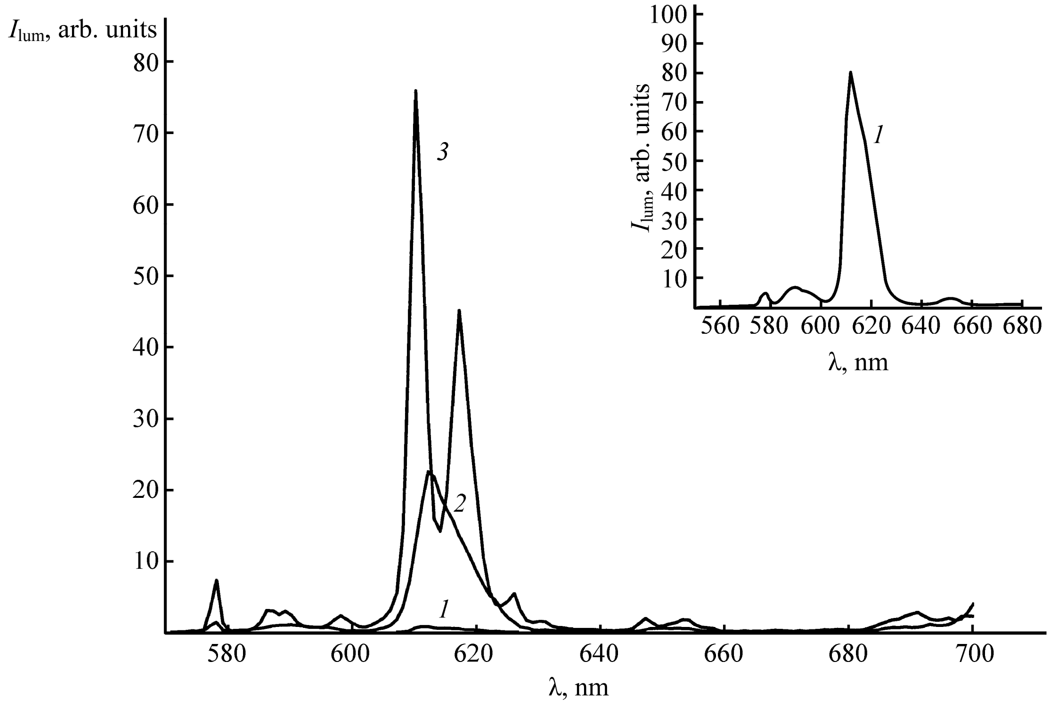


Fig. 2. Luminescence spectra of (*1*) Eu(III)–aldehyde **III**, (*2*) Eu(III)–aldehyde **III**–trioctylphosphine oxide, and (*3*) Eu(III)–aldehyde **III**–1,10-phenanthroline complexes. λ_{exc} = 367 nm; $c_{Eu} = 1 \times 10^{-4}$, $c_{III} = 4 \times 10^{-4}$, and $c_{surf} = 4 \times 10^{-4}$ M.

the 300–400 nm region with the maximum at 367 nm. In the presence of trioctylphosphine oxide the nature of the spectrum in the 200–300 nm region underwent certain changes, with appearance of a band peaked at λ = 292 nm, indicating the formation of mixed-ligand complexes. In the case of 1,10-phenanthroline the nature of the luminescence excitation spectrum remained unchanged (Fig. 3).

One of the main characteristics of luminescence is its duration which is determined by the lifetime of the excited state (τ). The luminescence decay kinetics was examined for the Tb(III) and Eu(III) ions in their complexes with the 2,4-dihydroxybenzoic acid derivatives (see the table). As seen from the tabulated data, in the presence of 1,10-phenanthroline and trioctylphosphine oxide, the lifetime of the excited state of the complex of Eu(III) with aldehyde **III** increases 3.5 and 2 times, respectively. These data also confirm an efficient energy transfer from the ligand to the lanthanide ion.

To evaluate the prospects of the complexes of Tb(III) and Eu(III) with the 2,4-dihydroxybenzoic acid derivatives for application as OLED emissive layers, the thermal stability ranges of these compounds were determined. It was found that, when the temperature increases to 100°C, the complexes undergo dehydration and with further increase in temperature to 300–320°C they are thermally stable. Above 330°C, thermolysis of the complexes begins. The thermal stability of the mixed-ligand complexes of europium(III) with 1,10-phenanthroline and trioctylphosphine oxide is determined by the temperature of the removal and decomposition of the neutral ligand. For all complexes, the onset of decomposition is at ~230°C and above. Due to good luminescent characteristics combined with high thermal stability, the compounds studied are suitable candidates for application as emissive materials in OLEDs.

EXPERIMENTAL

^{1}H NMR spectra of 5–10% solutions of the compounds in $CDCl_3$, DMSO-d_6 were measured on a Varian VXR-300 (operating frequency 300 MHz) and a Bruker AVANCE DRX 500 (operating frequency 500 MHz) spectrometers with TMS as internal reference. The mass spectra were measured on an MX-1321 spectrometer (direct admission, energy of ionizing electrons 70 eV, ionization chamber temperature 220°C) and on a VG 70-70EQ mass spectrometer [fast atom bombardment, 8-keV beam of Xe atoms, *m*-nitrobenzyl alcohol and poly(propylene glycol) matrix]. The IR spectra for solutions in $CHCl_3$ were recorded on a Specord IR-75 spectrophotometer.

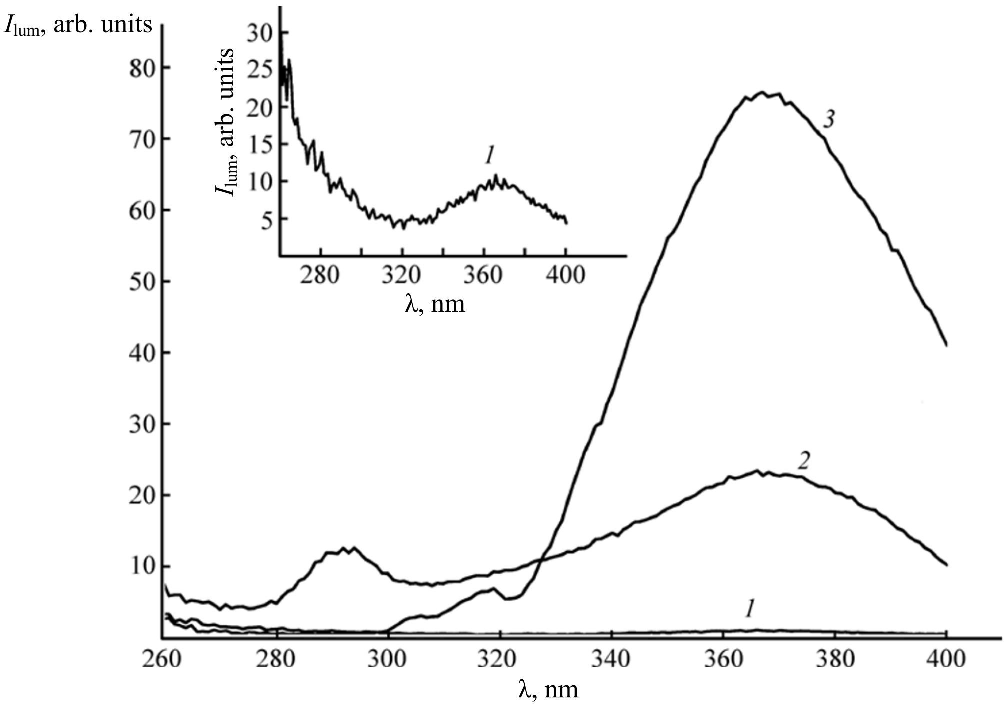


Fig. 3. Luminescence excitation spectra of (*1*) Eu(III)–aldehyde **III**, (*2*) Eu(III)–aldehyde **III**–trioctylphosphine oxide, and (*3*) Eu(III)–aldehyde **III**–1,10-phenanthroline complexes. $c_{Eu} = 1 \times 10^{-4}$, $c_{\mathbf{III}} = 4 \times 10^{-4}$, and $c_{add} = 4 \times 10^{-4}$ M.

The luminescence spectra of the Eu(III) and Tb(III) ions and the lifetimes of the complexes thereof were recorded in the 560–650 and 450–650 nm regions using a Cary Eclipse Varian (Australia) spectrometer with dual light sources (a 150-W continuous spectrum xenon lamp and a flash xenon lamp). The luminescence and excitation spectra of the ligands and complexes were recorded on a Fluorolog FL 3-22 (HORIBA Jobin-Yvon, France) spectrofluorometer with an ozone-free xenon lamp (450 W) and an InGaAs photoresistor (DSS-IGA020L, Electro-Optical Systems, the United States) cooled with liquid nitrogen (for measurements in the IR region).

The triplet-state energy levels of the organic reactants were determined from the phosphorescence spectra of their complexes with yttrium (77 K). The absorption spectra of solutions of the reactants were recorded on a UV-2401 PC Shimadzu (Japan) spectrophotometer. The pH measurements were carried out on an OP-211/1 (Radelkis, Hungary) pH-meter with a glass electrode, which was calibrated using standard buffer solutions.

To study the complexing of the lanthanides with the reactants synthesized, their stock solutions were prepared. The rare-earth element chlorides were obtained by dissolving high-purity (99.988%) oxides in hydrochloric acid (1 : 1), whose excess was subsequently removed by evaporation. The rare-earth element concentration was determined by complexometric titration. The solutions of compounds **III, IV** were prepared by dissolving precisely weighed portions of the substances in ethanol and acetone,

Decay kinetics and intensity of luminescence of Tb(III) and Eu(III) ions in complexes with 2,4-dihydroxybenzoic acid derivatives

Complex	τ, μs	I_{lum}, arb. units
Eu–aldehyde **III**	52	1.2
Eu–aldehyde **III**–1,10-phenanthroline	181	100
Eu–aldehyde **III**–trioctylphosphine oxide	96	30
Tb–acid **IV**	639	35

respectively. The surfactants were purified by recrystallization from ethanol, after which their precisely weighed portions were dissolved in bidistilled water. A solution of 1,10-phenanthroline was prepared by dissolving a precisely weighed portion of the substance in bidistilled water with acidifying to pH 5 using hydrochloric acid. Solutions of trioctylphosphine oxide and triphenylphosphine oxide for preparation of mixed-ligand complexes Eu(III)–aldehyde **III**–trioctylphosphine oxide (triphenylphosphine oxide) were obtained by dissolving the appropriate weighed portions of these substances in ethanol.

2,4-Dihydroxybenzaldehyde **II** was prepared by the procedure described in [16] from 33 g of resorcinol. Yield: 9.6 g (23.3%).

2-Hydroxy-4-[(4-decyloxy)benzoyloxy]benzaldehyde III. To a solution of compound **II** (3.036 g, 0.022 mol) in 50 mL of anhydrous methylene chloride, 4-decyloxybenzoic acid (4.4 g, 0.011 mol) and 4-dimethylaminopyridine (DMAP) (0.14 g, 0.0011 mol) were added. The reaction mixture was stirred for 15 min, after which *N,N*'-dicyclohexylcarbodiimide (DCC) (2.3 g, 0.011 mol) was added. The reaction mass was stirred at room temperature for 10 h. The resulting precipitate was filtered off and washed with anhydrous methylene chloride, after which the solvent was removed in a vacuum, and the residue was recrystallized from a 10 : 1 ethanol–benzene mixture. Yield 2.0 g (45.5%), mp 85°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.08 br.s (1H, OH), 10.25 s (1H, COH), 8.07 d (2H, $H^{8,12}$, ^3J8.56), 7.75 d (1H, H^6, ^3J 8.30), 7.12 d (2H, $H^{9,11}$, ^3J 8.05), 7.04–6.77 m (2H, $H^{3,5}$), 4.09 t (2H, CH_2O, ^3J 5.97), 1.86–1.63 m (2H, $C\underline{H}_2CH_2O$), 1.52–1.11 m (14H, CH_2), 0.86 t (3H, CH_3, ^3J 6.75). Mass spectrum, *m/z*: 399 $[M]^+$. Found, %: C 72.64; H 7.84. $C_{24}H_{30}O_5$. Calculated, %: C 72.36; H 7.54.

2-Hydroxy-4-[(4-decyloxy)benzoyloxy]benzoic acid IV was obtained by the procedure described in [17] from 0.4 g of 2-hydroxy-4-[(4-decyloxy)benzoyloxy]benzaldehyde **III** and 2 mL of freshly prepared Jones reagent [18]. Yield 0.302 g (72.95%), mp 172.9°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 11.25 br.s (1H, COOH), 10.57 s (1H, OH), 8.13 d (2H, $H^{8,12}$, ^3J 7.69), 7.98 d (1H, H^6, ^3J 7.96), 7.15–6.7 m (4H, $H^{3,5,9,11}$), 4.05 t (2H, CH_2O, ^3J 5.49), 2.00–1.70 m (2H, $C\underline{H}_2CH_2O$), 1.65–1.10 m (14H, CH_2), 0.89 t (3H, CH_3, ^3J 6.31). Mass spectrum, *m/z*: 415 $[M]^+$. Found, %: C 69.78; H 7.44. $C_{24}H_{30}O_6$. Calculated, %: C 69.56; H 7.25.

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