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Synthesis of new lanthanide naphthalocyanine complexes based on 6,7-bis(phenoxy)-2,3-naphthalodinitrile and their spectral and electrochemical investigation

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A number of naphthalocyanine and dinaphthalocyanine complexes of the rare-earth elements based on 6,7-bis(phenoxy)-2,3-naphthalodinitrile obtained for the first time has been synthesized and their spectral properties have been investigated. Electrochemical behavior of lutetium [bis(octaphenoxy)naphthalocyanine] in the thin hydrophobic films has been studied.

Key words: 6,7-bis(phenoxy)-2,3-naphthalodinitrile, naphthalocyanines, dinaphthalocyanine complexes, electronic absorption spectra, cyclic voltammetry, hydrophobic mark, lanthanides.

Phthalocyanine complexes are widely studied. Due to the presence of a long multicontour conjugation system in molecules of these compounds, they are used in catalysis,[1] nonlinear optics,[2] and cancer diseases therapy.[3] However, the structural phthalocyanine analogs, 2,3-naphthalocyanines, are studied considerably less.

It is known that the widening of the conjugation system causes a considerable (up to 100 nm) bathochromic shift of the Q-band in the electronic absorption spectra of naphthalocyanines in comparison with the spectra of phthalocyanines. An introduction of functional groups into naphthalocyanine ligands, a possibility of a metal ion incorporation into the center of a macrocycle, and an ability, similarly to phthalocyanines, to form two-deck complexes allows one to vary their properties within a wide range. Therefore, a directed synthesis of new substituted naphthalocyanines is an important problem, as well as a study of their properties in order to establish the structure—properties relationship and to broaden the scope of their application.

The present work deals with the synthesis of both the planar and the sandwich compounds on the basis of 6,7-bis(phenoxy)-2,3-naphthalodinitrile (**1**) synthesized for the first time. For obtaining of naphthalocyanine complexes, several methods were chosen: the synthesis with the use of 3,4,12,13,21,22,30,31-octaphenoxynaphthalocyanine (preliminary obtained by demetallation of the corresponding magnesium complex **2**) and the corresponding rare-earth element (REE) acetate; the reaction of naphthalodinitrile **1** and REE salt in a melt; as well as the synthesis under microwave irradiation carried out for naphthalocyanines for the first time.

The free ligand was obtained according to Scheme 1.

This approach allowed us increase the total yield of the target compound **3** to more than 2 times in comparison with the alternative one-step synthesis of unsubstituted free naphthalocyanine from naphthalodinitrile.[4]

The synthesis of compound **1** was carried out starting from 6,7-dibromo-2,3-naphthalodinitrile, obtained from 4,5-dibromo-*o*-xylene in 84% yield according to the standard procedure[5], and phenol in the presence of K_2CO_3 in anhydrous DMF under argon at 130 °C; the reaction mixture was kept at this temperature for 12 h. According to the TLC data, the formation of the target product was observed during 2 h. On elevation of the temperature above 130 °C, the yield of the target product decreases due to the phenol destruction. 6,7-Dibromo-2,3-naphthalodinitrile was isolated in a pure form by column chromatography, its composition and structure were confirmed by the elemental analysis, ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry data. The yield of compound **1** was 65%. Due to the decrease in the reaction time, as well as to the optimization of purification conditions, we succeeded in considerable increase in the reaction product yield relatively to its analog described in the procedure from Ref. 6.

To obtain magnesium complex **2** according to a modified procedure,[7] pre-synthesized naphthalodinitrile **1** and

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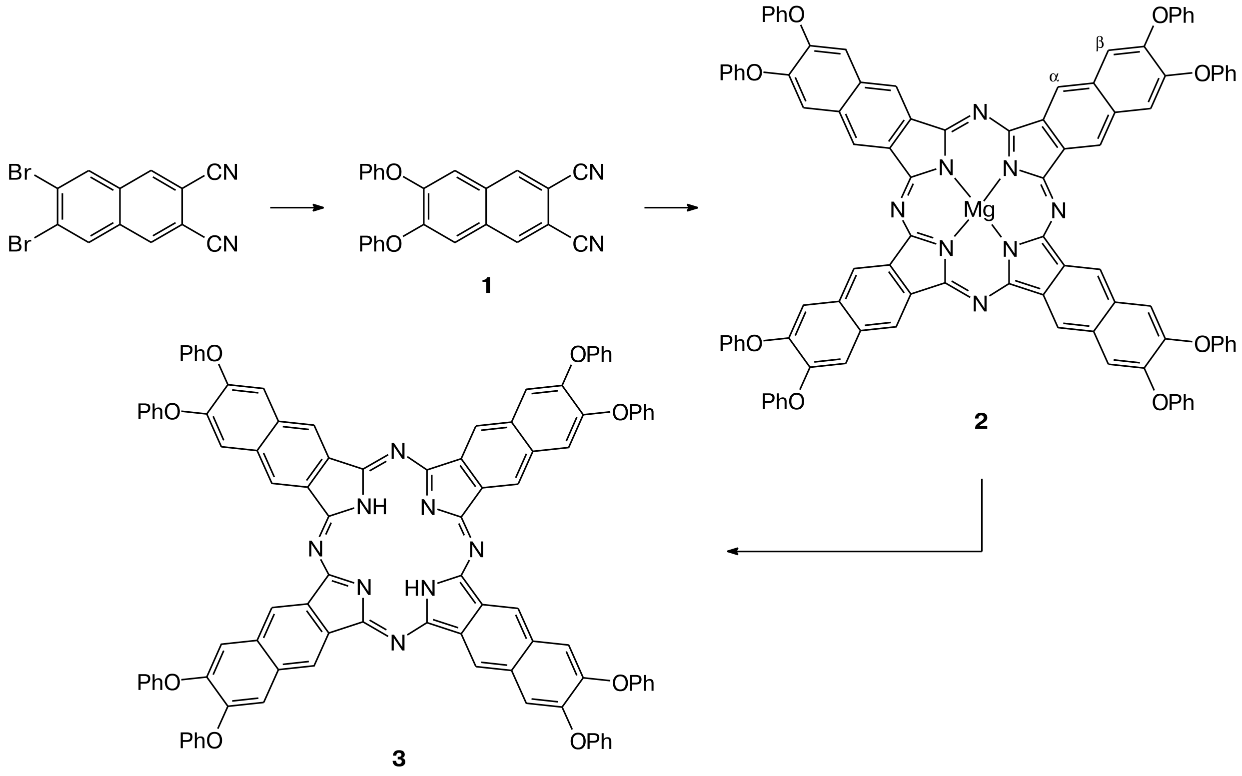
Scheme 1

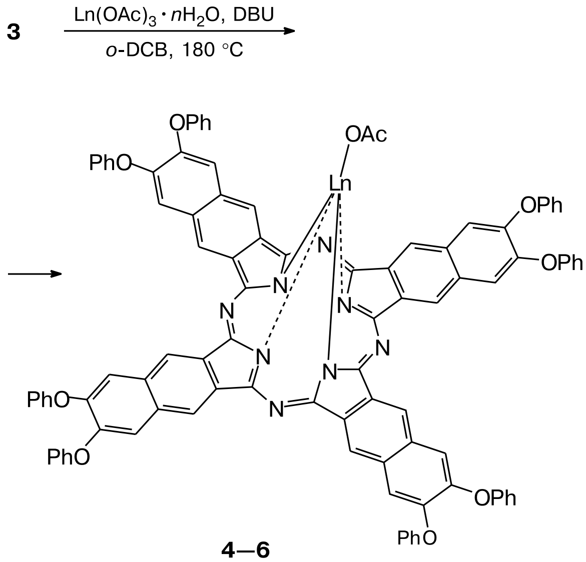


$Mg(OAc)_2 \cdot 2H_2O$ (4 : 1) were used in *n*-octanol in the presence of DBU. The synthesis was conducted until complete disappearance of the starting naphthalodinitrile **1**, that was estimated from TLC. As a rule, the process time was 3 h. Compound **2** was obtained in 68% yield. It was found that compound **2** is extremely unstable in solution, as it was observed earlier[6] for structurally similar naphthalocyanines.

Free ligand **3** was obtained by dissolution of magnesium complex **2** in concentrated sulfuric acid with subsequent pouring of the solution on ice. A precipitate formed was filtered off, washed with methanol and the solid residue was dried in a vacuum drying oven. The yield of product **3** was 92%.

Mononaphthalocyanines **4—6** were synthesized according to Scheme 2 starting from free ligand **3** and $Ln(OAc)_3 \cdot nH_2O$ by reflux in *o*-dichlorobenzene (*o*-DCB) in the presence of DBU.[8]

Scheme 2



Ln = Lu (**4**), Er (**5**), Eu (**6**)

According to the TLC and UV—Vis data, the target compounds **4—6** were obtained already in 15 min after the synthesis began. The reaction time was 1 h. It was found that there is no formation of dinaphthalocyanine under these conditions, even when the ligand : REE salt ratio was 2 : 1 and when the reaction time was increased to 1.5—2 h. Apparently, this results not only from the temperature effect on the coordination of the second macrocycle in the REE ion sphere, but also from the coordinating ability of DBU, as well as from the strength of the metal—counterion bond, that agrees with the literature data.[9] The yields of products **4—6** are given in Table 1.

Dinaphthalocyanine complexes **7—9** were synthesized by the reaction of naphthalodinitrile and REE salt in a melt

Table 1. Characteristics of naphthalocyanine **3** and naphthalocyanine complexes **2** and **4—9**

Complex	Yield (%)	λ_{max}/nm (THF)	MS*, *m/z*
2	68	359, 681, 727, 762	1473 $[M]^+$, 1381 $[M - OPh]^+$
3	92	330, 717, 779 332, 703, 751, 786**	1451 $[M]^+$, 1358 $[M - OPh]^+$
4	82	355, 682, 762	1685 $[M]^+$, 1777 $[MOAc + HY]^+$
5	84	352, 679, 760	1677 $[M]^+$, 1771 $[MOAc + HY]^+$.
6	83	352, 681, 760	1662 $[M]^+$, 1756 $[MOAc + HY]^+$
7	41	339, 590, 618, 677, 758	3073 $[M]^+$, 2980 $[M - OPh]^+$, 2888 $[M - 2\ OPh]^+$, 2796 $[M - 3\ OPh]^+$, 2703 $[M - 4\ OPh]^+$
8	47	336, 591, 615, 679, 762	3065 $[M]^+$, 2973 $[M - OPh]^+$, 2881 $[M - 2\ OPh]^+$
9	55	339, 594, 623, 682, 769	3050 $[M]^+$, 2958 $[M - OPh]^+$

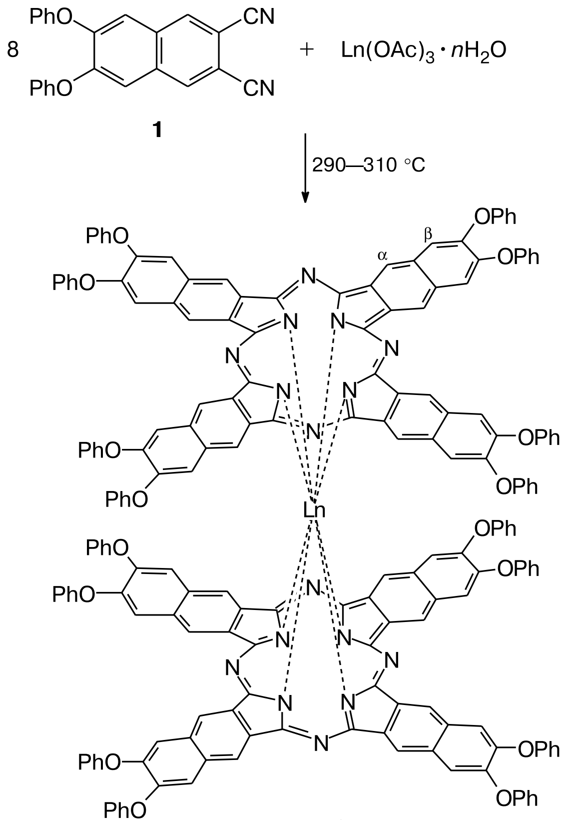
* HY is a matrix molecule (3,5-dihydroxybenzoic acid was used as the matrix).
** *o*-DCB.

(Scheme 3). This method considerably differs from the synthesis in solution since the starting nitrile serves simultaneously as the reagent and the reaction medium.[10,11]

According to this method, the synthesis of dinaphthalocyanines **7—9** was performed by melting of a mixture of dinitrile **1** with the corresponding REE acetates by the gradual increase of temperature from 220 to 310 °C and by keeping at this temperature until the reaction mixture was solidified (~2 h). The use of higher temperatures than it was in the procedure described earlier[10] allowed us to obtain the target compounds in considerably higher yields. The reaction course was monitored using spectrophotometry. When the syntheses were carried out at 310 °C, the formation of mononaphthalocyanine was not detected, that, apparently, is caused by its high reactivity under the reaction conditions. The reaction mixture was quenched by dissolution in DMF and further precipitation with methanol. The precipitate formed was filtered off, washed with methanol and water, and dried. Compounds **7—9** were purified using chromatography.

It was found that the yields of dinaphthalocyanine complexes gradually decrease on going from europium to lutetium, that agrees with the literature data.[12] It was noted[12] that the change of the yield correlates with the size of the central ion. Apparently, this is caused by a decrease in the REE ionic radius from europium to lutetium and by the corresponding increase in the sterical effect.

Scheme 3



7—9

Ln = Lu (**7**), Er (**8**), Eu (**9**)

In addition to the melting method, the europium and erbium dinaphthalocyanine complexes were synthesized using microwave irradiation (MW). This method has been suggested for the first time[13] for the synthesis of unsubstituted and octa-*tert*-butyl-substituted REE diphthalocyanines and so far has not been used for preparation of naphthalocyanine complexes.

Naphthalodinitrile **1** and acetates of the corresponding REE salts were used to obtain the dinaphthalocyanine complexes. The synthesis was carried out by irradiation of a mixture of reagents in a microwave oven (Samsung, a 1714R model). The power of irradiation was varied from 300 to 1000 W, the time, from 3 to 10 min. The following conditions were found to be optimal for the synthesis of dinaphthalocyanines with the use of the MW energy: the power of 700 W and the reaction time of 5—7 min. The use of microwave irradiation of higher power led to resinification of 2,3-naphthalodinitrile **1**. The use of MW allowed us to considerably simplify the synthesis (which can be carried out solvent-free), as well as to decrease the synthesis time from several hours to several minutes. The yields of dinaphthalocyanines given in Table 1 are comparable with the results obtained by the melting method.

To confirm the structures of the REE naphthalocyanine complexes obtained, ^{1}H NMR spectroscopy, MALDI-TOF mass spectrometry, and the UV—Vis spectroscopy were used. The presence of the $[Nc^{\bullet-}Ln^{3+}Nc^{2-}]^0$ radical fragment in the dinaphthalocyanine molecules hinders obtaining satisfactory NMR data in common solvent. Therefore, for recording the ^{1}H NMR spectra, the sandwich-like complexes were converted to the forms containing no radical fragments using procedure described earlier.[12]

Hydrazine hydrate (1—2 vol.%) was added to a solution of REE dinaphthalocyanine in deuterated THF, that resulted in the reduction of the radical fragment $Nc^{\bullet-}$ to dianion Nc^{2-} (Scheme 4).

Scheme 4

$$[Nc^{\bullet-}Ln^{3+}Nc^{2-}]^0 \longrightarrow [Nc^{2-}Ln^{3+}Nc^{2-}]^-$$

Thus, both macrocycles in the dinaphthalocyanine molecule become diamagnetic, that allows us to obtain satisfactory signals in the ^{1}H NMR spectrum. For europium and, especially, for erbium dinaphthalocyanines, the upfield shift of all the signals was observed, that is explained by the paramagnetic nature of these metal ions. Deshielding of the protons is the largest in the case of $[(PhO)_8Nc]_2Er$, that was noted earlier[9] for the symmetrically substituted phthalocyanine complexes, and for the first time was demonstrated by us for the naphthalocyanine complexes. In the ^{1}H NMR spectrum of magnesium naphthalocyanine **2**, the resonance signals characteristic of nitrile **1** upfield shifted by 0.4—0.9 ppm were also observed. The protons of the phenoxy substituents of erbium **8** and europium **9** dinaphthalocyanines, as well as of magnesium naphthalocyanine **5** resonate as wide signals, for which it is impossible to determine the spin-spin coupling constants.

The NMR data for compound **1**, magnesium naphthalocyanine **2**, lutetium **7**, erbium **8**, and europium **9** dinaphthalocyanines are given in Table 2.

The structures of all the naphthalocyanine complexes obtained were confirmed by MALDI-TOF mass spectra. This method is used the most widely for analysis of phthalocyanine compounds,[12,14] due to the mild conditions of their ionization and relatively simple analysis of the spectra obtained. In the spectra of compounds **7—9**, the peaks of the single-charged ions were observed with the masses corresponding to the molecular ions of the target substances. It was found that the fragmentation occurs by elimination of phenoxy groups from the macromolecule. In the series of Lu, Er, and Eu dinaphthalocyanine complexes the number of eliminating substituents decreases from four (in the case of lutetium complex) to one (in the case of europium complex). This fact, as well as the data in Table 1 suggest the higher stability of europium dinaphthalocyanine **9** in comparison with erbium complex **8** and, especially, with lutetium complex **7**. Similarly to compound **9**, the fragmentation with the loss of only one phenoxy group takes place also in the case of free ligand **3** and magnesium complex **2**. The mass spectrometric data are given in Table 1.

Table 2. ^{1}H NMR data for compound **1**, magnesium naphthalocyanine complex (**2**), and lutetium (**7**), erbium (**8**), and europium (**9**) dinaphthalocyanine complexes

Compound	δ* (*J*/Hz)		
	α-H_{Ar}	β-H_{Ar}	H_{OPh}
1	8.69 (s, 2 H)	7.66 (s, 2 H)	7.19 (d, 4 H_o, J = 7.8); 7.26 (t, 2 H_p, J = 7.3); 7.48 (t, 4 H_m, J = 7.3)
2	9.57 (s, 8 H)	8.04 (s, 8 H)	7.21—7.45 (м, 40 H)
7	9.09 (s, 16 H)	8.06 (s, 16 H)	7.21 (t, 16 H_p, J = 7.1); 7.29 (d, 32 H_o, J = 7.7); 7.50 (t, 32 H_m, J = 7.15)
8	36.71 (s, 16 H)	19.88 (s, 16 H)	9.96 (m, 16 H_p); 10.57 (m, 32 H_m) 12.06 (m, 32 H_o)
9	11.07 (s, 16 H)	8.98 (s, 16 H)	7.05—7.75 (m, 80 H)

* The spectra of compound **1** were recorded in DMSO-d_6, of compounds **2** and **7—9**, in THF-d_8 with $N_2H_4 \cdot H_2O$ (1—2 vol.%) as the additive.

Spectrophotometry allows the complete solution of the problem of identification of various forms of complexes during the synthesis and purification of naphthalocyanines. We have studied the UV—Vis spectra for all the compounds obtained.

The spectra of mononaphthalocyanines are characterized by an intensive Q-band in the region of 760 nm (which is typical of Nc^{2-} and corresponds[15] to the electronic transitions $a_{1u} \rightarrow e_g$), as well as by a vibrational satellite of lower intensity in the region of 680—720 nm. The Soret band, responsible for the transition $a_{2u} \rightarrow e_g$, has the maximum in the region of 340—350 nm. In contrast to the nonmetallated phthalocyanines, of which the splitting of the Q-band (Fig. 1) into two components in the region of 650—720 nm is characteristic,[9] in the UV—Vis of naphthalocyanine ligands, the splitting of the Q-band is not observed. It was found[15] by the MO calculations that this phenomenon results from the degeneration of the free naphthalocyanine b_{1g}- and b_{2g}-orbitals.

In the spectra of dinaphthalocyanines obtained, a Q-band in the region of 755—770 nm and a characteristic band in the region of 590 nm caused by the presence of an unpaired electron in the molecule are observed. The Soret band maximum is in the region of 335—340 nm (see Table 1).

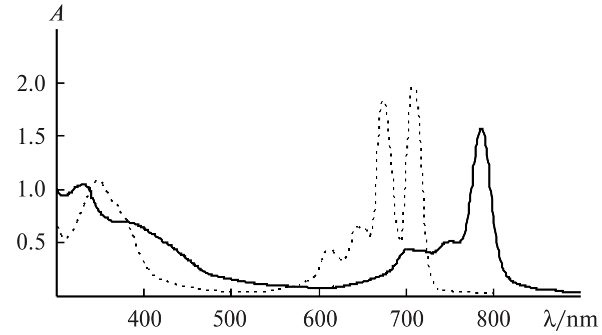


Fig. 1. The UV—Vis spectra of free phthalocyanine $^{Et}PcH_2$ (the dotted line) and naphthalocyanine $[(PhO)_8Nc]H_2$ (solid line) in *o*-DCB.

Analysis of the UV—Vis spectra of dinaphthalocyanine complexes obtained allowed us to reveal a number of features characteristic of these compounds. Thus, on going from $[(PhO)_8Nc]_2Lu$ to $[(PhO)_8Nc]_2Eu$ a bathochromic shift of the Q-band by 11 nm is observed caused by an increase in the ionic radius. In this case, the position of the Soret band changes inconsiderably.

The absorption spectra of the dinaphthalocyanine complexes in solution change on prolonged exposure to the light, in particular, a decrease in the Q-band intensity accompanied by appearance of the absorption bands in the regions of 600 and 800 nm is observed. It was found that addition of $N_2H_4 \cdot H_2O$ to the solution leads to the quantitative recovery of the starting compound, which is confirmed by the UV—Vis data. This allowed us to suggest a reversible character of the oxidation process of dinaphthalocyanines in air.

To confirm such a suggestion, a behavior of symmetrical lutetium and erbium dinaphthalocyanine complexes obtained has been investigated in the processes of chemical oxidation and reduction.

For oxidation, a solution of dinaphthalocyanine in THF was treated with bromine vapors. A decrease in intensity of absorption in the region of the Q-band, right up to its complete disappearance, was observed. Simultaneously, the appearance of two new absorption maxima (at 816 and 634 nm for lutetium dinaphthalocyanine and at 822 and 641 nm for erbium dinaphthalocyanine) was observed, whereas the position of the Soret band was not shifted. As an example, the UV—Vis spectra recorded during oxidation of $[(PhO)_8Nc]_2Lu$ in THF are given in Figure 2. On treatment with hydrazine hydrate, the starting neutral form of dinaphthalocyanine is slowly recovered, and further reduced to dianion in excess of hydrazine hydrate.

To carry out the reduction, a small amount of hydrazine hydrate (which did not considerably change the solution volume) was added to a solution of the starting dinaphthalocyanine in THF. During this, a decrease in intensity of the absorption in the region of the Q-band was observed with the simultaneous appearance of two new absorption maxima: the intensive one (at 698 nm) and the less intensive (at 820 nm) for lutetium dinaphthalocyanine, and at 701 and 808 nm, respectively, for erbium dinaphthalocyanine. A bathochromic shift of the Soret band (by 6—7 nm) also takes place. The change of UV—Vis spectra, recorded during the reduction of erbium dinaphthalocyanine complex, is given in Figure 3.

The redox-transformations in all the cases under study are characterized by the presence of the isobestic points. This suggests an ability of naphthalocyanines obtained to be reversibly oxidized and reduced under action of the corresponding chemical agents and the presence of electrochromic properties. Therefore, it was of interest to carry out more detailed study of electrochemical behavior of the complexes synthesized. As the example, the results of electrochemical study of complex **7** by cyclic voltammetry method are given in Figure 4.

A working disk electrode made of the side section of the highly oriented pyrolytic graphite was entirely covered with a thin film of the lutetium naphthalocyanine solution in nitrophenyl octyl ether. Since the latter does not mix with

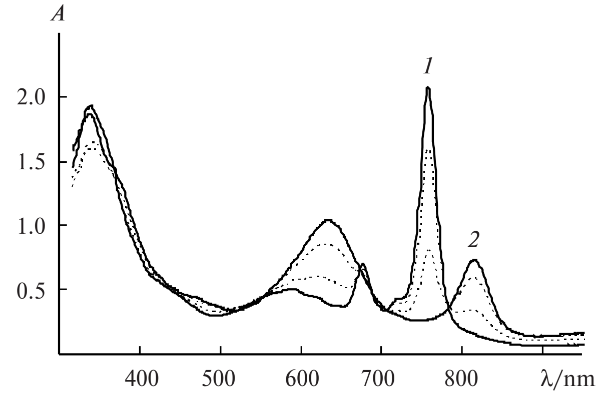


Fig. 2. The UV—Vis spectra of the neutral (*1*) and the oxidized with bromine (*2*) forms of $[(PhO)_8Nc]_2Lu$ in THF, the dotted lines correspond to the intermediate forms.

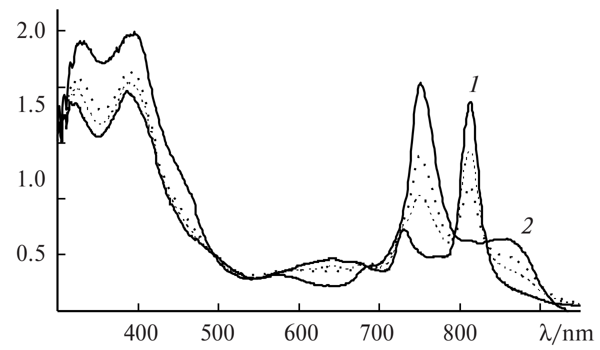


Fig. 3. The UV—Vis spectra of the neutral (*1*) and the reduced with hydrazine hydrate (*2*) forms of $[(PhO)_8Nc]_2Er$ in THF, the dotted lines correspond to the intermediate forms.

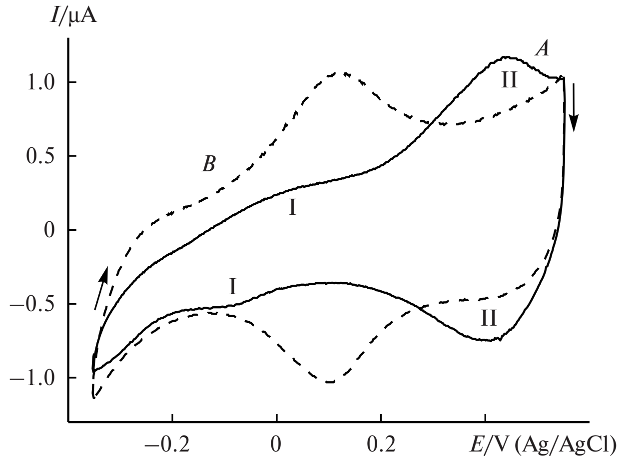


Fig. 4. Cyclic voltammograms of the liquid film of lutetium dinaphthalocyanine, 0.2 μL in nitrophenyl octyl ether (1 mg mL^{-1}) on the highly oriented pyrolytic graphite (~3 mm in diameter); 0.1 *M* KCl (*A*) or $KClO_4$ (*B*), the potential scan rate was 20 mV s^{-1}.

water, the working electrode turned out to be modified with a thin liquid film of solution of the hydrophobic redox-active lutetium naphthalocyanine when an aqueous solution of the supporting electrolyte was used.

To maintain the electroneutrality of the organic phase of the film, the oxidation of lutetium naphthalocyanine should be accompanied by a simultaneous crossing the interface between two phases (nitrophenyl octyl ether—water) by ions. In another words, the electrode process includes a simultaneous crossing the interface electrode—film by an electron and the interface film—water by ions.

In the cyclic voltammogram recorded at the modified electrode in aqueous solution of potassium chloride (curve *A*), two pairs of peaks, I and II, are observed corresponding to the redox-activity of lutetium naphthalocyanine. It is known[16,17] that the redox-transition I (one-electron reduction) is accompanied by the transfer of K^+ ions from water into the organic phase and back, whereas the redox-transition II (one-electron oxidation), by the transfer of Cl^- ions into the organic phase. The difference in intensities of peaks I and II is caused by the difference in the interface crossing rates for anions and cations. In curve *B* recorded in aqueous solution of potassium perchlorate, only one pair of peaks of redox-activity II is observed, which is related to the transfer of ClO_4^-. The potential of this redox-transition is shifted to cathode potentials region with respect to the position of the redox-activity peaks observed in the solution containing Cl^- ion (curve *A*). The difference in positions of the peaks of redox-activity II resulted from the difference in hydrophobic properties of the crossing anion: on its increase, the potential of redox-activity is shifted toward the cathode region. The peaks of redox-activity I accompanied by the transfer of cations through the interface was not observed in curve *B* due to the strong cathodic shift of the peaks of redox-activity II caused by the increase in hydrophobic properties of the aqueous phase anion (ClO_4^-). A similar shift of the redox-activity potential of a hydrophobic substance toward the cathodic region was observed earlier for decamethylferrocene,[18—20] metalloporphirines,[21,22] redox-active oils,[23—26] and redox-active polymers.[27]

In conclusion, lutetium naphthalocyanine can be used for the evaluation of hydrophobic properties of anions during their transfer through the interface of two unmixable liquids.

Experimental

Electronic absorption spectra in the visible region were obtained with Helios-α spectrophotometer in 0.5- and 1-cm thick quartz cuvettes using C_6H_6, THF, and *o*-DCB as the solvents. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM-300 (300.14 and 75.47 MHz, respectively) and Bruker WM-250 spectrometers (250.13 and 62.90 MHz, respectively) in $CDCl_3$, DMSO-d_6, or THF-d_8. Chemical shifts are given in δ scale relatively to Me_4Si. Preparative TLC was performed on Merck Silica Gel 60 F_{254} and Merck Aluminum Oxide F_{254} neutral plates, column chromatography, on Lancaster Silica Gel 60 (0.060—0.200 mm), Merck Silica Gel 40 (0.063—0.200 mm), and Merck Aluminum Oxide 90 sorbents. Mass spectra were recorded with a Finnigan MAT INSOC-50 (EI, 70 eV) and VISION-2000 instruments (MALDI-TOF). IR spectra were recorded with a Specord M-70 and Specord UR-20 spectrophotometers in Nujol. All solvents were purified according to the standard procedures just before use. Salts $Lu(OAc)_3 \cdot 4H_2O$, $Er(OAc)_3 \cdot 2H_2O$, $Eu(OAc)_3 \cdot 3H_2O$, and $Mg(OAc)_2 \cdot 2H_2O$ were kept before synthesis for 5 h in a vacuum drying oven at 100 °C. The synthesis of naphthalocyanines under microwave irradiation was performed using a Samsung 1714R device.

6,7-Bis(phenoxy)-2,3-naphthalodinitrile (1). 6,7-Dibromo-2,3-naphthalodinitrile (5.23 g, 0.016 mol), phenol (4.30 g, 0.046 mol), freshly calcined potash (26.86 g, 0.195 mol), and anhydrous DMF (100 mL) were placed into a 250-mL three-neck flask equipped with a reflux condenser, thermometer, and a drying tube packed with $CaCl_2$. The mixture was heated to 130 °C and kept for 12 h under argon. Monitoring of the reaction course was performed by TLC (SiO_2 F_{254}, eluent: C_6H_6). After the reaction was complete, the cooled reaction mixture was poured into water (400 mL). A precipitate formed was filtered off, washed with water until neutral pH, and dried at 60 °C. The mass obtained was subjected to column chromatography (SiO_2, eluent: C_6H_6), the target product isolated was dried at 60 °C to obtain compound **1** (3.71 g, 64%) as white needle-like crystals, m.p. 219—220 °C, R_f = 0.33 (SiO_2 F_{254}, eluent: C_6H_6). Found (%): C, 79.36; H, 4.08; N, 7.61. $C_{24}H_{14}N_2O_2$. Calculated (%): C, 79.56; H, 3.87; N, 7.73. ^1H NMR ($(CD_3)_2SO$), δ: 7.19 (d, 4 H, *o*-H_{PhO}, *J* = 7.8 Hz); 7.26 (t, 2 H, *p*-H_{PhO}, *J* = 7.4 Hz); 7.48 (t, 4 H, *m*-H_{PhO}, *J* = 7.3 Hz); 7.66 (s, 2 H, β-H_{Ar}(5), β-H_{Ar}(8)); 8.70 (s, 2 H, α-H_{Ar}(1), α-H_{Ar}(4)). ^{13}C NMR ($(CD_3)_2SO$), the atoms numeration is given according to the IUPAC rules, δ: 107.2 (C_{Ar}(2), C_{Ar}(3)); 115.3 (CN); 116.0 (C_{Ar}(5), C_{Ar}(8)); 118.6 (C_{OPh}(2), C_{OPh}(6)); 124.3 (C_{Ar}(9), C_{Ar}(10)); 127.8 (C_{OPh}(4)); 129.9 (C_{Ar}(1), C_{Ar}(4)); 134.5 (C_{OPh}(3), C_{OPh}(5)); 150.4 (C_{Ar}(6), C_{Ar}(7)); 154.7 (C_{OPh}(1)). IR, ν/cm^{-1}: 2245 ($\nu_{C\equiv N}$), 1592 ($\nu_{C=C}$), 1496 ($\nu_{C=C}$), 1465 ($\nu_{C=C}$), 1385 (ν_{C-O}). MS (EI, 70 eV), *m/z*: 362 $[M]^+$.

Magnesium (3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine (2). Compound **1** (500 mg, 1.38 mmol), *n*-octanol (4 mL), and magnesium acetate (240 mg, 1.35 mmol) were placed in a 20-mL two-neck flask equipped with a distilling column, and a drying tube packed with $CaCl_2$. The mixture was heated until complete dissolution of the nitrile followed by addition of DBU (70 mg, 0.46 mmol) and then refluxed for 3 h under Ar. Monitoring of the reaction course was performed by TLC (SiO_2, eluent: C_6H_6). After the reaction was complete, methanol (80 mL) was added to the cooled reaction mixture. A precipitate formed was filtered off, washed with water, aq. methanol, and dried in air. The mass obtained was dissolved in THF and precipitated with methanol. A bright green precipitate formed was filtered off, washed with hot methanol (4×10 mL), and dried in a vacuum drying oven at 60 °C to obtain compound **2** (345 mg, 68%) as a dark-green powder. ^{1}H NMR (THF-d_8), δ: 7.18—7.42 (m, 20 H, H_{OPh}); 8.03 (s, 8 H, β-H_{Ar}); 9.54 (s, 8 H, α-H_{Ar}). MS (MALDI-TOF), *m/z*: 1473 $[M]^+$, 1381 $[M - OPh]^+$. UV—Vis (THF), λ_{max}/nm: 359, 681, 727, 762.

(3,4,12,13,21,22,30,31-Octaphenoxy)-2,3-naphthalocyanine (3). Concentrated H_2SO_4 (17 mL, $\rho = 1.84$ g mL^{-1}) was added to a solution of compound **2** (100 mg, 0.07 mmol) in THF (15 mL). The mixture was vigorously stirred for 2—3 min under cooling in an ice-water bath until complete dissolution. The reaction mixture obtained was poured on ice. A precipitate formed was filtered off, sequentially washed with deionized water until neutral pH, aq. methanol, and hot methanol, and dried in a vacuum drying oven at 60 °C to obtain compound **3** (92 mg, 92%) as a dark-green powder. MS (MALDI-TOF), *m/z*: 1451 $[M]^+$, 1358 $[M - OPh]^+$. UV—Vis (THF), λ_{max}/nm: 330, 717, 779.

Synthesis of lanthanide (3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanines (general procedure). Compound **3** (110 mg, 0.076 mmol), $Ln(OAc)_3 \cdot nH_2O$ (0.380 mmol), and *o*-DCB (3 mL) were placed in a 20-mL two-neck flask equipped with a distilling column and a drying tube packed with $CaCl_2$. The mixture was heated until complete dissolution of the starting substances followed by addition of catalytic amount of DBU and reflux for 1 h under Ar. Monitoring of the reaction course was performed by TLC (Al_2O_3, eluent: chloroform) and UV—Vis spectra. After the reaction was complete, the mass was treated similarly to the procedure for compound **2**.

Lutetium (3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine acetate (4). The yield was 105 mg (82%). UV—Vis (THF), λ_{max}/nm: 355, 682, 762. MS (MALDI-TOF), *m/z*: 1685 $[M]^+$, 1777 $[M - OAc + HY^*]^+$.

Erbium (3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine acetate (5). The yield was 107 mg (84%). UV—Vis (THF), λ_{max}/nm: 352, 679, 760. MS (MALDI-TOF), *m/z*: 1677 $[M]^+$, 1771 $[M - OAc + HY]^+$.

Europium (3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine acetate (6). The yield was 105 mg (83%). UV—Vis (THF), λ_{max}/nm: 352, 681, 760. MS (MALDI-TOF), *m/z*: 1662 $[M]^+$, 1756 $[M - OAc + HY]^+$.

Synthesis of lanthanide bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanines] 7—9 in a melt of compound 1 (general procedure). Compound **1** (0.3 g, 0.83 mmol) and $Ln(OAc)_3 \cdot nH_2O$ (0.17 mmol) (Ln = Lu, Er, Eu) were placed in a round-bottom flask equipped with a distilling column and thermometer, the mixture was started to be heated with gradual elevation of temperature from 220 to 310 °C, then, the reaction mixture was kept at this temperature for 2 h until the reaction mass solidified. After the synthesis was complete, the reaction mixture was dissolved in DMF and dinaphthalocyanine was precipitated with methanol. The precipitate was filtered off and dried at 70 °C, dissolved in benzene, and subjected to chromatography on a column with Al_2O_3 with THF—C_6H_6 (1 : 10) as the eluent.

Lutetium bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine] (7). The yield was 130 mg (41%). UV—Vis (THF), λ_{max}/nm: 339, 590, 618, 677, 758. MS (MALDI-TOF), *m/z*: 3073 $[M]^+$, 2980 $[M - OPh]^+$, 2888 $[M - 2\ OPh]^+$, 2796 $[M - 3\ OPh]^+$, 2703$[M - 4\ OPh]^+$. ^{1}H NMR (THF-d_8), δ: 7.21 (t, 16 H, *p*-H_{OPh}, $J = 7.1$ Hz); 7.29 (d, 32 H, *o*-H_{OPh}, $J = 7.7$ Hz); 7.50 (t, 32 H, *m*-H_{OPh}, $J = 7.2$ Hz); 8.04 (s, 16 H, β-H_{Ar}); 9.07 (s, 16 H, α-H_{Ar}).

Erbium bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine] (8). The yield was 150 mg (47%). UV—Vis (THF), λ_{max}/nm: 336, 591, 615, 679, 762. MS (MALDI-TOF), *m/z*: 3065 $[M]^+$, 2973 $[M - OPh]^+$, 2880 $[M - 2\ OPh]^+$. ^{1}H NMR (THF-d_8), δ: 9.95—12.04 (m, 40 H, H_{OPh}); 19.87 (s, 16 H, β-H_{Ar}); 36.72 (s, 16 H, α-H_{Ar}).

Europium bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanine] (9). The yield was 174 mg (55%). UV—Vis (THF), λ_{max}/nm: 339, 594, 623, 682, 769. MS (MALDI-TOF), *m/z*: 3050 $[M]^+$, 2958 $[M - OPh]^+$. ^{1}H NMR (THF-d_8), δ: 7.07—7.70 (m, 40 H, H_{OPh}); 8.96 (s, 16 H, β-H_{Ar}); 11.06 (s, 16 H, α-H_{Ar}).

Synthesis of lanthanide bis[(3,4,12,13,21,22,30,31-octaphenoxy)-2,3-naphthalocyanines] (8, 9) using microwave irradiation (general procedure). Compound **1** (0.3 g, 0.83 mmol) and $Ln(OAc)_3 \cdot nH_2O$ (0.17 mmol) (Ln = Er, Eu) were placed into a round-bottom flask and the mixture was placed into a microwave oven with the power of irradiation of 700 W. The reaction time was 5—7 min. After the synthesis was complete, the reaction mixture was dissolved in DMF, and dinaphthalocyanine was precipitated with methanol. The precipitate was filtered off and dried at 70 °C, dissolved in benzene, and subjected to chromatography on a column with Al_2O_3 and THF—C_6H_6 (1 : 10) as the eluent. The yields of compounds **8** and **9** were 105 (33%) and 123 mg (39%), respectively.

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* HY is a matrix molecule.

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