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Hexadecapropyloxy-substituted diphthalocyanine complexes of rare-earth elements: synthesis, spectroscopic and electrochemical studies

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Hexadecapropyloxy-substituted diphthalocyanine complexes of rare-earth elements (REE = Lu, Tm, Sm) were synthesized. The new symmetrically substituted diphthalocyanine complexes prepared starting from 4,5-dipropyloxyphthalodinitrile (phthalogen) are characterized by better solubilities compared to the known hexadecamethyl-substituted diphthalocyanine complexes of the same REE. Spectral and electrochemical characteristics of the complexes were studied. The compounds can be used as materials for high-contrast electrochromic devices.

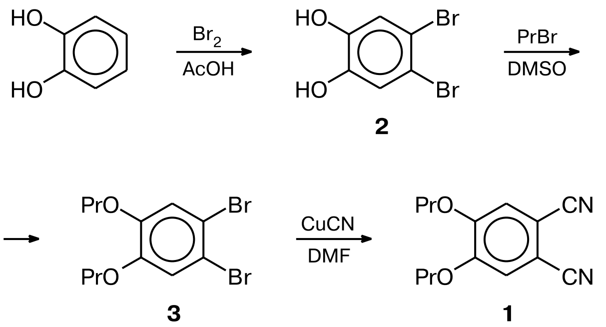
Key words: diphthalocyanines, rare-earth elements, complexes, electrochemistry, electronic absorption spectra.

Recently, phthalocyanines and their complexes with various metals have attracted considerable attention because of their distinct electrochromic and semiconductor properties and unique spectral characteristics that open up new fields of application.[1—7] Many of these characteristics are particularly pronounced with diphthalocyanine complexes. This makes the synthesis of new, functionally substituted diphthalocyanine complexes topical.

The subject of our earlier studies[8,9] were *tert*-butyl-substituted diphthalocyanines. In this work we report on the synthesis of hexadecapropyloxy-substituted diphthalocyanine complexes of some rare-earth elements (REE = Lu, Tm, Sm). With 4,5-dipropyloxyphthalodinitrile (**1**) as the phthalogen, we prepared a number of new, symmetrically substituted diphthalocyanine complexes characterized by higher solubilities compared to the known hexadecamethyl-substituted diphthalocyanine complexes of the same REE.[10,11]

Synthesis of complexes. The starting phthalodinitrile **1** was obtained from 4,5-dibromopyrocatechol (**2**) synthesized by treating pyrocatechol with bromine in AcOH [12] (Scheme 1). The reaction of *n*-propyl bromide with dibromide **2** at 20 °C resulted in 1,2-dibromo-4,5-dipropyloxybenzene (**3**). The product yield exceeded 70%. Cyanation of dibromide **3** was accomplished by heating it with excess CuCN under reflux for 8 h in DMF.[13,14] Phthalodinitrile **1** was obtained after recrystallization from EtOH in 68% yield.

Scheme 1



Lutetium, thulium, and samarium diphthalocyanine complexes (**4—6**, respectively) were prepared by treating the REE acetates or formates with an eight-fold excess of phthalodinitrile **1** in amyl alcohol under reflux in the presence of DBU in an inert atmosphere. The reaction mixtures were heated until disappearance of the starting phthalodinitrile (TLC-monitoring).

The diphthalocyanine complexes **4—6** were separated and purified by column chromatography (Al_2O_3, with $CHCl_3$—MeOH (10 : 1) as eluent) and finally obtained in 61 to 66% yields. Compounds **4—6** are water insoluble but readily soluble in most of organic solvents ($CHCl_3$, CH_2Cl_2, C_6H_6, Me_2CO). Both TLC-monitoring and the electronic absorption spectra (EAS) showed that the reaction mixtures contained not only the target

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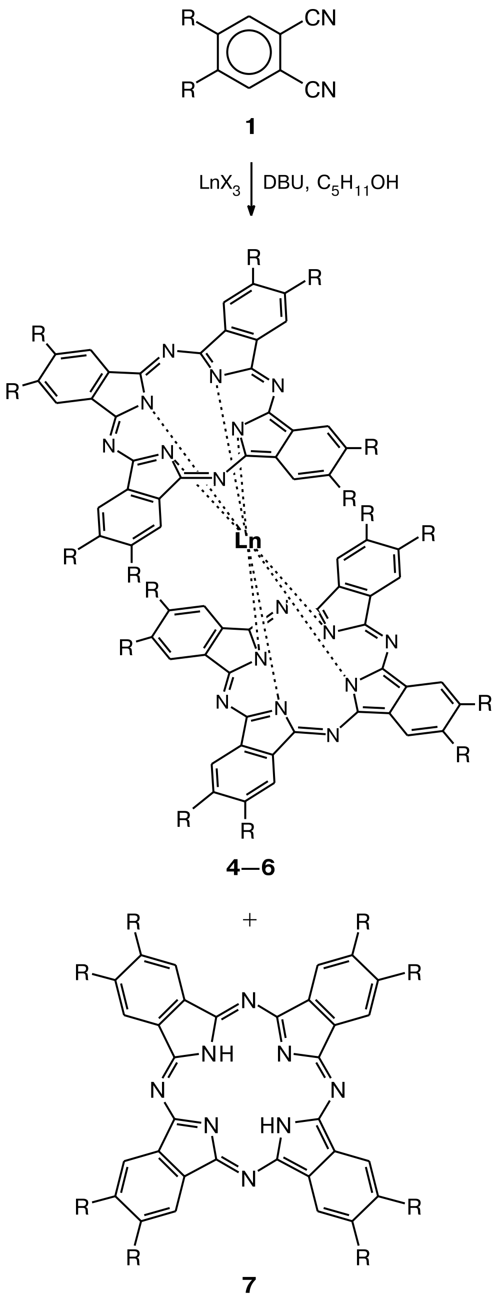
products **4—6** but also small amounts of phthalocyanine **7** (Scheme 2).

Scheme 2



Ln = Lu (**4**), Tm (**5**), Sm (**6**); X = OCHO, OAc; R = PrO

The absorption spectra of complexes **4—6** follow an identical pattern and exhibit a characteristic maximum in the region 660—680 nm and a Soret band near 320 nm. For the diphthalocyanine complexes of the late REE (**4**, **5**) the Q-band position varies only slightly (660 and 662 nm). As the ionic radius of the central metal ion increases (complex **6**), the main absorption maximum is shifted toward the long-wavelength region (680 nm). The EAS of all the complexes synthesized in this work exhibit maxima in the region 460—480 nm. This is yet another characteristic feature of the REE diphthalocyanine complexes, which appears due to the presence of the unpaired electron since these compounds are stable radicals. On going from lutetium phthalocyanine to samarium phthalocyanine this maximum behaves similarly to the main absorption maximum, namely, it experiences a bathochromic shift, while its intensity increases (probably, due to an increase in the distance between the phthalocyanine rings).

Electrochemical studies. The electrochemical properties of the hexadecapropyloxy-substituted diphthalocyanine complexes of Lu, Tm, and Sm were studied by cyclic voltammetry (CV) in *o*-dichlorobenzene (DCB). Three reversible redox transitions were detected for the complexes, one in the oxidation region and the other two in the reduction region (Fig. 1). The potentials of the redox transitions are listed in Table 1.

Electrochemical measurements were carried out using a working electrode made of a graphite-like material with highly developed surface (pyrolyzed polyacrylontrile, PA). This allowed operation at lower concentrations of the compounds under study compared to the measurements with compact platinum electrodes.[11,13] This is of considerable importance for the electrochemical studies of phthalocyanine complexes, since many of them are poorly soluble in most of organic solvents used for electrochemical measurements. The PA electrode is characterized by a

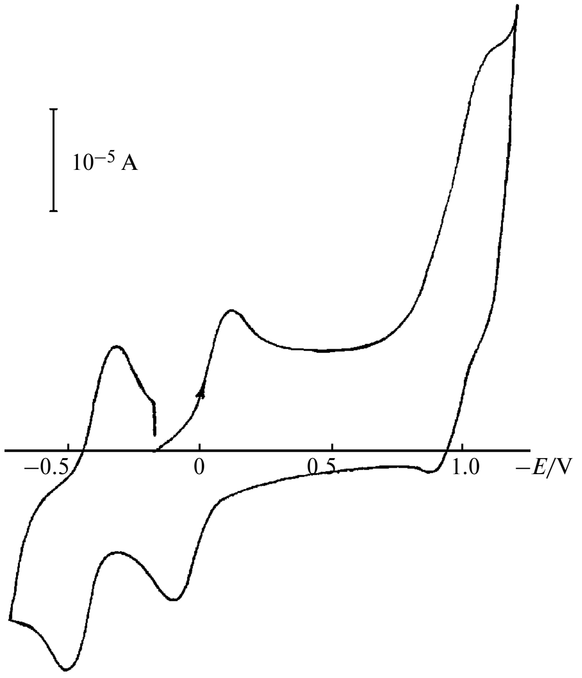


Fig. 1. Cyclic voltammogram of complex **4** (graphite electrode; DCB; 0.15 M Bu$^n{}_4$NBF$_4$; Ag|AgCl|KCl; υ = 200 mV s^{-1}; 20 °C).

Table 1. Potentials of redox transitions of complexes **4**—**6**[a]

Complex	E^b/V		
	Oxidation	Reduction	
4	0.38	−0.02	−0.97
4[c]	0.39	−0.02	−0.99
5	0.42	0.02	−1.02
6	0.50	0.10	−0.98

[a] Graphite electrode; DCB; 0.15 *M* $Bu^n_4NBF_4$; Ag|AgCl|KCl; v = 200 mV s^{-1}; 20 °C.

[b] Arithmetic mean of the direct and reverse peaks.

[c] Pt electrode.

higher signal-to-noise ratio compared to the smooth Pt electrode and, hence, provides better results despite the increase in the surface area of the Pt electrode. The potentials measured with the PA electrode and the smooth Pt electrode are very close (see Table 1), which allows a comparison of the results obtained using the two electrodes.

The potentials of the first redox transitions of the complexes studied in this work are in good agreement with the published data[13] for the REE diphthalocyanines containing pentyloxy groups in the same positions of phthalocyanine macrocycles (0.39—0.50 V for oxidation and −0.06—0.05 V for reduction). The propyloxy-substituted complexes are characterized by small narrowing of the electrochemical gap ($G = E^{Ox} - E^{Red}$) from 0.45 to 0.40 V. Earlier,[13,15—17] it was shown that, depending on substituents, the *G* value for the substituted diphthalocyanine complexes of REE can vary from 0.33 to 0.54 V.

The potentials of the first redox transitions of the complexes correlate with the REE ionic radii (R = 0.9931, see Fig. 2), which is due to π—π-interaction between phthalocyanine rings.[18] The slopes of the corresponding straight lines (0.874 V A^{-1}) are somewhat larger than those obtained for pentyloxy-substituted complexes (0.798 V A^{-1})[13] and are characteristic of the diphthalocyanine complexes of REE.[13,15,19] Thus, enhancement of the effect of the REE ionic radius on the first redox potentials and the narrowing of the electrochemical gap for the REE diphthalocyanine complexes occur simultaneously. A similar trend was also observed earlier (see, *e.g.*, Ref. 13). The effect of the REE ionic radii on the second reduction potentials of the complexes is much less pronounced (see Fig. 2).

Both the first redox and the second reduction potentials of the complexes studied in this work also correlate with the sums of the Hammett constants of substituents (quantitative characteristic of electronic changes due to the presence of substituents in the phthalocyanine rings).[13]

The spectral and electrochemical properties of the complexes were studied using a quartz cell, which allowed the detection of spectral changes directly in the course of electrolysis. The positions of the absorption maxima in the EAS of the neutral, reduced, and oxidized forms of the complexes are listed in Table 2. In Fig. 3 we present the EAS of the neutral, reduced, and oxidized forms of diphthalocyanine **5** obtained by bulk electrolysis. The pattern of the EAS of the redox forms of the complexes is typical of the REE diphthalocyanine complexes[20] and indicate that the first redox processes involve one electron and localization of electronic changes on the phthalocyanine macrocycles.[18,21—23]

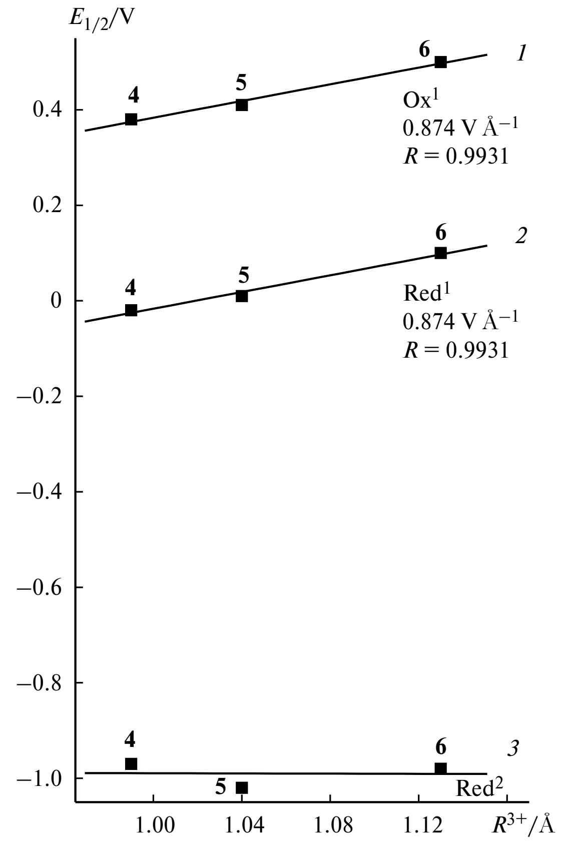


Fig. 2. Effect of the REE ionic radius on the potentials of the first oxidation transition (*1*) and of the first (*2*) and second (*3*) reduction transitions of complexes **4**—**6**.

Comparison of the spectral parameters of the redox forms of the complexes studied in this work reveals a bathochromic shift of the absorption bands with an increase in the radius of the central metal ion (see Table 2). This is a characteristic feature of diphthalocyanine complexes of REE.[9] The red shift of the absorption bands of the redox forms compared to the unsubstituted complexes (see Table 2) is due to the presence of electron-donor *n*-propyloxy groups, which is in agreement with the published data.[13,24] The complexes exhibit high color contrast between the neutral, reduced, and oxidized redox forms (see Table 2), which can be assessed as arrangements of hues in the equally contrast Munsell color circle.

Table 2. Maxima of the electronic absorption spectra of the neutral, reduced, and oxidized forms of complexes **4—6** and Pc_2Lu in DCB and colors of the corresponding solutions

Complex	R^{3+} /A	$\lambda_{max}{}^{a}$/nm		
		$[^{x}Pc_2Ln]^-$	$[^{x}Pc_2Ln]^0$	$[^{x}Pc_2Ln]^+$
4	0.99	361, 570 sh, $\underline{624}$, $\underline{702}$ (blue)	367, 481, 576 sh, 600, 634 sh, $\underline{664}$ (green)	387, $\underline{499}$, 632 sh, $\underline{697}$ (orange)
5	1.04	363, 596 sh, $\underline{626}$, $\underline{700}$ (blue)	369, 480, 581 sh, 603, 640 sh, $\underline{666}$ (green)	389, $\underline{502}$, 634 sh, $\underline{701}$ (orange-pink)
6	1.13	365, 583 sh, $\underline{634}$, $\underline{684}$ (blue)	374, 494, 586 sh, 613, 643 sh, $\underline{674}$ (green)	391, $\underline{520}$, 640 sh, $\underline{724}$ (pink)
Pc_2Lu^b	0.99	333, 560 sh, $\underline{616}$, $\underline{690}$ (dark blue)	339, 459, 573 sh, 596, 629 sh, $\underline{659}$ (green)	350, $\underline{477}$, 623, $\underline{693}$ (orange)

[a] The most intense absorption bands are underlined.
[b] DCB—MeCN (1 : 1).

Thus, these compounds can be used as materials for electrochromic devices.

Experimental

The starting pyrocatechol of "purum" grade was used as received. 4,5-Dibromopyrocatechol (**2**) was synthesized following the known procedure[12] that was modified in some way. Amyl alcohol ("pure" grade) and propyl bromide ("chemically pure" grade) were distilled prior to use; DMF and DMSO (both of "chemically pure" grade) were vacuum distilled over BaO; *o*-dichlorobenzene (DCB) of "chemically pure" grade was passed through a column with neutral Al_2O_3 immediately prior to use; and $Bu^n{}_4NBF_4$ (Aldrich) was twice recrystallized from propan-2-ol ("extra pure" grade) and then vacuum dried at 110 °C. Phthalocyanines were synthesized from the corresponding lanthanide formates and acetates (analytical grade).

NMR spectra were recorded on a Bruker DPX-200 spectrometer (200 MHz) in $CDCl_3$, containing Me_4Si (0.05%) as internal reference. Absorption spectra were recorded on a Specord M-800 spectrophotometer in the region 200—800 nm.

4,5-Dibromopyrocatechol (2). To a solution of pyrocatechol (44 g, 0.4 mol) in AcOH (150 mL), a solution of Br_2 (135.8 g, 0.85 mol) in AcOH (100 mL) was added dropwise with stirring and cooling with ice—water mixture. Once bromine was added, the mixture was allowed to stand for 12 h at ca. 20 °C. Then the solvent was partially distilled off and the residue was poured into ice—water mixture (1.2 L). The white precipitate that formed was filtered off, dried in air, and recrystallized from $CHCl_3$ to give compound **2** (80.1 g, 89%), m.p. 119—120 °C (*cf.* Ref. 12: 119—120 °C).

1,2-Dibromo-4,5-dipropyloxybenzene (3). To a stirring mixture of KOH powder (11.11 g, 0.198 mol) in anhydrous DMSO (50 mL), 4,5-dibromopyrocatechol (**2**; 6.63 g, 0.025 mol) and *n*-propyl bromide (12.18 g, 0.099 mol) were added at 20 °C and the reaction mixture was stirred for 1.5 h. The resulting mixture was poured into water—ice mixture (200 mL), extracted with CH_2Cl_2 (4×30 mL), washed with dilute NaOH solution (2×30 mL), water, and dried over $MgSO_4$. The orange oil obtained after removal of the solvent was dissolved in benzene and the product was separated by column chromatography (Al_2O_3, with C_6H_6 as the eluent). Dibromide **3** (6.34 g, 73%) was obtained as colorless crystals, m.p. 60—61 °C. Found (%): C, 40.90; H, 4.53; Br, 45.45. $C_{12}H_{16}Br_2O_2$. Calculated (%): C, 40.94;

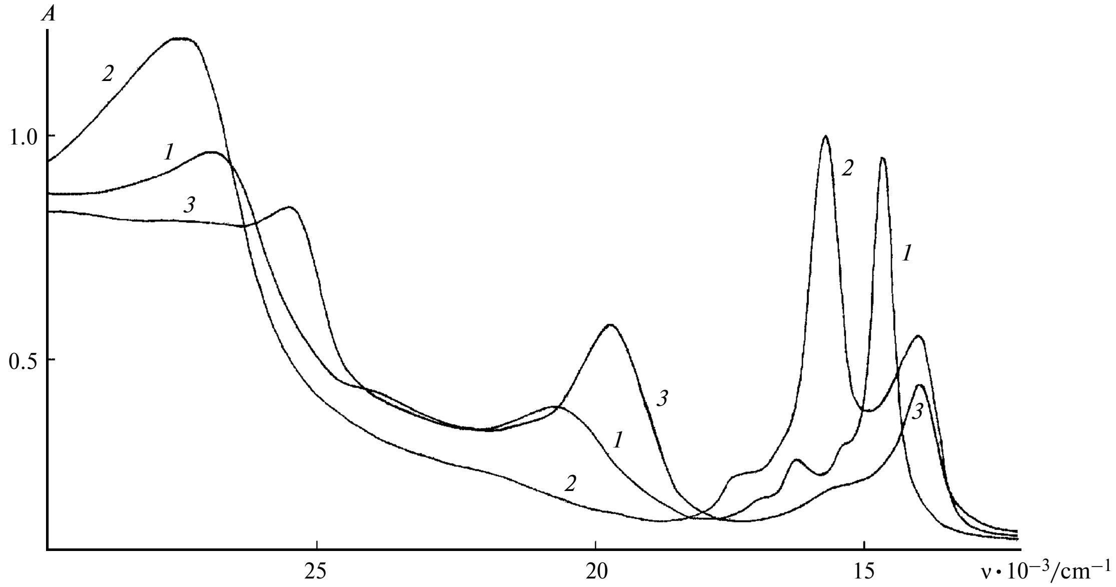


Fig. 3. Electronic absorption spectra of the neutral (*1*), reduced (*2*), and oxidized (*3*) forms of complex **5** generated at potentials of −0.5 and +1.0 V (*vs.* Ag|AgCl|KCl) at the Pt electrode in DCB with 0.15 *M* $Bu^n{}_4NBF_4$ as the background electrolyte.

H, 4.58; Br, 45.39. ^{1}H NMR ($CDCl_3$, J/Hz), δ: 1.02 (t, 6 H, 2 Me, J = 6.7); 1.85 (m, 4 H, 2 CH_2); 3.90 (t, 4 H, 2 CH_2, J = 6.7); 7.04 (s, 2 H, C_6H_2).

4,5-Dipropyloxyphthalodinitrile (1). A mixture of 1,2-dibromo-4,5-dipropyloxybenzene (**3**; 6.34 g, 0.018 mol) and CuCN (4.84 g, 0.054 mol) in anhydrous DMF (80 mL) was refluxed for 8 h. After cooling the solvent was evaporated *in vacuo*, CH_2Cl_2 (80 mL) and 30% aqueous ammonia (150 mL) were added to the residue, and the resulting mixture was vigorously stirred for 24 h. The aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with water, and the combined organic extracts were dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was recrystallized from EtOH to give compound **1** (2.71 g, 68%) as colorless crystals, m.p. 151—152 °C. Found (%): C, 68.81; H, 6.58; N, 11.27. $C_{14}H_{16}N_2O_2$. Calculated (%): C, 68.83; H, 6.60; N, 11.47. ^{1}H NMR ($CDCl_3$, J/Hz), δ: 1.09 (t, 6 H, 2 Me, J = 6.7); 1.90 (m, 4 H, 2 CH_2); 4.02 (t, 4 H, 2 CH_2, J = 6.7); 7.10 (s, 2 H, C_6H_2).

Bis(octapropyloxyphthalocyanine)lutetium(III) (4). A mixture of 4,5-dipropyloxyphthalodinitrile (**3**; 340 mg, 1.4 mmol), $Lu(OCHO)_3 \cdot 2H_2O$ (60 mg, 0.17 mmol), and DBU (106 mg, 0.70 mmol) was refluxed in amyl alcohol (5 mL) for 8 h in Ar atmosphere. After cooling the solvent was removed *in vacuo*, the residue was reprecipitated with water from DMF, washed with aqueous MeOH, and dried in air. After separation with column chromatography (Al_2O_3, with $CHCl_3$—MeOH (10 : 1) as the eluent) diphthalocyanine **4** (182 mg, 61%) was obtained as dark-green fine-crystalline powder. Solubility (benzene) $1.41 \cdot 10^{-2}$ mol L^{-1}. Found (%): C, 63.44; H, 6.29; N, 10.18. $C_{112}H_{128}LuN_{16}O_{16}$. Calculated (%): C, 63.18; H, 6.06; N, 10.53.

Bis(octapropyloxyphthalocyanine)thulium(III) (5) was synthesized similarly from dinitrile **3** (250 mg, 1 mmol) and $Tm(OAc)_3 \cdot 4H_2O$ (53 mg, 0.13 mmol). Diphthalocyanine **5** (180 mg, 66%) was obtained as dark-green powder. Found (%): C, 63.52; H, 6.44; N, 10.21. $C_{112}H_{128}N_{16}O_{16}Tm$. Calculated (%): C, 63.36; H, 6.08; N, 10.55.

Bis(octapropyloxyphthalocyanine)samarium(III) (6) was synthesized similarly from dinitrile **3** (370 mg, 1.5 mmol) and $Sm(OAc)_3$ (75 mg, 0.19 mmol). Diphthalocyanine **6** (247 mg, 62%) was obtained as dark-green fine-crystalline powder. Found (%): C, 63.54; H, 6.44; N, 10.93. $C_{112}H_{128}N_{16}O_{16}Sm$. Calculated (%): C, 63.91; H, 6.13; N, 10.65.

Electrochemical measurements were carried out using a PI-50-1 potentiostat, a PR-8 programmer, and a PDA-1 XY-recorder at a graphite electrode (pyrolyzed acrylonitrile with a specific area of 12 m^2 g^{-1}, m ~1 mg) and at a Pt wire (d = 1.0 mm, a working area of 32.2 mm^2) against 0.15 M $Bu^n{}_4NBF_4$ at 20 °C. The three-electrode scheme was employed. A Pt wire served as an auxiliary electrode and an AgCl electrode was used as the reference electrode. Oxygen was removed from the cell by passing a dry argon stream. The current-*vs.*-voltage curves were recorded by cyclic voltammetry (CV) technique at a scan rate of 200 mV s^{-1}. The measured peak potentials were corrected for the ohmic losses (electrolyte resistance) calculated from the shifts of the anodic and cathodic oxidation peaks of ferrocene: $(E^c - E^a) - 0.059 = I \cdot R$, where E^c and E^a are respectively the cathodic and anodic oxidation peak potentials of ferrocene, I is the sum of the currents of the cathodic and anodic processes, and R is the electrolyte resistance. DCB was used as the solvent. The concentrations of solutions of the complexes under study ranged from $7 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mol L^{-1}.

The electrochemically generated redox forms used in the spectroelectrochemical studies of phthalocyanine complexes were obtained in the potentiostatic mode in a tailor-made quartz cell with anodic and cathodic compartments separated by a porous glass membrane at 20 °C. The cell was connected to the potentiostat by the three-electrode scheme. The working electrode was a Pt grid with a surface area of nearly 9.7 cm^2 (estimated by comparing the electrochemical responses of ferrocene at the Pt grid and at a Pt electrode of a simple shape), the supporting electrolyte was 0.15 M $Bu^n{}_4NBF_4$, and the auxiliary electrode was a Pt plate. The potentials were measured *vs.* an AgCl electrode. DCB was used as the solvent. The concentrations of solutions of the complexes under study ranged from $2 \cdot 10^{-5}$ to $3 \cdot 10^{-5}$ mol L^{-1}. Passing dry argon stream was used both to remove oxygen prior to the experiments and to stir the solutions in the cell. The electronic spectra of the electrochemically generated redox forms of the complexes were recorded on a Specord UV-VIS spectrophotometer (Carl Zeiss) immediately in the quartz cell in the range 30000—13500 cm^{-1} (333—800 nm) with 0.15 M $Bu^n{}_4NBF_4$ in the same solvent as the reference solution.

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