# New diphthalocyanine complexes of rare-earth metals based on 4,5-isopropylidenedioxyphthalonitrile

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A series of the earlier unknown diphthalocyanine complexes of rare-earth metals based on 4,5-isopropylidenedioxyphthalonitrile were prepared. Their compositions and yields depend on the radius of the complexing ion. The synthesized compounds were studied by spectroscopy and electrochemical methods. The redox potentials of the complexes studied change nonlinearly with a decrease in the lanthanide ion radius.

**Key words:** 4,5-isopropylidenedioxyphthalonitrile, diphthalocyanines, electronic absorption spectra, cyclic voltammetry.

Diphthalocyanine complexes of rare-earth metals (REM) have interesting spectral and electrochemical properties, which attracts researchers´ attention to this class of compounds.[1—5] We have recently synthesized symmetric lanthanide hexadecapropyloxy-[6] and hexadeca-alkyl-substituted diphthalocyanines.[7,8] In this work, we present the results of studying diphthalocyanines based on 4,5-isopropylidenedioxyphthalonitrile (**1**). The syntheses of the starting nitrile and its monophthalocyanine complexes have been published earlier.[9]

Two methods for the synthesis of the diphthalocyanine complexes are known presently.[6—8,10,11] The first of them is the reaction of phthalonitriles with REM salts on refluxing in high-boiling solvents or on melting of the starting compounds.[6—8] The second method is the deprotonation of free phthalocyanine (Pc) ligands and interaction of the dianion that formed with monophthalocyanines or REM salts.[10,11] We examined both approaches.

The reaction of dinitrile **1** with lanthanide acetates **2** in a ratio of 10 : 1 in boiling isoamyl alcohol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) affords diphthalocyanine complexes **3** in 8—32% yields (Scheme 1).

The course of reactions was monitored by TLC and spectrophotometry. The data obtained show that monophthalocyanine complexes **4** are formed in the first step as nitrile **1** is consumed in the reaction mixture. Metal-free phthalocyanine **5** was also found. The free ligand disappears further with accumulation of diphthalocyanines **3** in the mixture. However, in the case of Ln = Nd, compound **5** becomes the single reaction product. The use of europium acetate results in a mixture of free ligand **5** and europium monophthalocyanine **4b** rather than in diphthalocyanine **3b**.

These results suggest that the REM ion radius exerts a strong effect on complex formation. The metals of the beginning of the row with a larger ion radius, most likely, cannot produce stable phthalocyanine complexes under the reaction conditions (the latter decompose to form metal-free phthalocyanine **5**). The metals of the middle of the row, whose ion radius is smaller than that of the metals of the beginning of the series, form more stable planar phthalocyanine complexes due to stronger binding of the metal ion with the macrocyclic ligand and are also capable of forming diphthalocyanine complexes. However, for the metals of the end of the row, steric repulsion of the rigidly fixed Me groups of the isopropylidene fragment decreases the yield of the target complexes. Note that the melting of dinitrile **1** with lanthanide salts or under microwave irradiation of these mixtures (see Ref. 11) results in dinitrile polymerization.

Since the yields of the diphthalocyanine complexes of REM for the synthesis from nitrile **1** and a metal salt are low, we used the second method of their preparation.

The treatment of free phthalocyanine **5** with butyllithium in DMSO generates the phthalocyanine dianion in solution (Scheme 2). The reactions of the latter with REM monophthalocyanines afford reduced forms of diphthalocyanines.

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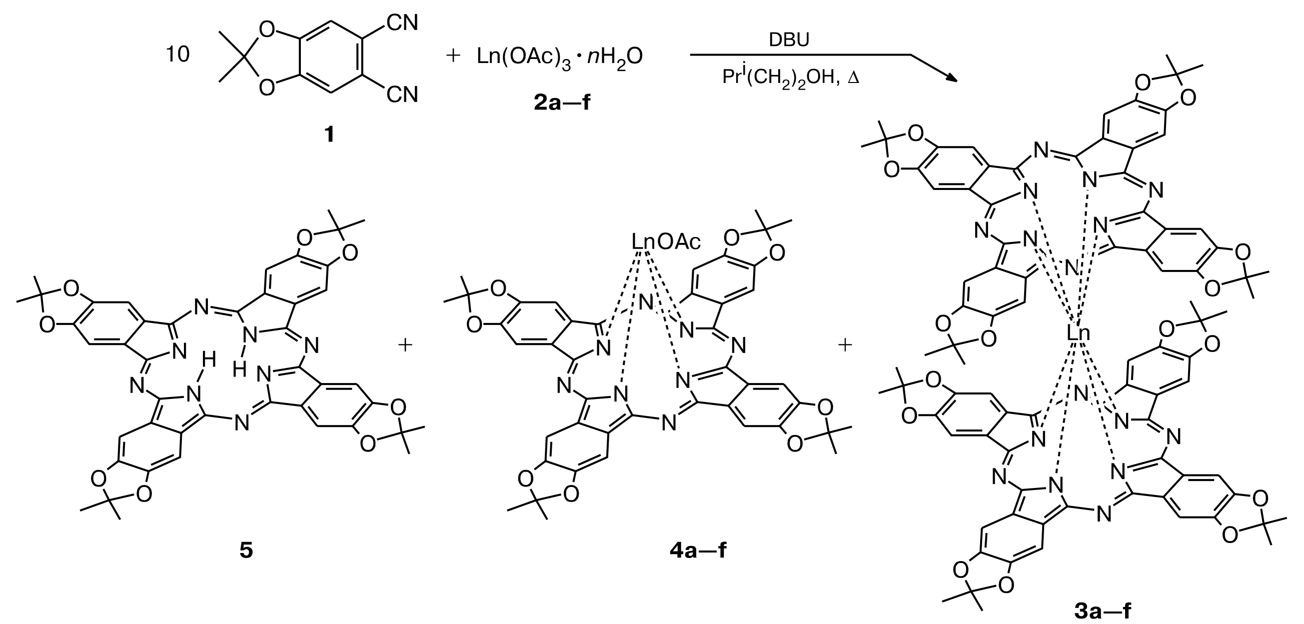
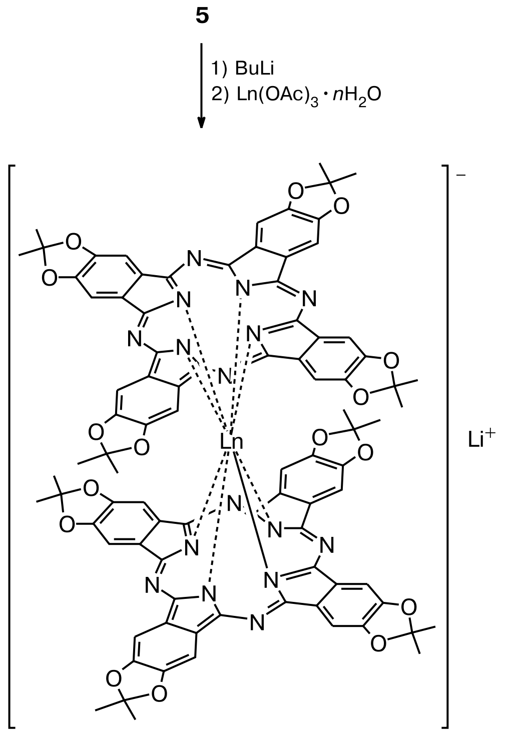
**Scheme 1**



Ln = Nd (**a**), Eu (**b**), Tb (**c**), Dy (**d**), Yb (**e**), Lu (**f**)

**Scheme 2**



The spectra of thus prepared octa(isopropylidenedioxy)diphthalocyanine complexes $[Pc'_2Ln]^-$ are identical to the spectra of compounds formed by the chemical reduction of neutral forms of diphthalocyanines **3**. The reduced forms of the diphthalocyanine complexes are readily oxidized with atmospheric oxygen to compounds **3b,f**.

Neodymium diphthalocyanine **3a** was synthesized by the reaction of free ligand **5** with neodymium triacetate on boiling in *o*-dichlorobenzene (*o*-DCB) in the presence of DBU.

It should be noted that the $Pc'_2Nd$ (**3a**) and $Pc'_2Eu$ (**3b**) complexes are unstable in air and decompose with time to form free $Pc'H_2$.

The yields of the target complexes prepared by different methods of synthesis are given in Table 1.

The synthesized compounds were studied by MALDI-TOF mass spectrometry. The spectra of the diphthalocyanine complexes contain peaks of molecular ions of $Pc'_2Ln$ with *z*/*e* 1700—1800. In addition, the spectra exhibit signals belonging to the monophthalocyanine

**Table 1.** Yields of complexes **3a—f** in different methods of synthesis

| Compound | Yield (%) | Compound | Yield (%) |
|---|---|---|---|
| **3a** | 0[a], 3[b] | **3d** | 10[a] |
| **3b** | 0[a], 11[c] | **3e** | 12[a] |
| **3c** | 32[a] | **3f** | 8[a], 19[c] |

[a] See Experimental, general procedure *A*.
[b] Synthesis from ligand **5** and $Nd(OAc)_3 \cdot H_2O$ in the presence of DBU.
[c] See Experimental, general procedure *B*.

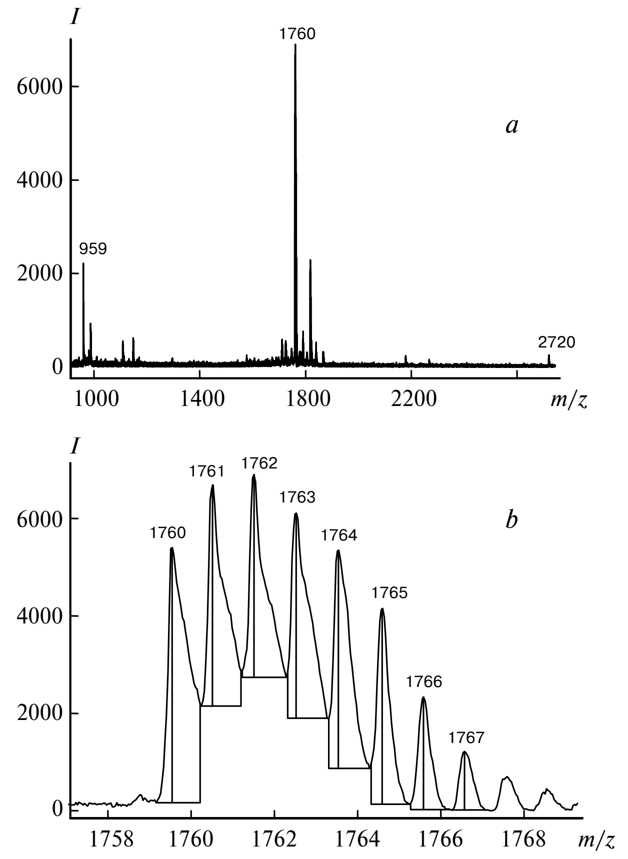


**Fig. 1.** Mass spectrum of complex **3c**: general view (*a*) and molecular ion peak (*b*).

fragments (*z/e* 950—1050), free ligand (*z/e* 802), and three-decker complexes (*z/e* 2400—2500). The typical mass spectrum is shown in Fig. 1.

The mass spectrum of the $Pc'_2Nd$ compound obtained by chemical ionization exhibits peaks corresponding to the single- and double-charged ions of the complex (*m/z* 1746 and 873, respectively).

The spectrophotometric studies of compounds **3a—f** confirmed that they are complexes of the $[Pc^{\bullet-}M^{3+}Pc^{2-}]^0$ type. Their spectra contain the Q band at 665—675 nm, which is inherent in $Pc^{2-}$ and corresponds to the electronic transition between the π- and π*-orbitals of the phthalocyanine ring, and the characteristic band at 470 nm caused by the $Pc^{\bullet-}$ radical fragment in the molecule. The Soret band has absorption maxima at 330 and 360—370 nm (Table 2).

The electronic absorption spectra of the oxidized and reduced forms of terbium diphthalocyanine **3c** were obtained (Fig. 2). The action of bromine in a $CHCl_3$ solution results in the reversible oxidation of the complex to form the red form $[2Pc^{\bullet-}M^{3+}]^+$. When a solution of the oxidized form is treated with an equivalent amount of triethylamine, the initial neutral form is quantitatively regenerated.

**Table 2.** Absorption maxima in the EAS of solutions of compounds **3a—f** in $CHCl_3$

| Compound | $\lambda_{max}$/nm |
|---|---|
| **3a** | 338, 371, 486, 612, 676 |
| **3b** | 342, 371, 478, 613, 672 |
| **3c** | 333, 370, 476, 603, 671* |
| **3d** | 332, 367, 472, 602, 670 |
| **3e** | 331, 365, 468, 602, 668 |
| **3f** | 330, 363, 465, 601, 665 |

* $\varepsilon = 9.8 \cdot 10^4$.

The $[Pc^{\bullet-}M^{3+}Pc^{2-}]^0$ neutral form is easily reduced to $[Pc^{2\bullet-}M^{3+}Pc^{2-}]^-$ when treated with 1 equiv. of triethylamine or hydrazine hydrate. The spectrum of the redox form of compound **3c** is shown in Fig. 2.

The electrochemical properties of the synthesized compounds were studied for the neodymium, terbium, and lutetium complexes. Measurements were carried out by cyclic voltammetry (CV) in a potential region of −0.2—1.0 V using *o*-DCB as the solvent. Two one-electron redox pairs corresponding to the first oxidation and reduction processes are observed in this potential region in the CV curves for all the complexes under study. The cyclic voltammogram of lutetium diphthalocyanine **3f** is presented in Fig. 3. These redox processes are quasireversible in the CV time scale at a sweep rate of 200 mV $s^{-1}$: the backward peak values are equal to the values of the forward peaks, and the potential difference between them does not exceed 130 mV. The potentials of the redox transitions of the studied complexes are given in Table 3.

The isopropylidenedioxy-substituted diphthalocyanine complexes manifest an unusual electrochemical behavior. The potentials of the redox transitions of the lutetium complex under study (see Table 3) are substantially shifted

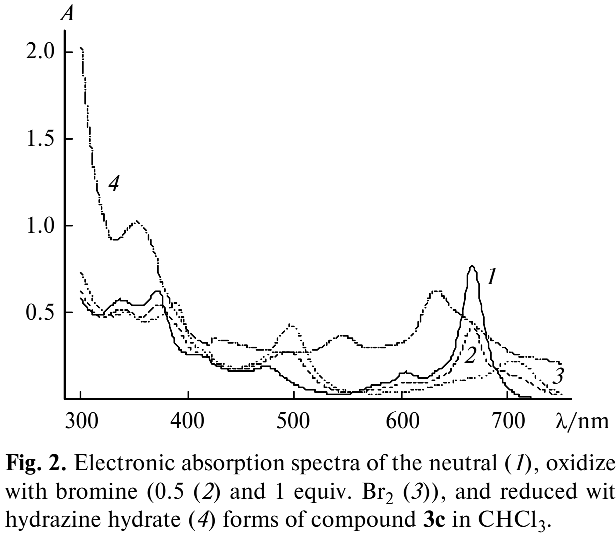


**Fig. 2.** Electronic absorption spectra of the neutral (*1*), oxidized with bromine (0.5 (*2*) and 1 equiv. $Br_2$ (*3*)), and reduced with hydrazine hydrate (*4*) forms of compound **3c** in $CHCl_3$.

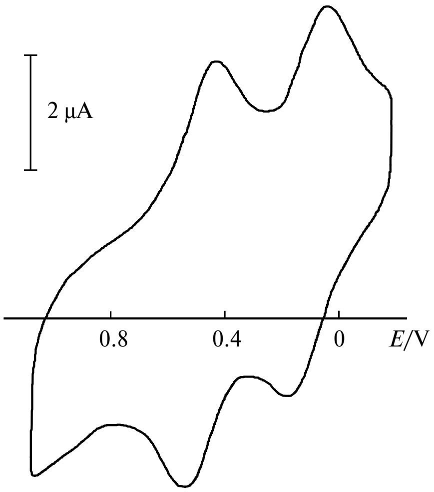


**Fig. 3.** Cyclic voltammogram of complex **3f** (graphite electrode, *o*-DCB, 0.15 *M* solution of $Bu^n{}_4NBF_4$, *vs.* Ag/AgCl/KCl, ν = 200 mV $s^{-1}$, 20 °C).

**Table 3.** Potentials of the redox transitions of the REM diphthalocyanine complexes and unsubstituted lutetium diphthalocyanine[a]

| Complex | $R_{Ln^{3+}}$/Å | $E_{1/2}{}^b$/V | |
|---|---|---|---|
| | | Oxidation | Reduction |
| **3a** | 1.15 | 0.61 | 0.31 |
| **3c** | 1.09 | 0.53 | 0.14 |
| **3f** | 0.99 | 0.51 | 0.12 |
| $[(n\text{-}C_3H_7O)_8Pc']_2Lu$[1] | 0.99 | 0.38 | −0.02 |
| $[(n\text{-}C_5H_{11}O)_8Pc']_2Lu$[7] | 0.99 | 0.39 | −0.06 |
| $Pc_2Lu$[c] [7] | 0.99 | 0.53 | 0.13 |

[a] Graphite electrode (pyrolyzed polyacrylonitrile), *o*-DCB, 0.15 *M* solution of $Bu^n{}_4NBF_4$, *vs.* Ag/AgCl/KCl, ν = 200 mV $s^{-1}$, 20 °C.

[b] The arithmetic mean of peaks of the forward and backward potentials.

[c] *o*-DCB—MeCN = 1 : 1.

to the anodic region compared to other hexadecaalkoxy-substituted diphthalocyanine analogs. A similar regularity has previously[9] been observed for isopropylidenedioxy-substituted monophthalocyanines as well. It is most likely that the isopropylidenedioxy groups manifest a lower electron-donor effect than other alkoxy substituents.

The dependences of the redox potentials of the octa(isopropylidenedioxy)- and earlier studied hexadecapropyloxy-substituted diphthalocyanine complexes[6] on the radius of the central metal ion are presented in Fig. 4. Usually these values correlate linearly for the diphthalocyanine complexes (see Fig. 4; Refs 12 and 13). This correlation is caused by a decrease in the π—π-interaction of the phthalocyanine macroligands with each other with an increase in the lanthanide ion size and a decrease in the energy of the partially occupied $a_2$-MO of the complexes involved in the first processes of their oxidation and reduction.[14] However, the redox potentials for isopropylidenedioxy complexes **3a,c,f** change nonlinearly (see Fig. 4). Lanthanide ions with small radii exert a weak effect on the redox potentials of the complexes. This dependence is probably caused by steric hindrance to approaching of the phthalocyanine ligands, which appears in the case of the lanthanide ions with small radii, or by a decrease in the electron-donor effect of the isopropylidenedioxy groups due to the distortion of their geometry upon approaching of the phthalocyanine ligands.

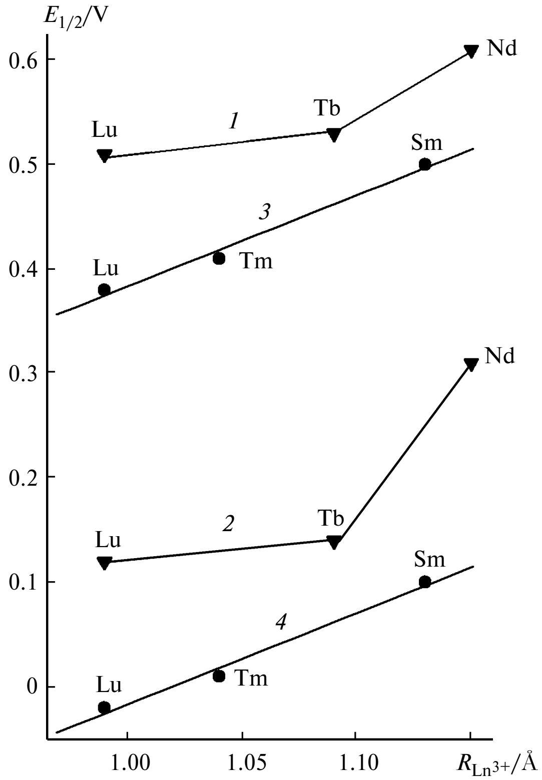


**Fig. 4.** Influence of the lanthanide ion radius ($R_{Ln^{3+}}$) on the potentials of the redox transitions of octa(isopropylidenedioxy)- (*1*, *2*) and hexadecapropyloxy-substituted (*3*, *4*) diphthalocyanine complexes: *1* and *3* are oxidation; *2* and *4* are reduction.

Thus, the electrochemical properties of the complexes under study change nonlinearly and depend on the metal ion radius. The first processes of oxidation and reduction of the diphthalocyanine complexes are related to the removal or addition of an electron to the partially occupied $a_2$-MO. The band in the electronic absorption spectrum at 470—480 nm is also caused by the electron transition to this orbital.[14] The dependence between the potentials of the redox transitions and wave number of this spectral band is presented in Fig. 5. A good linear correlation between these values is observed for the complexes of different lanthanides.

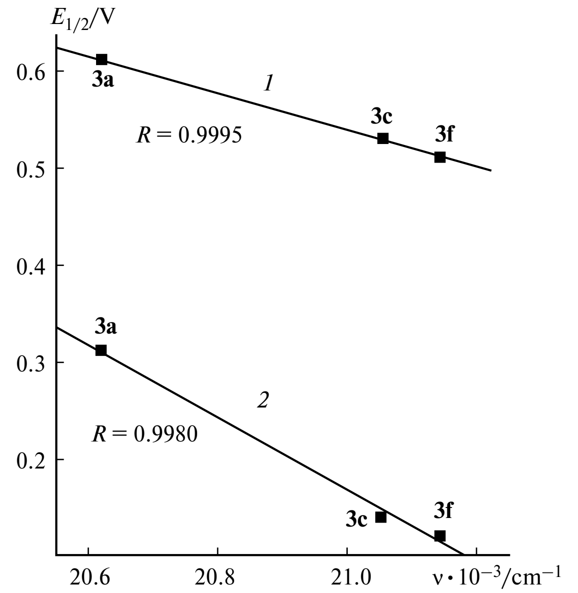


**Fig. 5.** Correlation of potentials of the first redox transitions of isopropylidenedioxy-substituted diphthalocyanine complexes **3a,c,f** with the wave number (ν) of the band in the electronic absorption spectra at 470—480 nm: *1* is oxidation; *2* is reduction.

Thus, a correlation between the electrochemical and spectral properties of the diphthalocyanine complexes of lanthanides is observed even in the case when these properties change nonlinearly with a change in the radius of the central metal ion.

## Experimental

Prior to use *o*-dichlorobenzene (Aldrich, HPLC grade) was passed through a column packed with neutral $Al_2O_3$; $Bu^n{}_4NBF_4$ (Aldrich) was twice recrystallized from $Pr^iOH$ (special-purity grade) and dried in a vacuum desiccator at 110 °C.

$^1$H NMR spectra were recorded on a Bruker AC-200 instrument (200 and 50.3 MHz) in $CDCl_3$ or $(CD_3)_2SO$. Chemical shifts are presented in the δ scale relatively to $Me_4Si$. Thin-layer chromatography was carried out on Silufol UV-254 plates. Mass spectra were obtained on Finnigan MAT INCOS-50 (chemical ionization) and VISION-2000 (MALDI-TOF) instruments.

Electronic absorption spectra of solutions of the complexes in $CHCl_3$ or *o*-DCB ($10^{-3}$—$10^{-5}$ mol $L^{-1}$) were recorded on a Helios-α instrument in quartz cells with a solution layer thickness of 0.2—1.0 cm.

Electrochemical measurements were carried out using a PI-50-1 potentiostat, a PR-8 programmer, and a PDA1 two-coordinate recorder *via* the three-electrode scheme on a graphite electrode (VMN-4 pyrolyzed polyacrylonitrile, $T_f = 2400$ °C, specific surface 12 $m^2 g^{-1}$, $m \approx 0.5$ mg) *vs.* 0.15 *M* solution of $Bu^n{}_4NBF_4$ at 20 °C. A Pt plate served as an auxiliary electrode, and a silver—silver chloride electrode was used as a reference electrode. Oxygen was removed from the cell with a dry argon flow. Voltammetric curves were detected by the CV method at a sweep rate of 200 mV $s^{-1}$. The measured peak potentials were recalculated with allowance for the resistance of the electrolyte, which was calculated from the shift of the anodic and cathodic peaks of ferrocene oxidation

$$(E^c - E^a) - 0.059 = IR,$$

where $E^c$ and $E^a$ are the potentials of the cathodic and anodic oxidation peaks of ferrocene, respectively; *I* is the sum of currents of the cathodic and anodic processes, and *R* is the electrolyte resistance. The solvent was *o*-DCB. The concentration of solutions of the complexes under study was $7 \cdot 10^{-5}$—$1 \cdot 10^{-4}$ mol $L^{-1}$.

**Neodymium(III) 2,3,9,10,16,17,23,24,2′,3′,9′,10′,16′,17′,23′,24′-octa(isopropylidenedioxy)diphthalocyaninate (3a).** A mixture of ligand **5** (0.56 g, 0.7 mmol), $Nd(OAc)_3 \cdot H_2O$ (0.1 g, 0.3 mmol), and DBU (0.5 mL) in *o*-DCB (20 mL) was refluxed for 5 h. After cooling, the reaction mixture was filtered, the solvent was evaporated *in vacuo*, and the residue was purified by column chromatography ($SiO_2$, 1.5×10 cm). The starting phthalocyanine **5** was eluted with chloroform, and then the target compound was eluted with acetonitrile. After MeCN was evaporated, the residue was dissolved in $CHCl_3$, and the resulting solution was left for ~14 h. The oxidation product was additionally purified on a column ($SiO_2$, 1.5×10 cm, $CHCl_3$ as eluent). After the eluent was evaporated, compound **3a** was obtained as a green powder in a yield of 0.017 g (3%). Found (%): C, 59.85; H, 3.57; N, 12.65. $C_{88}H_{64}N_{16}NdO_{16}$. Calculated (%): C, 60.54; H, 3.70; N, 12.84. Mass spectrum, *m/z*: 1746 $[M]^+$, 873 $[M]^{2+}$. EAS (*o*-DCB), $\lambda_{max}$/nm: 371, 485, 585 sh, 607, 639 sh, 672, 900.

**2,3,9,10,16,17,23,24,2′,3′,9′,10′,16′,17′,23′,24′-Octa(isopropylidenedioxy)diphthalocyaninates of REM 3a—f (general procedure).** ***A.*** A mixture of dinitrile **1** (2.5 mmol, 0.5 g), DBU (2.5 mmol, 0.378 g), and the corresponding REM acetate **2a—f** (0.25 mmol) was refluxed in isoamyl alcohol (5 mL) under an argon flow until the reaction ceased (6—8 h). The reaction course was monitored by TLC. The reaction mixture was successively treated with benzene and chloroform. The solid residue that formed was dissolved in DMF. Water was added to the resulting solution until a precipitate formed, and the mixture was left for ~14 h for precipitation completeness. The green finely dispersed mixture was filtered off, washed with water, and dried *in vacuo* at 100 °C. The synthesized phthalocyanines were purified by column chromatography on silica gel ($CHCl_3$ as eluent). The corresponding monophthalocyanines **4b—f** were isolated as by-products by chromatography of the filtrate of the reaction mixtures.

***B.*** A 1.6 *M* solution of BuLi in hexane (0.5 mL) was added with stirring to a solution of metal-free phthalocyanine **5** (0.08 g, 0.1 mmol) in anhydrous DMSO (10 mL). The reaction mixture was stirred for 20 min until the end of gas release, and a solution of the corresponding REM monophthalocyanine **4** (0.1 mmol) in DMSO (5 mL) was added dropwise. The reaction mixture was stirred for 2 h at 80—90 °C. After cooling, the solution was diluted with ethyl acetate (50 mL), washed with water (3×100 mL), and dried with magnesium sulfate. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography on $Al_2O_3$ ($CHCl_3$ as eluent).

**Europium(III) 2,3,9,10,16,17,23,24,2′,3′,9′,10′,16′,17′,23′,24′-octa(isopropylidenedioxy)diphthalocyaninate (3b).** Mass spectrum, *m/z*: 1753 $[M]^+$.

**Terbium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´, 23´,24´-octa(isopropylidenedioxy)diphthalocyaninate (3c).** The yield was 32%. Found (%): C, 59.85; H, 3.57; N, 12.65. $C_{88}H_{64}N_{16}O_{16}Tb$. Calculated (%): C, 60.04; H, 3.66; N, 12.73. $^1H$ NMR, δ: 2.69, 2.86 (both s, 48 H, $CMe_2$); 7.90 (s, 16 H, H arom.). Mass spectrum, *m/z*: 1760 $[M]^+$. EAS (*o*-DCB), $\lambda_{max}$/nm: 371, 475, 576 sh, 604, 634 sh, 667, 896.

**Dysprosium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´, 17´,23´,24´-octa(isopropylidenedioxy)diphthalocyaninate (3d).** Mass spectrum, *m/z*: 1764 $[M]^+$.

**Ytterbium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´, 23´,24´-octa(isopropylidenedioxy)diphthalocyaninate (3e).** Mass spectrum, *m/z*: 1774 $[M]^+$.

**Lutetium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´, 23´,24´-octa(isopropylidenedioxy)diphthalocyaninate (3f).** Mass spectrum, *m/z*: 1776 $[M]^+$. EAS (*o*-DCB), $\lambda_{max}$/nm: 372, 473, 574 sh, 602, 633 sh, 664, 895.

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