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Hexadecabenzyloxy(diphthalocyanines) of rare-earth elements: synthesis and spectroscopic and electrochemical characteristics

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Reactions of 4,5-dibenzyloxyphthalonitrile with salts of rare-earth elements afforded symmetrical lutetium, dysprosium, samarium, and neodymium complexes with hexadecabenzyloxy(diphthalocyanine), which are well soluble in organic solvents. The spectroscopic and electrochemical characteristics of the complexes obtained were studied.

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

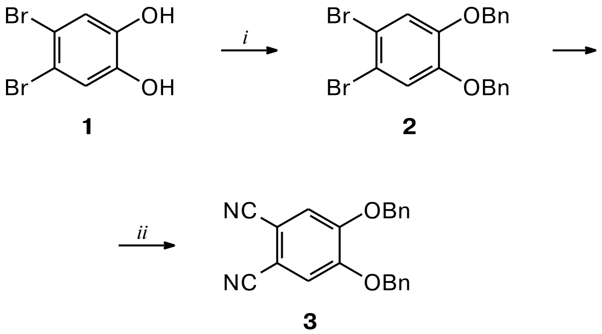
Recent steady interest in the studies of phthalocyanines, which are synthetic analogs of porphyrins, is due to a unique variety of their physicochemical, coordination, and electrochemical properties. Compounds of this class have found a wide use as organic dyes,[1,2] catalysts for redox processes[3,4] and electrochemical reactions,[1,5,6] gas sensors,[7] semiconducting materials,[8,9] photosensitive compounds, and drugs.[10,11]

Both free phthalocyanine and many its derivatives (including metal complexes) are usually poorly soluble in organic solvents, which complicates purification and analysis of these compounds and limits the area of their applications. In contrast, sandwich-type diphthalocyanine complexes of rare-earth elements are usually well soluble in organic solvents and are characterized by unique physicochemical, electrochemical, and electrochromic properties.[12—14] Sandwich compounds were first mentioned in the mid-1960s.[15,16]

Earlier,[17,18] we have offered routes to symmetrical alkoxydiphthalocyanine complexes and described their electrochemical characteristics. In the course of the investigations, we obtained symmetrical 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecabenzyloxy(diphthalocyanine) complexes $[(BnO)_8Pc]_2Ln$.

The starting substituted phthalonitrile was prepared from 4,5-dibromopyrocatechol **1** according to Scheme 1. 1,2-Dibenzyloxy-4,5-dibromobenzene **2** was synthesized by a reaction of compound **1** with BnBr in DMSO in the presence of KOH at room temperature. The reaction with BnCl also gives compound **2** in high yield;[19] however, the formation of KCl, which is less soluble than KBr, hinders stirring of the reaction mixture, thus increasing the reaction time and making the product isolation more difficult. 4,5-Dibenzyloxyphthalonitrile **3** was obtained by treatment of compound **2** with CuCN in boiling dry DMF as described earlier.[20—22]

Scheme 1



Reagents: *i.* BnBr, KOH, DMSO; *ii.* CuCN, DMF.

Diphthalocyanines of Lu^{III}, Dy^{III}, Sm^{III}, and Nd^{III} were obtained by reactions of 4,5-dibenzyloxyphthalonitrile **3** with the corresponding metal acetates or formates in *n*-hexanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under argon according to Scheme 2.

The course of the reaction was monitored by TLC and electronic absorption spectroscopy. Fifteen to twenty minutes after the beginning of the reaction, the solution turned characteristically green and the spectra contained a peak at 665 to 685 nm. The electronic absorption spectra of the final reaction mixtures are shown in Fig. 1. It can be seen that the nature of the central metal ion affects the spectral pattern of the target complex. For instance, the spectra of crude complexes of late lanthanides with smaller ion radii

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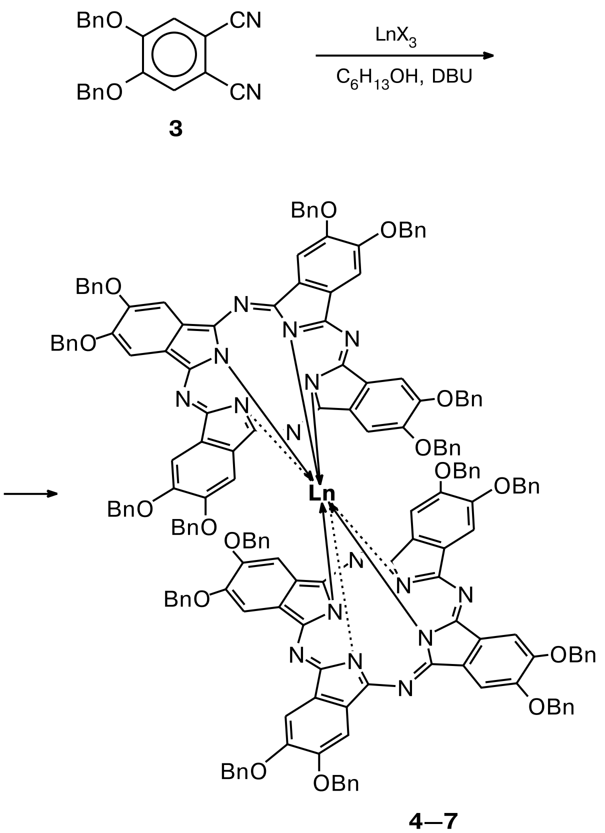
Scheme 2



Ln = Lu (**4**), Dy (**5**), Sm (**6**), Nd (**7**); X = HCO_2 or $MeCO_2$

(lutetium (**4**) and dysprosium complexes (**5**)), are typical of diphthalocyanines. They contain an intense Q-band at 660 to 670 nm with a satellite band at 605 to 620 nm and a peak at 450 to 480 nm due to the presence of an unpaired electron characteristic of sandwich complexes, which are stable radicals. The Soret band usually observed at 360 to 370 nm was indistinct in the spectra of the reaction mixture, which is probably due to contamination. A low "shoulder" at 720 nm indicates the presence of little metal-free phthalocyanine in the crude product.

The absorption spectra of crude samarium (**6**) and neodymium complexes (**7**) (early lanthanides) differ from those described above. They show a bifurcate Q-band with peaks of different intensities at 630 to 640 and 670 to 680 nm. Such electronic absorption spectra are characteristic of the reduced form of phthalocyanine complexes.

The complexes obtained are dark green solids, which are well soluble in benzene and chloroform, virtually insoluble in alcohols, and insoluble in water. Chromatographic purification of diphthalocyanines **4—6** gave good results. The electronic absorption spectra of these complexes became like those of neutral forms: they contain the Q-band at 660 to 680 nm and a characteristic band at 480 to 500 nm (Fig. 2). In contrast, chromatography of Nd diphthalocyanine (**7**) resulted in its intensive decomposition. We found it more efficient to purify this complex by extraction of impurities with hot MeOH in a Soxhlet apparatus. The spectrum of product **7** corresponds to its neutral form.

The complexes obtained were identified by electronic absorption spectroscopy and MALDI-TOF mass spectrometry (Table 1). The electronic absorption spectra revealed that with an increase in the radius of the central metal ion, the major absorption peak experiences a bathochromic shift from 662 to 679 nm for Lu and Nd diphthalocyanines, respectively. The mass spectrum of complex **5** is shown as an example in Fig. 3.

The electrochemical characteristics of the Lu^{III}, Dy^{III}, Sm^{III}, and Nd^{III} complexes obtained were determined by cyclic voltammetry (CV) in *o*-dichlorobenzene (*o*-DCB). In the potential range studied (from –2.0 to 1.1 V), the CV curve shows five reversible redox peaks: two in the anodic and three in the cathodic voltammograms (Fig. 4).

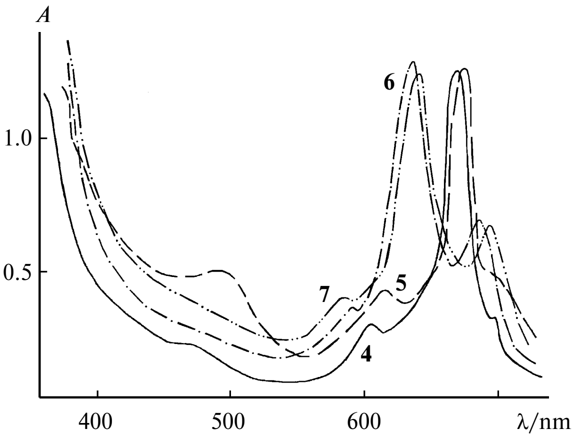


Fig. 1. Electronic absorption spectra of the final reaction mixtures in the synthesis of complexes **4—7**.

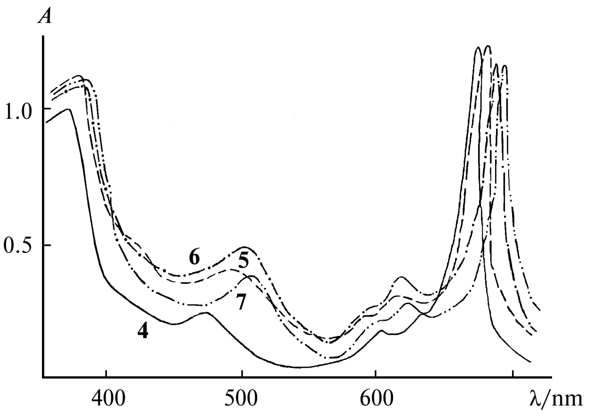


Fig. 2. Electronic absorption spectra of purified diphthalocyanines **4—7**.

Table 1. Physicochemical characteristics of complexes **4—7**

Complex	Molecular formula	M /g mol^{-1}	MALDI-TOF MS, m/z	UV, λ_{max}/nm ($CHCl_3$)	Solubility in C_6H_6, $S\cdot10^4$/mol L^{-1}
4	$C_{176}H_{128}N_{16}O_{16}Lu$	2898.03	2898	662	4.2
5	$C_{176}H_{128}N_{16}O_{16}Dy$	2885.56	2885	667	4.6
6	$C_{176}H_{128}N_{16}O_{16}Sm$	2873.42	2873	675	2.9
7	$C_{176}H_{128}N_{16}O_{16}Nd$	2867.30	2867	679	3.5

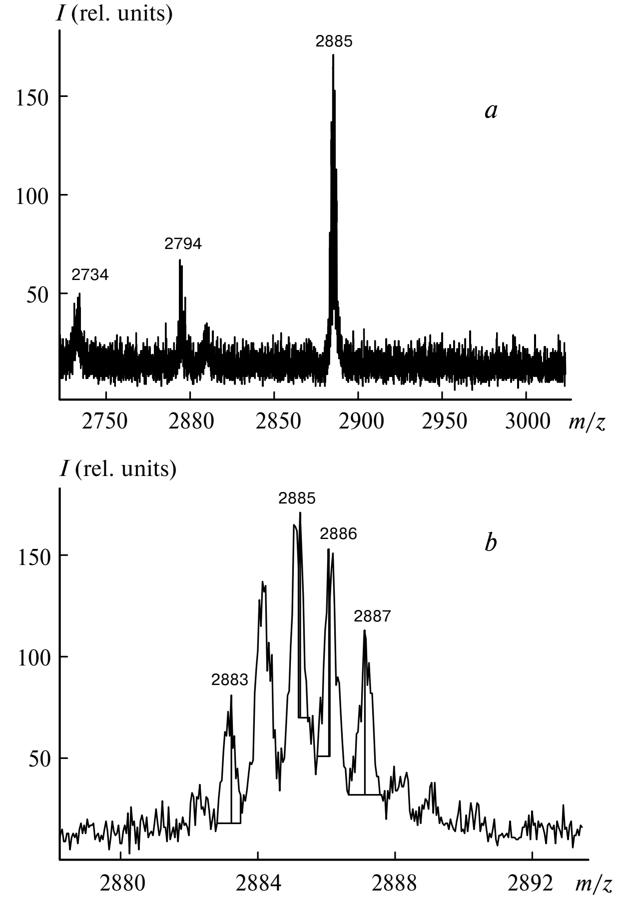


Fig. 3. MALDI-TOF mass spectrum of $[(BnO)_8Pc]_2Dy$ (**5**) (*a*) and the molecular ion peak (*b*).

The first anodic peak appears at 0.51 to 0.65 V, corresponding to the transition

$$[(BnO)_8Pc]_2Ln \underset{+e}{\overset{-e}{\rightleftharpoons}} \{[(BnO)_8Pc]_2Ln\}^+.$$

Ln = Lu, Dy, Sm, Nd

The second anodic peak and three cathodic peaks correspond to the sequential transfer of four electrons to $[(BnO)_8Pc]_2Ln$; the peak potentials are given in Table 2.

The spectroelectrochemical properties of the complexes obtained were examined in a quartz cell that allows spectral changes to be registered during the electrolysis.

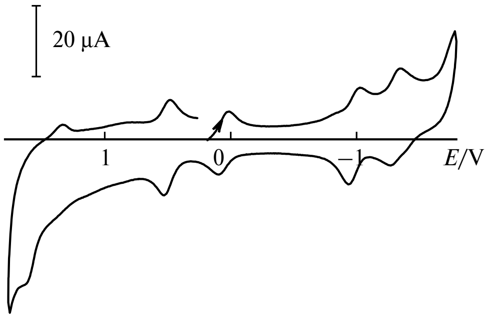


Fig. 4. Cyclic voltammogram of $[(BnO)_8Pc]_2Lu$ (graphite electrode; *o*-dichlorobenzene; 0.15 *M* $Bu^n{}_4NBF_4$; Ag/AgCl/KCl; ν = 200 mV s^{-1}; 20 °C).

Table 2. Potentials of the redox transitions for lanthanide hexadecabenzyloxy(diphthalocyanines)[a]

Complex	$R_{M^{3+}}$/Å	$E_{1/2}{}^b$/V				
		Oxidation		Reduction		
		1	2	3	4	5
$[(BnO)_8Pc]_2Nd$	1.15	0.65	1.27	0.22	−0.98	−1.31
$[(BnO)_8Pc]_2Sm$	1.13	0.61	1.35	0.18	−0.99	−1.29
$[(BnO)_8Pc]_2Dy$	1.07	0.55	1.43	0.11	−0.99	−1.33
$[(BnO)_8Pc]_2Lu$	0.99	0.51	1.50	0.06	−0.98	−1.32

[a] Graphite electrode; *o*-dichlorobenzene; 0.15 *M* $Bu^n{}_4NBF_4$; Ag/AgCl/KCl; ν = 200 mV s^{-1}; 20 °C.

[b] The arithmetic mean of the forward and reverse peak potentials.

The electronic absorption spectra of the neutral, reduced, and oxidized forms of complex **4** are shown in Fig. 5. The character of the spectra is typical of diphthalocyanine complexes of rare-earth elements. The absorption peaks in the electronic absorption spectra and the potentials of the redox transitions of the neutral, reduced, and oxidized forms of all the complexes studied are given in Tables 3 and 2, respectively. The tabulated data show that the spectroscopic and electrochemical characteristics of the complexes are linear functions of the metal ion radius. Earlier,[17] it has been noted that the first processes of oxidation and reduction of diphthalocyanine complexes are associated with electron removal from and addition to, respectively, a partially occupied MO a_2. In the elec-

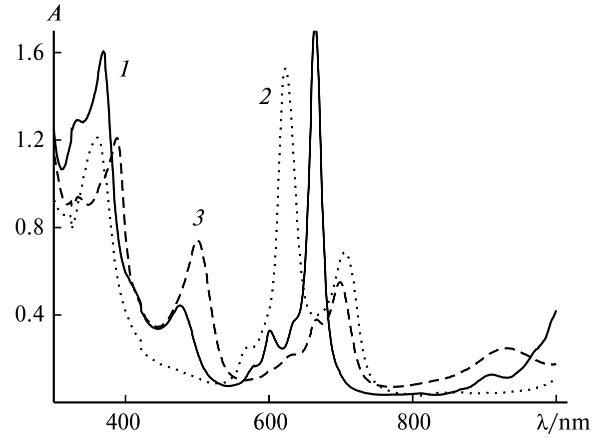


Fig. 5. Electronic absorption spectra of the neutral (*1*), reduced (*2*), and oxidized forms (*3*) of $[(BnO)_8Pc]_2Lu$ generated at $E = -0.5$ and 1.0 V at a platinum electrode (*vs.* Ag/AgCl/KCl) in *o*-dichlorobenzene with 0.15 *M* $Bu^n{}_4NBF_4$ as a supporting electrolyte.

Table 3. Peaks in the electronic absorption spectra of the oxidized, neutral, and reduced forms of the lanthanide complexes with benzyloxyphthalocyanine in *o*-dichlorobenzene

Complex	λ_{max}/nm		
	$(^*Pc_2Ln)^+$	$(^*Pc_2Ln)^0$	$(^*Pc_2Ln)^-$
$[(BnO)_8Pc]_2Nd$	390; 523; 644 sh; 719	374; 500; 587 sh; 613; 646 sh; 676	358; 583 sh; 634; 681
$[(BnO)_8Pc]_2Sm$	390; 520; 648 sh; 717	371; 493; 584 sh; 610; 642 sh; 673	360; 581 sh; 632; 684
$[(BnO)_8Pc]_2Dy$	388; 510; 636 sh; 702	369; 483; 576 sh; 603; 635 sh; 665	362; 574 sh; 623; 688
$[(BnO)_8Pc]_2Lu$	388; 500; 629 sh; 699	369; 476; 577 sh; 602; 634 sh; 664	359; 571 sh; 623; 705

Note. *Pc stands for benzyloxyphthalocyanine. The most intense absorption bands are underlined.

tronic absorption spectra, the band at 470 to 480 nm is due to electron transfer just to this orbital.

Experimental

Freshly distilled *n*-hexanol (high-purity grade) and benzyl bromide (reagent grade) were used; DMF and DMSO (reagent grade) were distilled *in vacuo* over CaH_2. For the synthesis of phthalocyanine complexes with lanthanides, the corresponding metal formates and acetates (analytical grade) were used. *o*-Dichlorobenzene (Aldrich, HPLC grade) for electrochemical studies was passed through a layer of neutral Al_2O_3 immediately before use. Tetra(*n*-butyl)ammonium tetrafluoroborate (Aldrich) was twice recrystallized from Pr^iOH (special purity grade) and dried in a vacuum desiccator at 110 °C.

Electrochemical measurements were carried out on an IPC-Pro potentiostat in a three-electrode cell with a graphite working electrode (pyrolyzed polyacrylonitrile, specific surface 12 m^2 g^{-1}, $m \approx 1$ mg) and 0.15 *M* $Bu^n{}_4NBF_4$ as a supporting electrolyte at 20 °C. A platinum plate served as a counter electrode and a silver chloride reference electrode was used. The cell was deoxygenated by bubbling dry argon. Cyclic voltammograms were recorded at a scan rate of 200 mV s^{-1}. Automatic *IR*-compensation was applied. The resistance *R* of an electrolyte was calculated from the difference between the anodic and cathodic oxidation peaks of ferrocene: $(E^c - E^a) - 0.059 = I \cdot R$, where E^c and E^a are the potentials of the cathodic and anodic oxidation peaks of ferrocene, respectively; *I* is the sum of the cathodic and anodic currents. The concentrations of solutions of the complexes under study in *o*-dichlorobenzene were $1 \cdot 10^{-4}$ mol L^{-1}.

In the spectroelectrochemical studies, the electrochemically generated redox forms of phthalocyanine complexes were accumulated with the use of a P-5827 potentiostat at 20 °C in a quartz cell with the anodic and cathodic compartments separated by a porous glass membrane. The cell was connected to the potentiostat according to a three-electrode scheme. A platinum grid (surface area ~9.7 cm^2) served as a working electrode and a platinum plate, as a counter electrode; 0.15 *M* $Bu^n{}_4NBF_4$ was used as a supporting electrolyte. Potentials were given with reference to a silver chloride electrode. *o*-Dichlorobenzene was used as a solvent. During the electrolysis, the solution in the cell was stirred and the cell was deoxygenated by bubbling dry argon. The electronic absorption spectra of the electrochemically generated redox forms of the complexes were recorded directly in the cell on a Specord UV-VIS spectrophotometer (Carl Zeiss) at 30 000 to 12 500 cm^{-1} (333—800 nm) with 0.15 *M* $Bu^n{}_4NBF_4$ in the same solvent as a standard. The concentrations of solutions of the complexes under study were $1 \cdot 10^{-5}$ mol L^{-1}.

NMR spectra were recorded on a Bruker DPX-200 instrument (200 MHz) relative to Me_4Si. The mass spectra of compounds **2** and **3** were recorded on a Finnigan MAT INSOC-50 instrument; the mass spectra of diphthalocyanine complexes were recorded on a VISION-2000 instrument (MALDI-TOF). Column chromatography was carried out on silica gel 60 (Lancaster, 0.060—0.200 mm) and aluminum oxide (Brockmann II, neutral).

4,5-Dibromopyrocatechol **1** was prepared by bromination of pyrocatechol in acetic acid in 89% yield according to a known procedure[23] and recrystallized from $CHCl_3$ immediately before use.

1,2-Dibenzyloxy-4,5-dibromobenzene (2). Powdered KOH (16.42 g, 0.290 mol) was stirred at ~20 °C in dry DMSO (60 mL). 4,5-Dibromopyrocatechol (9.80 g, 0.037 mol) and then benzyl bromide (25.04 g, 0.14 mol) were added. The reaction mixture was stirred at ~20 °C for 8 h and poured into water with ice (200 mL). The product was extracted with CH_2Cl_2 (4×60 mL). The extract was washed with a dilute solution of NaOH (2×40 mL) and twice with water, dried over $MgSO_4$, and concentrated. The resulting light crystals were recrystallized from 2-methoxyethanol to give compound **2** (8.80 g, 54%), m.p. 144—145 °C. Found (%): C, 53.49; H, 3.65; Br, 35.59. $C_{20}H_{16}Br_2O_2$. Calculated (%): C, 53.60; H, 3.60; Br, 35.66.

^{1}H NMR ($CDCl_3$), δ: 5.11 (s, 4 H, CH_2); 7.15 (s, 2 H, C_6H_2); 7.42 (m, 10 H, Ph). MS (EI, 70 eV), *m/z*: 448 $[M]^+$.

4,5-Dibenzyloxyphthalonitrile (3). A mixture of 1,2-dibenzyloxy-4,5-dibromobenzene (**2**) (7.00 g, 0.016 mol) and CuCN (4.90 g, 0.055 mol) was refluxed in dry DMF (80 mL) for 8 h. After cooling, the solvent was removed *in vacuo*, conc. aqueous NH_3 (300 mL) was added, and the mixture was vigorously stirred for a day. The precipitate was filtered off, washed with water, and dried at 50 °C. The product was extracted with CH_2Cl_2 in a Soxhlet apparatus. The extract was concentrated *in vacuo* to give greenish crystals. Column chromatography on silica gel with chloroform as an eluent followed by recrystallization from ethanol gave compound **3** (2.78 g, 51%) as colorless crystals, m.p. 179—181 °C. Found (%): C, 77.38; H, 4.68; N, 8.17. $C_{22}H_{16}N_2O_2$. Calculated (%): C, 77.63; H, 4.74; N, 8.23. ^{1}H NMR ($CDCl_3$), δ: 5.20 (s, 4 H, CH_2); 7.13 (s, 2 H, C_6H_2); 7.38 (m, 10 H, Ph). MS (EI, 70 eV), *m/z*: 340 $[M]^+$.

Lutetium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecabenzyloxy(diphthalocyanine) (4). A mixture of 4,5-dibenzyloxyphthalonitrile (**3**) (340 mg, 1.00 mmol), lutetium formate dihydrate (42 mg, 0.12 mmol), and DBU (106 mg, 0.70 mmol) was refluxed in *n*-hexanol (5 mL) under argon for 8 h. After cooling, the product was filtered off and washed with aqueous 70% MeOH. The residue was reprecipitated from DMF with water and chromatographed on silica gel with benzene—MeOH (10 : 1) as an eluent to remove resins. Additional chromatography on Al_2O_3 gave complex **4** (153 mg, 44%) as dark green crystals.

Dysprosium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecabenzyloxy(diphthalocyanine) (5) was obtained analogously from dinitrile **3** (200 mg, 0.59 mmol) and dysprosium acetate tetrahydrate (30 mg, 0.74 mmol). The yield of complex **5** was 118 mg (55%).

Samarium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecabenzyloxy(diphthalocyanine) (6) was obtained analogously from dinitrile **3** (200 mg, 0.59 mmol) and samarium acetate tetrahydrate (29 mg, 0.74 mmol). The yield of complex **6** was 100 mg (47%).

Neodymium(III) 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecabenzyloxy(diphthalocyanine) (7) was obtained analogously from dinitrile **3** (200 mg, 0.59 mmol) and neodymium acetate hydrate (25 mg, 0.74 mmol). After cooling, the dark green precipitate that formed was filtered off, washed with MeOH, reprecipitated from DMF with water, and placed in a Soxhlet apparatus to extract impurities with hot MeOH. The residue in the extractor body was pure complex **7** (78 mg, 37%).

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