Synthesis and spectroscopic study of hexadecaalkyl-substituted rare-earth diphthalocyanines

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New hexadecaalkyl-substituted diphthalocyanine complexes of lanthanides $^{R}Pc_2Ln$ (R = Et, or Bu; Ln = Lu, Dy, or Eu) were synthesized by three methods: in solution in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene, in a melt of a mixture of the reagents, and under microwave irradiation. The first of the above-mentioned procedures has an advantage for the preparation of Dy and Eu diphthalocyanines, whereas the melt synthesis is a method of choice for the preparation of Lu complexes. The reaction time decreases in going from the first to the third method. The structures of the complexes were confirmed by mass spectrometry, NMR spectroscopy, and electronic absorption spectroscopy.

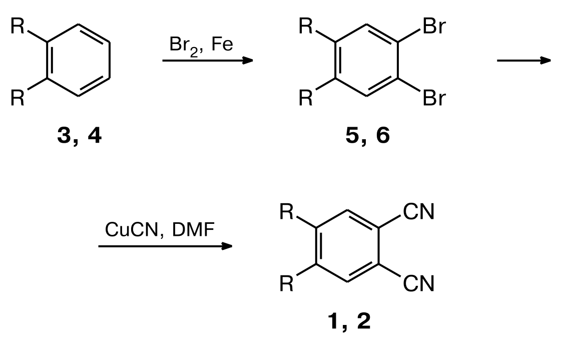
Key words: diphthalocyanines, rare-earth elements, ^{1}H NMR spectra, electronic absorption spectra.

Diphthalocyanine complexes of rare-earth elements have attracted considerable attention for more than three decades because of their practically important properties, such as spectroscopic,[1] electrochromic,[2] gas-sensor,[3,4] semiconducting,[5] mesogenic,[6] magnetic,[7] *etc.* However, in spite of extensive studies of diphthalocyanine complexes, many data on the properties of these compounds are insufficiently reliable and often contradictory. Hence, important challenges now are to synthesize new, including symmetrically substituted, complexes, investigate their properties with the aim of revealing the structure—property relationship, and extend the field of their application.

In the present study, we synthesized hexadecaalkyl-substituted diphthalocyanine complexes of rare-earth metals (REM), in particular, of Lu, Dy, and Eu. The reactions with the use of 4,5-diethylphthalodinitrile (**1**) and 4,5-dibutylphthalodinitrile (**2**) as the starting phthalogens afforded symmetrically substituted diphthalocyanine complexes (unlike unsymmetrical *tert*-butyl-substituted diphthalocyanines studied in-depth[8,9]), which are better soluble compared to rare-earth hexadecamethyl-substituted diphthalocyanines prepared earlier.[10,11]

Phthalodinitriles **1** and **2** were synthesized according to Scheme 1 with the use of 1,2-diethylbenzene (**3**) and 1,2-dibutylbenzene (**4**), respectively, as the starting reagents. Compound **3** is a commercially available product. Compound **4** was prepared according to known procedures[12—14] by cross-coupling of *o*-dichlorobenzene with two equivalents of *n*-butylmagnesium bromide in the presence of dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) as a catalyst. The reactions of dialkylbenzenes **3** and **4** with Br_2 in dichloromethane in the presence of catalytic amounts of an iron powder and iodine afforded compounds **5** and **6** in 62 and 50% yields, respectively. Cyanation of dibromodialkylbenzenes **5** and **6** with dibromide and CuCN (in a molar ratio of 1 : 3) according to procedures described earlier[15,16] gave rise to dinitriles **1** and **2**, respectively, in ~50% yields. A change in the dibromide-to-CuCN ratio to 1 : 5 made it possible to increase the yields of dinitriles **1** and **2** to 61—64%.

Scheme 1



R = Et (**1**, **3**, **5**), Bu (**2**, **4**, **6**)

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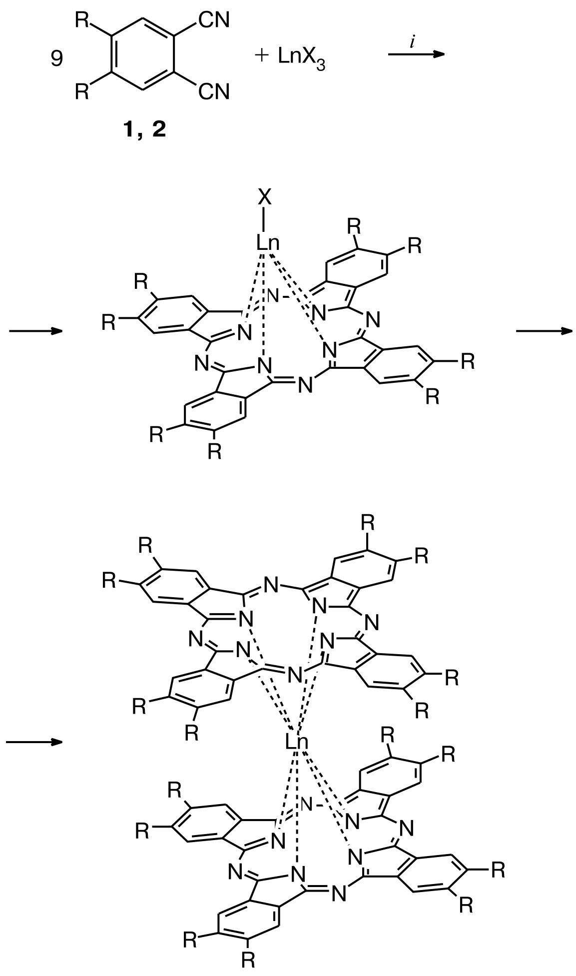
Three methods were used for the synthesis of diphthalocyanines **7a—f** (Scheme 2). One of these methods is based on procedures[17—19] developed for the preparation of complexes containing alkoxy or heptyl groups at positions 2, 3, 9, 10, 16, 17, 23, and 24 of the phthalocyanine macroligands. Complexes **7a—f** were synthesized according to this method by refluxing compound **1** or **2** and the corresponding rare-earth acetate or acetylacetonate in isoamyl alcohol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under argon for 15—20 h. The target complexes were isolated in yields from 5 to 53% depending on the nature of metal and substituents in the macroligand (Table 1). In going from europium to lutetium, the yields of diphthalocyanines **7a—f** in the reactions with rare-earth acetates and acetylacetonates decrease from 35 to 5% and from 53 to 14%, respectively. This fact is, presumably, associated with a decrease in the ionic radius of REM in going from europium to lutetium, which leads to an enhancement of the influence of the steric factors caused by the presence of alkyl substituents in the phthalocyanine rings. Higher yields obtained in the reactions with rare-earth acetylacetonates are, apparently, attributable to the fact that the acetylacetonate ligand is more prone to the replacement by the second phthalocyanine ring compared to the acetate ligand.

Scheme 2



7a—f

i. Method *1*: $C_5H_{11}{}^iOH$, DBU, reflux for 15—20 h;
method *2*: 250—290 °C, 2—8 h;
method *3*: MW (300—450 W), 5—8 min.

Ln = Lu (**7a**, **7d**), Dy (**7b**, **7e**), Eu (**7c**, **7f**); X = OAc, acac;
R = Et (**1**, **7a—c**), Bu (**2**, **7d—f**).

Table 1. Yields of the diphthalocyanine complexes depending on the nature of the starting reagents and the synthesis methods

Compound	R	LnX_3	Synthesis method*	Yield (%)
7a	Et	$Lu(OAc)_3$	1	11
		$Lu(acac)_3$	1	21
7b	Et	$Dy(OAc)_3$	1	15
		$Dy(acac)_3$	1	33
7c	Et	$Eu(OAc)_3$	1	26
		$Eu(acac)_3$	1	53
7d	Bu	$Lu(OAc)_3$	1	6
			2	35
			3	16
		$Lu(acac)_3$	1	14
			2	49
			3	23
7e	Bu	$Dy(OAc)_3$	1	21
		$Dy(acac)_3$	1	39
7f	Bu	$Eu(OAc)_3$	1	24
			2	22
			3	20
		$Eu(acac)_3$	1	46
			2	31
			3	17

* See Scheme 2.

Another procedure for the synthesis was described in-depth in the literature.[20—25] However, this method was used for the preparation of symmetrical structures only in the case of hexadecamethyl-substituted diphthalocyanines.[10] Complexes **7d,f** were synthesized by fusing a mixture of dinitrile **2** with rare-earth acetates or acetylacetonates (in a molar ratio of 1 : 8) with a gradual increase in the temperature from 100 to 290 °C and keeping the reaction mixture at this temperature from 2 to 8 h depending on the nature of the starting rare-earth compounds. In the spectroscopic characteristics, the resulting complexes are identical to the complexes prepared earlier in solutions. This method made it possible to reduce the reaction time by at least one half and led to a substantial increase in the yield of lutetium diphthalocyanine **7d** (see Table 1). Hence, this approach can be considered as a method of choice for the synthesis of such compounds.

The third method was first described[26] for the synthesis of unsubstituted and octa-*tert*-butyl-substituted REM diphthalocyanines. Up to now, this method has not been used for the preparation of symmetrically substituted alkyl complexes. This method differs from the method based on thermal fusion primarily in that the complex formation is initiated by microwave (MW) irradiation. The use of MW enabled us to substantially simplify the synthesis by performing it in the absence of solvents as well as to decrease the reaction time from several hours to several minutes. The synthesis was performed by irradiation of a mixture of the reagents in a microwave oven. The microwave power was varied from 300 to 850 W. The irradiation time was varied from 30 s to 10 min. The optimum conditions for the synthesis of sandwich-like complexes **7d,f** in relation to the nature of the starting reagents and their ratio were found experimentally. It was demonstrated that the power of 300 W and the irradiation time of 5 min are optimum for the synthesis with the use of lutetium acetate and 4,5-dibutylphthalonitrile **2**. More prolonged irradiation (8 min) and a higher microwave power (450 W) are required in the case of europium acetate. The synthesis according to this method with the use of rare-earth acetylacetonates as the starting compounds did not lead to an increase in the yield of the target diphthalocyanines (see Table 1).

The structures of the sandwich-like rare-earth phthalocyanines were studied by ^{1}H NMR spectroscopy and mass spectrometry. The presence of the radical fragment $\mathrm{Pc}^{\bullet -}$ in the diphthalocyanine molecules does not allow one to obtain reliable NMR spectroscopic data in usual solvents. Hence, to record the ^{1}H NMR spectra, we transformed the complexes into forms devoid of radical fragments using a procedure, which has been proposed in the studies.[27,28] According to this procedure, hydrazine hydrate (from 1 to 5 vol.%) was added to a solution of rare-earth diphthalocyanine in a mixture of deuterated chloroform and DMSO (1 : 1, v/v). In the presence of hydrazine hydrate, the $\mathrm{Pc}^{\bullet -}$ fragment is reduced to the Pc^{2-} dianion.

$$[\mathrm{Pc}^{\bullet -}\mathrm{Lu}^{3+}\mathrm{Pc}^{2-}]^0 \underset{-e}{\overset{+e}{\rightleftharpoons}} [(\mathrm{Pc}^{2-})_2\mathrm{Lu}^{3+}]^-$$

Table 2. ^{1}H NMR spectra of compounds **1** and **2** and the Lu and Eu diphthalocyanine complexes synthesized on their basis

Compound	δ^a
1^b	1.26 (t, 3 H, CH_3); 2.74 (q, 2 H, CH_2); 7.58 (s, 1 H, ArH)
2^c	0.90 (t, 3 H, CH_3); 1.25—1.60 (m, 4 H, CH_2CH_2); 2.70 (t, 2 H, $ArCH_2$); 7.93 (s, 1 H, ArH)
7a^d	1.75 (t, 48 H, CH_3); 3.31 (m, 32 H, $ArCH_2$); 8.65 (s, 16 H, ArH)
7c^d	2.57 (t, 48 H, CH_3); 4.21—4.41 (m, 32 H, $ArCH_2$); 10.91 (s, 16 H, ArH)
7d^d	1.26 (t, 48 H, CH_3); 1.79—2.15 (m, 64 H, CH_2CH_2); 3.28 (t, 32 H, $ArCH_2$); 8.61 (s, 16 H, ArH)
7f^d	1.77 (t, 48 H, CH_3); 2.57—3.09 (m, 64 H, CH_2CH_2); 4.27 (t, 32 H, $ArCH_2$); 10.94 (s, 16 H, ArH)

[a] $J = 7.3$ Hz.
[b] In $CDCl_3$.
[c] In $(CD_3)_2SO$.
[d] In $CDCl_3 + (CD_3)_2SO + N_2H_4 \cdot H_2O$.

In the diphthalocyanine molecule, both macrocycles become diamagnetic, which allowed us to record NMR signals. The ^{1}H NMR spectra of lutetium and europium phthalocyanines show signals, which are characteristic of the corresponding nitriles but are shifted downfield by 0.6—0.7 and 2.9—3.3 ppm, respectively (Table 2, Fig. 1).

We failed to obtain satisfactory ^{1}H NMR spectroscopic data for dysprosium diphthalocyanines, apparently, because of the paramagnetic nature of the triple-charged metal ion. This fact has been observed earlier[17] in at-

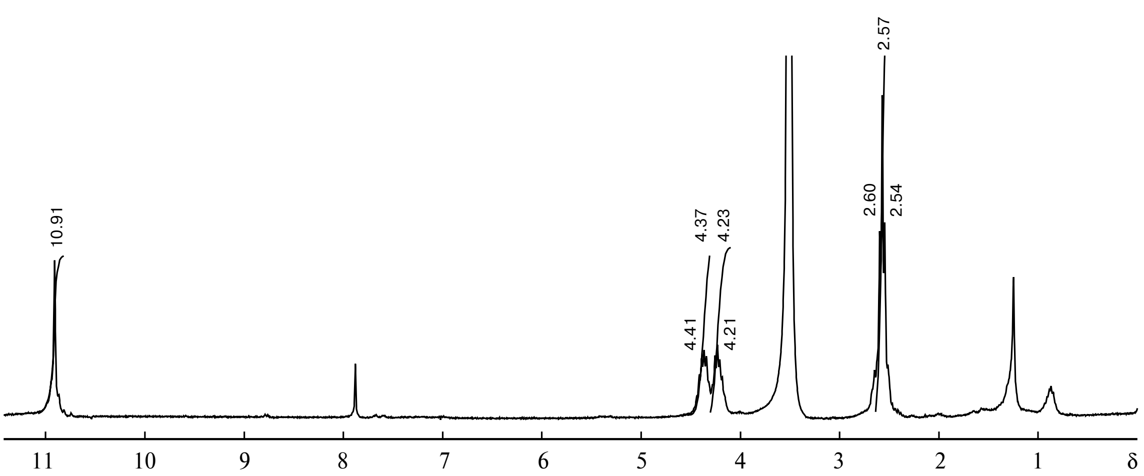


Fig. 1. ^{1}H NMR spectrum of diphthalocyanine $^{(\mathrm{Et})}\mathrm{Pc}_2\mathrm{Eu}$ (**7c**) ($CDCl_3$, $(CD_3)_2SO$, $N_2H_4 \cdot H_2O$).

Table 3. MALDI-TOF and electronic absorption spectra of solutions of diphthalocyanines

Compound	M_r (calculations)	MS,* m/z, $[M]^+$	λ_{max}/nm, $CHCl_3$
7a	1649	1648	325, 350, 476, 608, 675
7b	1637	1636	328, 354, 483, 612, 681
7c	1627	1626	329, 355, 491, 617, 687
7d	2098	2098	325, 352, 479, 610, 677
7e	2085	2084	328, 354, 485, 615, 684
7f	2075	2075	330, 357, 494, 618, 690

* The most intense isotope peak of the molecular ion is given.

tempting to record NMR spectra of the reduced forms of alkyl- and alkoxy-substituted gadolinium diphthalocyanines.

The complexes were studied by MALDI-TOF mass-spectrometry (Table 3, Fig. 2). The spectra of compounds **7a—f** have peaks of single-charged ions with masses corresponding to molecular ions.

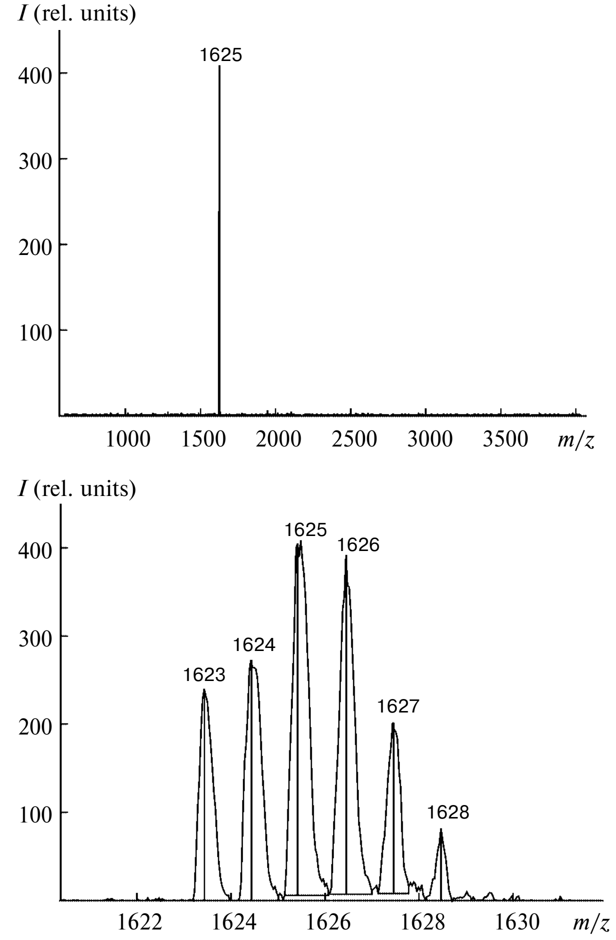


Fig. 2. MALDI-TOF spectrum of diphthalocyanine $^{(Et)}Pc_2Eu$ (**7c**) and the molecular ion peak.

The complexes were characterized also by spectrophotometry. According to the results of electronic absorption spectroscopy, diphthalocyanines **7a—f** were synthesized as the green $[Pc^{\bullet -}M^{3+}Pc^{2-}]^0$ forms. The electronic absorption spectra of these compounds have a Q band at 675—690 nm corresponding to the electron transition between the π and π* orbitals of the phthalocyanine ring and a characteristic band at 480—490 nm associated with the presence of the $Pc^{\bullet -}$ radical fragment. The Soret band has maxima at 330 and 350 nm (see Table 3).

Analysis of the electronic absorption spectra of the diphthalocyanine complexes revealed some features, which are characteristic of these compounds and are consistent with the published data.[10,17,19] The more pronounced bathochromic shift of the Q band (by 12—13 nm) is observed in going from Lu to Eu due to an increase in the ionic radius. In addition, a vibrational satellite and the band corresponding to the $Pc^{\bullet -}$ fragment are shifted bathochromically by 8—9 and 15 nm, respectively. The position of the Soret band changes only slightly (Fig. 3).

A slight (2—3 nm) but characteristic shift of the Q band to longer wavelengths is observed in going from the ethyl to butyl substituents (see Table 3). These data as well as the results published in the literature[10,17] allow us to conclude that the electron-donating groups in the complexes under study are responsible for a bathochromic shift of the Q band compared to the unsubstituted complexes. At the same time, the σ-donor properties of the alkyl groups lead to a gradual disappearance of this shift as the length of the carbon chain in the substituents increases (Table 4).

We studied chemical oxidation and subsequent reverse reduction of symmetrical butyl-substituted lutetium diphthalocyanine complex **7d**. For this purpose, a solution of phthalocyanine in chloroform was treated with bromine vapor. Oxidation of diphthalocyanine leads to a decrease in the intensity of absorption in the region of the Q band up to its complete disappearance accompanied by the simultaneous appearance of two new absorption

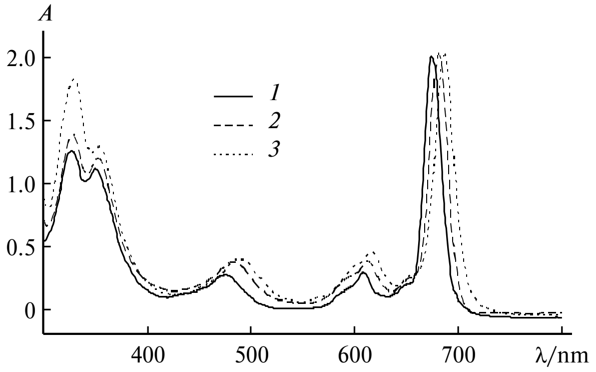


Fig. 3. Electronic absorption spectra of diphthalocyanines $^{(Et)}Pc_2Ln$ (**7a—c**) in $CHCl_3$; Ln = Lu (*1*), Dy (*2*), Eu (*3*).

Table 4. Positions of the Q band in electronic absorption spectra (λ_{max}/nm, $CHCl_3$) of selected unsubstituted and 2,3,9,10,16,17,23,24,2′,3′,9′,10′,16′,17′,23′,24′-hexadecaalkyl-substituted diphthalocyanines

Central atom	Substituent				
	H	Me	Et	Bu^n	n-C_7H_{15}
Lu	654[10]	674[10]	675	677	—
Eu	671[17]	—	687	690	690[17]

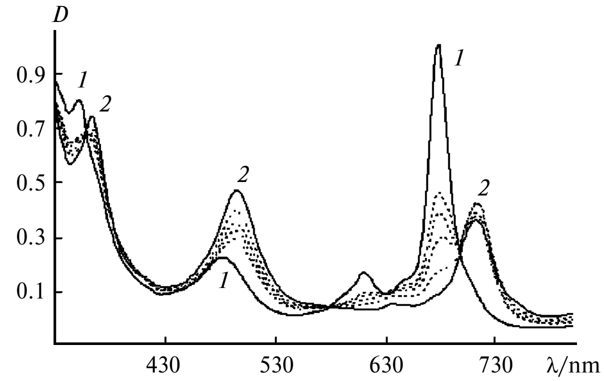


Fig. 4. Electronic absorption spectra of the neutral (*1*) and oxidized (with bromine) (*2*) forms of **7d** in $CHCl_3$. Intermediate spectra are indicated by dashed lines.

maxima at 494 and 713 nm, the Soret band being bathochromically shifted from 352 to 362 nm (Fig. 4).

The electronic absorption spectra of the oxidation product are indicative of the formation of the radical cation.[29] Treatment with triethylamine led to regeneration of the starting green form of diphthalocyanine. The redox transformations are characterized by the presence of isobestic points. This indicates that the phthalocyanines synthesized can be reversibly oxidized with the corresponding chemical reactants (see Fig. 4). Hence, these compounds hold promise as materials for electrochromic devices.

Experimental

Solvents were purified according to standard procedures immediately before use.

The electronic absorption spectra in the visible region were recorded on a Helios-α spectrophotometer in 0.5- and 1-cm quartz cells using $CHCl_3$, AcOEt, and C_6H_6 as solvents. Thin-layer chromatography was carried out on Merck Silica Gel 60 F_{254} and Merck Aluminium Oxide F_{254} neutral plates. Column chromatography was performed on Lancaster Silica Gel 60 (0.060—0.200 mm) and Merck Silica Gel 40 (0.063—0.200 mm). The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument (200 and 50 MHz, respectively) in $CDCl_3$ or $(CD_3)_2SO$. The chemical shifts are given in the δ scale relative to Me_4Si. The mass spectra of diphthalocyanines were obtained on a VISION-2000 (MALDI-TOF) instrument. The mass spectra of phthalodinitriles were recorded on a Finnigan MAT INSOC-50 instrument (EI, 70 eV). The IR spectra of phthalodinitriles were measured on Specord M-70 and Specord UR-20 spectrophotometers in Nujol mulls.

The syntheses of the phthalocyanine complexes by the MW method were carried out in a Samsung 1714R microwave oven.

1,2-Dibromo-4,5-diethylbenzene (5). Diethylbenzene **3** (Aldrich) (17.4 g, 0.130 mol), CH_2Cl_2 (40 mL), a Fe powder (0.9 g, 16 mmol), and crystalline I_2 (~0.35 g, 1.4 mmol) were placed in a three-neck flask equipped with a magnetic stirrer, a thermometer, a dropping funnel, and an HBr outlet adapter. The reaction mixture was cooled to 2 °C. The flask was protected from light, and Br_2 (14 mL, 0.275 mol) was added dropwise with stirring for 2 h, the temperature being maintained below 5 °C. The reaction mixture was stirred at ~20 °C for 10 h and then at 40 °C for 10 h, after which it was washed with 5% Na_2SO_3 (3×100 mL) and H_2O (3×100 mL) and dried with calcined $MgSO_4$. The solution was filtered off from the drying agent and concentrated. The residue was distilled *in vacuo* and the fraction with b.p. 151—152 °C (14 Torr) was collected. Compound **5** was obtained in a yield of 23.5 g (62%) as a colorless viscous liquid. ^1H NMR ($CDCl_3$), δ: 1.18 (t, 3 H, CH_3, J = 7.3 Hz); 2.56 (q, 2 H, CH_2, J = 7.3 Hz); 7.38 (s, 1 H, ArH). ^{13}C NMR ($CDCl_3$), δ: 14.86 (CH_3); 24.90 (CH_2); 121.51 (C(3), C(6)); 133.13 (C(1), C(2)); 142.87 (C(4), C(5)). MS (EI, 70 eV), m/z: 292 $[M]^+$.

1,2-Dibromo-4,5-dibutylbenzene (6). Compound **4** (7.07 g, 0.037 mol), CH_2Cl_2 (10 mL), a Fe powder (0.257 g, 4.6 mmol), and crystalline I_2 (0.1 g, 0.4 mmol) were placed in a three-neck flask equipped with a magnetic stirrer, a thermometer, a dropping funnel, and an HBr outlet adapter. The reaction mixture was cooled to 2 °C. The flask was protected from light, and Br_2 (4 mL, 0.079 mol) was added dropwise with stirring for 1.5 h, the temperature being maintained below 5 °C. The reaction mixture was stirred at ~20 °C for 28 h, then washed with 5% Na_2SO_3 (3×30 mL) and H_2O (3×100 mL), dried with calcined $MgSO_4$, and concentrated. The residue was recrystallized from acetone. Compound **6** was obtained in a yield of 6.39 g (50%) as colorless small crystals, m.p. 33—34 °C (*cf.* lit. data[16]: 34—35 °C).

4,5-Diethylphthalodinitrile (1). Compound **5** (8 g, 0.027 mol), CuCN (12.33 g, 0.135 mol), and DMF (150 mL) were placed in a round-bottom flask equipped with a reflux condenser. The reaction mixture was refluxed for 4.5 h and poured into a 7.5% aqueous $FeCl_3 \cdot 6H_2O$ solution (150 mL). After the formation of a precipitate, H_2O (400 mL) was added to the reaction mixture. After 30 min, the precipitate that formed was filtered off from the solution on a sinter funnel and dried in a vacuum desiccator. The dry residue was rinsed off the filter with $CHCl_3$, washed with water (3×100 mL), dried with calcined $MgSO_4$, filtered, and concentrated. Subsequent purification was carried out by column chromatography (Lancaster silica gel, C_6H_6 as the eluent). The fraction containing the pure target compound and the fraction containing an impurity of 2-bromo-4,5-diethylbenzonitrile were isolated. The latter fraction was purified by recrystallization from n-hexane. Compound **1** was obtained in a yield of 3.09 g (61.3%) as colorless crystals, m.p. 104 °C (*cf.* lit. data[15]: 103.5—104 °C), R_f 0.65 (SiO_2 F_{254}, C_6H_6). Found (%): C, 78.21, 78.40; H, 6.39, 6.51; N, 15.08, 15.30. $C_{12}H_{12}N_2$. Calculated (%): C, 78.26; H, 6.52; N, 15.22. ^{13}C NMR ($CDCl_3$), δ: 13.50 (CH_3); 25.12 (CH_2); 112.87 (C(1), C(2)); 115.67 (CN);

132.77 (C(3), C(6)); 148.12 (C(4), C(5)). IR (Nujol mulls), ν/cm^{-1}: 2930 s, 2860 s, 2235 s, 1598 m, 1467 s, 1380 m, 1245 m, 1070 m, 930 m, 900 m, 882 m, 795 m, 730 m. MS (EI, 70 eV), *m/z*: 184 [M]$^+$.

4,5-Dibutylphthalodinitrile (2). Compound **6** (6.53 g, 0.019 mol), CuCN (8.44 g, 0.094 mol), and DMF (110 mL) were placed in a round-bottom flask equipped with a reflux condenser. The reaction mixture was refluxed for 4 h and poured into a 7.5% aqueous $FeCl_3 \cdot 6H_2O$ solution (80 mL). After the formation of a precipitate, H_2O (200 mL) was added to the reaction mixture. After 30 min, the precipitate that formed was filtered off from the solution on a sinter funnel and dried in a vacuum desiccator. The dry residue was rinsed off the filter with $CHCl_3$, washed with water (3×100 mL), and dried with calcined $MgSO_4$. Subsequent purification was carried out by column chromatography (Merck silica gel, C_6H_6 as the eluent), and the target compound containing impurities of 2-bromo-4,5-dibutylbenzonitrile and octabutyl-substituted copper phthalocyanine was isolated. The crude product was purified by repeated extraction from a hot hexane solution with 80% aqueous EtOH. After evaporation of the aqueous-alcoholic extract, the dry residue was recrystallized from *n*-hexane. Compound **2** was obtained in a yield of 2.86 g (63.5%) as colorless needle-like crystals, m.p. 51 °C (*cf.* lit. data**16**: 51—52 °C), R_f 0.55 (SiO_2 F_{254}, C_6H_6). Found (%): C, 80.20, 80.50; H, 8.25, 8.30; N, 11.86. 11.76. $C_{16}H_{20}N_2$. Calculated (%): C, 80.00; H, 8.33; N, 11.67. ^{13}C NMR ($(CD_3)_2SO$), δ: 13.66 (CH_3); 22.01 ($CH_3\underline{C}H_2CH_2CH_2$); 31.35 ($CH_3CH_2\underline{C}H_2CH_2$); 32.05 ($CH_3CH_2CH_2\underline{C}H_2$); 111.65 (C(1), C(2)); 116.08 (CN); 134.33 (C(3), C(6)); 147.44 (C(4), C(5)). IR (Nujol mulls), ν/cm^{-1}: 2950 s, 2930 s, 2870 s, 2235 s, 1598 m, 1492 m, 1467 s, 1380 m, 1245 m, 1108 m, 939 m, 912 m, 882 m, 741 m. MS (EI, 70 eV), *m/z*: 240 [M]$^+$.

Synthesis of bis(2,3,9,10,16,17,23,24-octaalkylphthalocyanine)lanthanides 7a—f in solution (general procedure). Phthalonitrile **1** (**2**) (0.820 mmol), $Ln(OAc)_3 \cdot nH_2O$ or $Ln(acac)_3 \cdot 3H_2O$ (Ln = Lu, Dy, or Eu) (0.089 mmol), and isoamyl alcohol (2 mL) were placed in a round-bottom flask and the reaction mixture was heated until a transparent solution was obtained. Then DBU (70 mg, 0.460 mmol) was added and the reaction mixture was refluxed under a stream of Ar until the starting nitrile was completely disappeared (15—20 h). The course of the reaction was monitored by TLC (Merck Aluminium Oxide F_{254} neutral, C_6H_6 as the eluent). After completion of the reaction, the mixture was diluted with $CHCl_3$ (25 mL) and filtered off from insoluble impurities on a sinter funnel. The solvent was distilled off and the dry residue was refluxed in 80% aqueous MeOH (3×50 mL) followed by filtration and drying in a vacuum desiccator to prepare a powder, which was dissolved in C_6H_6 and chromatographed on a column (Merck Silica Gel 40 (0.063—0.200 mm), C_6H_6 as the eluent). Preparative purification of diphthalocyanines was carried out by TLC (Merck Aluminium Oxide F_{254} neutral, C_6H_6 as the eluent). The yields and spectroscopic data for the compounds synthesized are given in Tables 1—3.

Synthesis of bis(2,3,9,10,16,17,23,24-octabutylphthalocyanine)lanthanides 7d and 7f by fusing reagents (general procedure). Phthalonitrile **2** 0.2 г (0.820 mmol) and $Ln(OAc)_3 \cdot nH_2O$ or $Ln(acac)_3 \cdot 3H_2O$ (Ln = Lu, Dy, or Eu) (0.089 mmol) were placed in a round-bottom flask equipped with a reflux condenser. The reaction mixture was heated with a gradual increase in the temperature from 100 to 290 °C and then kept at 290 °C for 2—8 h until the mixture was solidified. After completion of the synthesis, the reaction mixture was dissolved in $CHCl_3$ and filtered off from insoluble impurities on a sinter funnel. The solvent was distilled off. Subsequent purification was carried out as described above.

Synthesis of bis(2,3,9,10,16,17,23,24-octabutylphthalocyanine)lanthanides 7d and 7f under microwave irradiation (general procedure). Phthalonitrile **2** (0.2 g, 0.820 mmol) and $Ln(OAc)_3 \cdot nH_2O$ or $Ln(acac)_3 \cdot 3H_2O$ (Ln = Lu, Dy, or Eu) (0.089 mmol) were placed in a round-bottom flask and the flask was placed in a microwave oven. The microwave power was 300—450 W. The reaction time was 5—8 min. After completion of the synthesis, the reaction mixture was dissolved in $CHCl_3$ and filtered off from insoluble impurities on a sinter funnel. The solvent was distilled off. Subsequent purification was carried out as described above.

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