

An Amphiphilic Lutetium Bisphthalocyanine: Lu[(PEO)₄Pc][{(DodO)₄Pc}]

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The synthesis of an amphiphilic lutetium bisphthalocyanine is described. One phthalocyanine of the sandwich complex bears four hydrophobic chains (C₁₂H₂₅O = DodO), and the other bears four hydrophilic polyether groups (CH₃(OCH₂CH₂)_nO = PEO). The molecule has been characterized by ¹H NMR and ESI mass spectrometry. The mean value for *n*, the number of polyethyleneoxy units in the starting PEOH, is 8 with a Gaussian distribution around that value; however, for the most abundant lutetium bisphthalocyanine, 4*n* = 26. On the spectrum, the peak corresponding to the adduct with two Na⁺ is higher than the one of the singly charged ion, a result of the affinity of polyethers for alkali ions.

Introduction

Interest in the chemistry of the phthalocyanines and their metallic complexes is due to remarkable electronic properties that make them particularly attractive for the design of molecular materials for electronics and optoelectronics.^{1,2} Various methods have been used to order them as multilayers, especially the Langmuir–Blodgett technique.^{3,4} Amphiphilic molecules are best suited to the formation of well-organized films as the interaction with the aqueous subphase is strengthened. Amphiphilic monophthalocyanines that have been used until now bear hydrophilic substituents on one or two of the outer benzene rings of the macrocycle and alkyl or alkoxy groups on the others.^{3–9} The characteristics of the ordered films thus obtained vary according to the nature of the molecular units.⁴

Because of their peculiar electronic properties, building Langmuir–Blodgett films of lanthanide bisphthalocyanines, which requires the synthesis of an amphiphilic sandwich complex, appeared stimulating. Multilayers of unsubstituted bisphthalocyanines of various lanthanides

(LnPc₂) have been obtained;^{10–12} however, films of better quality are expected from suitably substituted derivatives.^{13–15} Up to the present work, no real amphiphilic lanthanide bisphthalocyanine has been described. Simon and co-workers have synthesized lutetium bisphthalocyanines in which the two macrocycles are hydrophobic and the ethyleneoxy side chains are hydrophilic. This is not really convenient for the orientation at the water/air interface and consequently for the formation of Langmuir–Blodgett films on solid substrates.¹⁶ The synthetic path to unsymmetrically substituted Ln(III) sandwich complexes developed in our group appears to be appropriate.¹⁷ This article describes the synthesis and some properties of a lutetium bisphthalocyanine in which one of the two macrocycles is substituted by four hydrophilic methoxypolyethyleneoxy (PEO) chains and the second phthalocyanine bears four hydrophobic dodecyloxy (DodO) groups; the substituents are connected to the macrocycles via an ether linkage (Figure 1).

Results and Discussion

Preparation of the substituted phthalonitriles is the first stage of the synthesis. This is done by reacting 4-nitrophthalonitrile with the appropriate long-chain alcohol in dimethylformamide (DMF) in the presence of

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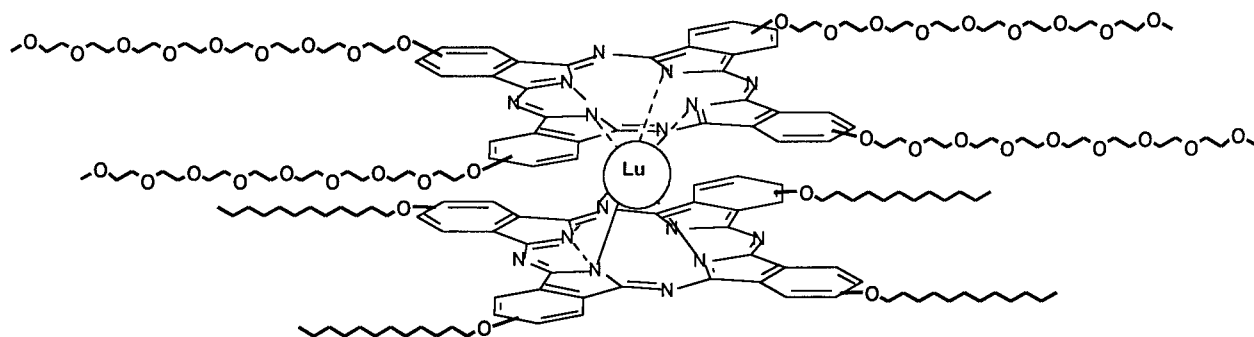
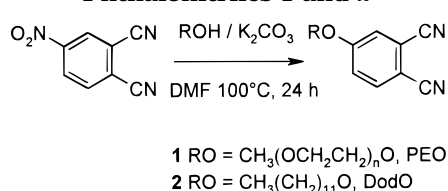


Figure 1. Lu[(PEO)₄Pc][(DodO)₄Pc] (**7**).

Scheme 1. Synthesis of the Substituted Phthalonitriles 1 and 2



an insoluble base, K₂CO₃ (Scheme 1).^{18,19} The carbonate, finely powdered, is added at once to the other reactants to avoid the formation of the usually reported byproducts, 4-hydroxyphthalonitrile and 4,4'-oxybis(phthalonitrile).²⁰

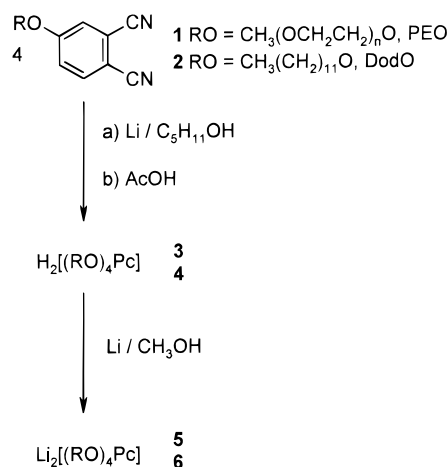
After evaporation of DMF, **1** is recovered with the unreacted poly(ethylene glycol)monomethyl ether (PEOH), which will be eliminated in the second stage of the synthesis. The phthalonitrile **2** is purified by chromatography on a silica gel column. The lithium phthalocyanine and the metal-free phthalocyanine have been synthesized following an already published procedure.^{21, 22}

The purification of the phthalocyanines is much easier when they are protonated. The hydrophilic, water soluble derivative **3** is separated from the low molecular weight impurities, the poly(ethylene glycol)monomethyl ether particularly, by ultrafiltration of its aqueous solution. Being totally insoluble in acetone, **4** is purified by washing in a Soxhlet apparatus. The pure lithium phthalocyanines **5** and **6** are obtained by reaction of the metal-free phthalocyanines (**3** and **4**) with lithium methoxide in refluxing methanol, a procedure precedently applied to naphthalocyanines (Scheme 2).²³

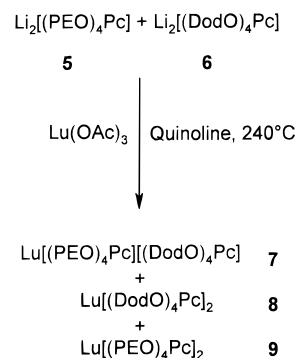
The amphiphilic lutetium bisphthalocyanine **7** is prepared by condensation of 1 equiv of each of the lithium monophthalocyanines **5** and **6** with 1 equiv of lutetium acetate, in quinoline, at high temperature (Scheme 3).

After evaporation of quinoline, the residue is chromatographed on silica gel. The symmetrical bisphthalocyanine **8**, with both macrocycles bearing four dodecyloxy substituents, is isolated by elution with pure dichloromethane (yield, 22%). From a second elution with dichloromethane/methanol (90/10 to 60/40 by volume), a

Scheme 2. Synthesis of the Phthalocyanines 3–6



Scheme 3. Synthesis of the Lutetium Bisphthalocyanines 7–9



mixture of **7** and **9** is obtained. These two compounds are separated by another chromatography on silica gel, with a ternary mixture of solvents, dichloromethane/ethyl acetate/methanol (60/30/10).

The amphiphilic lutetium bisphthalocyanine **7** (Figure 1) has been characterized by physicochemical methods. This compound is paramagnetic; however, its NMR study is possible after solubilization in deuterated DMF and addition of hydrazine hydrate. The molecular form of **7** bears one unpaired electron (Lu³⁺, Pc²⁻, Pc⁻), but its reduced form (Lu³⁺, Pc²⁻, Pc²⁻) is diamagnetic.^{17b}

Each Pc macrocycle, substituted by either four dodecyloxy groups or four methoxypolyethyleneoxy groups, has four regioisomers. Of course, the sandwich complex has many more isomers; however, it is not possible to identify them by NMR.² The two kinds of substituents are linked to the aromatic ring by the same OCH₂CH₂ unit, and thus the methylene protons near the Pc core

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have identical shifts (4.70 ppm). The other protons of the dodecyl chain appear at higher field, from 0.80 to 2.30 ppm. All the methylene protons of the ethyleneoxy units are shifted between 3.20 and 4.20 ppm, depending on their distance to the ring. The aromatic protons on each of the two macrocycles have approximately the same environment; however, their signals are broad owing to the number of isomers. The outer protons of the macrocycle are more shielded than usually observed,^{17b} a consequence of the adjacent electron-donating dodecyloxy or ethyleneoxy groups. The chemical shift, toward lower fields, of the two kinds of inner protons is due to the ring current of the two macrocycles.

Molecular analysis cannot be used for the identification of this compound as the poly(ethylene glycol)monomethyl ether is a mixture of chains of various lengths, $O(CH_2CH_2O)_nCH_3$. Mass spectrometry is more appropriate to the identification of such a molecule. In a previous work, monophthalocyanine derivatives with side chains containing about 10 ethyleneoxy subunits have been studied by fast atom bombardment mass spectrometry (FAB-MS).^{22c} Electrospray ionization mass spectrometry (ESI-MS) provides a fast, sensitive, and accurate method for high molecular mass measurements. ESI-MS has already been used to characterize lanthanide bisphthalocyanine.²⁴

Compounds **3** and **7**, as well as the starting material poly(ethylene glycol)monomethyl ether (PEOH), have been studied by ESI-MS; the m/z values of the sodium adducts $[M + Na]^+$ are presented in Figure 2. A small amount of potassium adducts $[M + K]^+$ is also observed. The peak at m/z 1645.8 (Figure 2c), corresponding to $[M + 2Na]^{2+}$, is higher than the one of the singly charged ion ($m/z = 3224.7$, Figure 2c). $[M + 3Na]^{3+}$ is present in the spectrum of compound **9**, the symmetrical lutetium bisphthalocyanine with four PEO chains on each of the macrocycles (see Experimental Section). Triply charged ions are seldom observed, but PEO derivatives are known to form complexes with alkali cations.

The mass spectra of the compounds appear like series of peaks separated by 44 mass units for singly charged ions (CH_2CH_2O) and 22 mass units for doubly charged ions, with a Gaussian distribution around a maximum. From Figure 2 the terms n and Σn_i , corresponding to the number of ethyleneoxy subunits, are deduced for each compound. Figure 3 represents the relative abundance of the (CH_2CH_2O) subunits in PEOH, **3**, and **7**.

For PEOH ($CH_3(OCH_2CH_2)_nOH$) (Figures 2a and 3) the maximum abundance at $m/z = 407.2$ corresponds to a number of eight ethyleneoxy subunits; however, n varies from 4 to 15. The spectrum of the metal-free phthalocyanine $H_2[(PEO)_4Pc]$ **3** (Figures 2b and 3) has a maximum m/z value at 1977.9, which indicates that $\Sigma n_{i,max} = 30$. The fact that $\Sigma n_{i,max}$ is not equal to 32 means that the average distribution on the macrocyclic compound is lower than that of PEOH, the starting material. This could result from the purification of **3** by chromatography. The lutetium bisphthalocyanine **7** has also been characterized by ESI-MS; Σn_i varies for the different fractions of **7** collected during chromatography, the highest abundance for $[M + Na]^+$ corresponding to $\Sigma n_i = 26$ ($m/z = 3223.7$, Figures 2c and 3). The experimental isotopic distribution of the sodium adduct of **7** matches perfectly the theoretical isotopic distribution (Figure 4). The exact

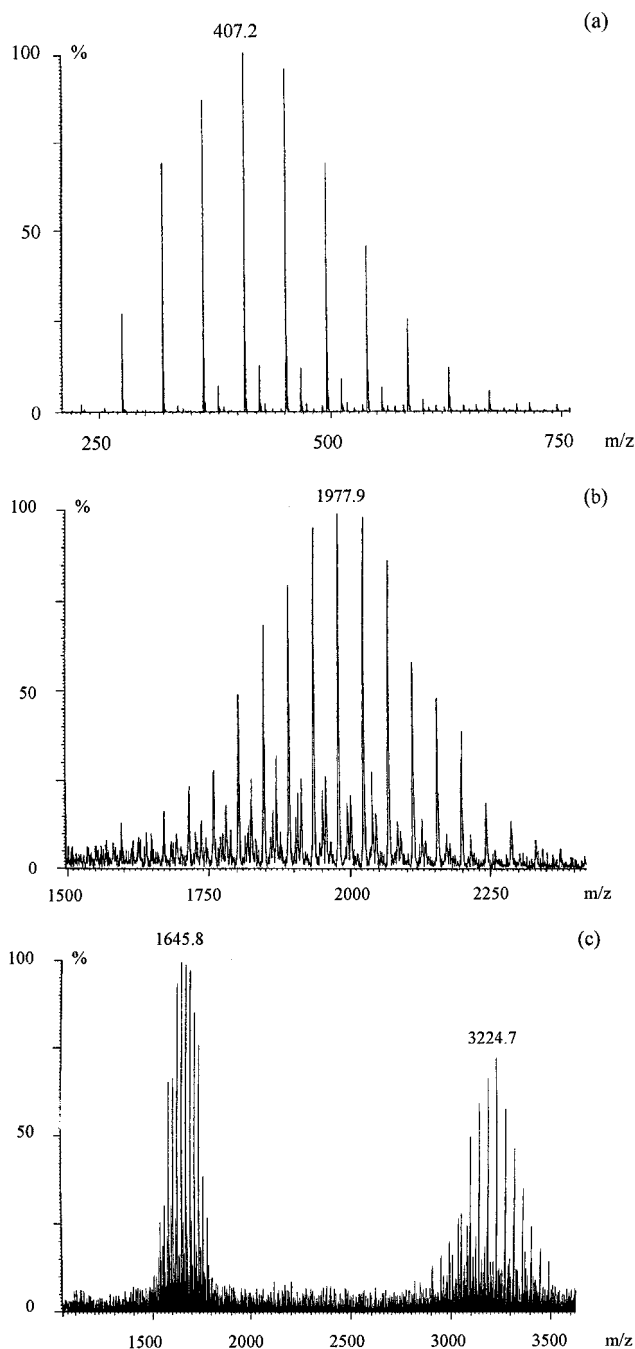


Figure 2. ESI MS spectra: (a) PEOH = $CH_3(OCH_2CH_2)_nOH$; (b) $H_2[(PEO)_4Pc]$ (**3**); (c) $Lu[(PEO)_4Pc][(DodO)_4Pc]$ (**7**).

mass measurement confirms the molecular formula of the molecular ion (less than 2 ppm between experimental and theoretical values), which ascertains that **7** is the asymmetrical bisphthalocyanine. From the 1H NMR (400 MHz) spectrum, the compound is estimated to be pure.

Even if the two macrocycles of this sandwich complex have different affinities for solvents, they are identical from an electronic point of view because both bear OCH_2CH_2 substituents. Consequently this compound can be considered as a symmetrical lutetium bisphthalocyanine, formally a complex of Lu^{3+} with Pc^{2-} and Pc^- (the oxidized form of the phthalocyanine ring), where the unpaired electron is delocalized over the two macrocycles.²⁵ The UV-visible spectrum is very typical of this class of compounds, with a Q-band maximum at 672 nm.²⁶ The redox potentials (CH_2Cl_2 , 0.1 M, Bu_4NPF_6) of this mol-

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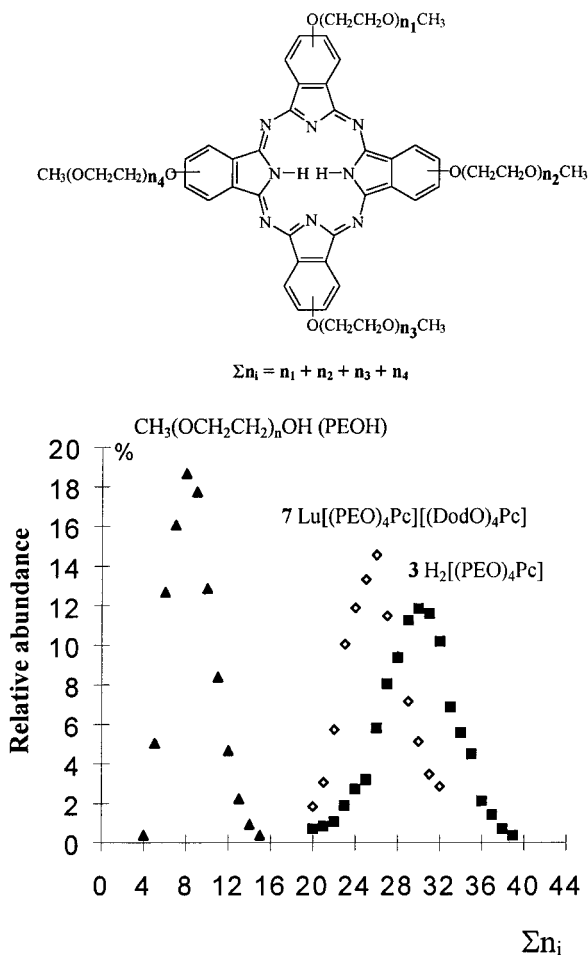


Figure 3. ESI mass spectrometry; relative abundances of ethyleneoxy subunits in PEOH, **3**, and **7**.

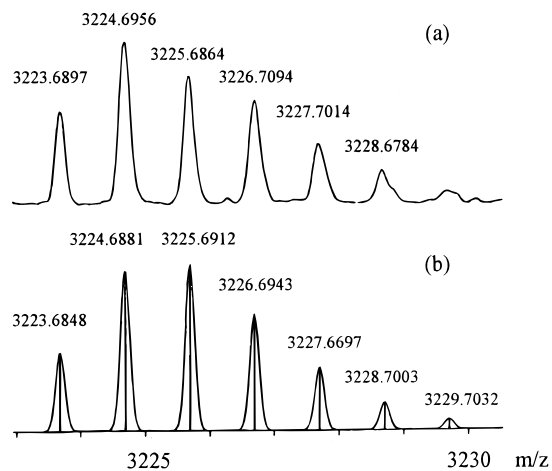


Figure 4. High-resolution ESIMS of **7** ($\Sigma n_i = 26$): (a) experimental isotopic distribution; (b) theoretical isotopic distribution.

ecule are influenced by the electron-donating substituents on the macrocycles. They are shifted to more negative values than those of LuPc_2 : $E_{\text{red}}^{\circ} = -0.55 \text{ V}$, $E_{\text{ox}}^{\circ} = -0.19 \text{ V}$ (-0.42 V and -0.02 V for LuPc_2 vs $E^{\circ}(\text{Fc}^+/\text{Fc})$).

This first amphiphilic lanthanide bisphthalocyanine, **7**, which has been synthesized, purified, and fully characterized, will be used to build up organized films at the water–air interface and to transfer them on transparent ITO electrodes by the technique of Langmuir–Blodgett.

Experimental Section

Materials. 4-Nitrophthalonitrile was purchased from ACROS, and 1-dodecanol and poly(ethylene glycol)monomethyl ether 350 were purchased from Aldrich. Organic solvents were distilled before use.

Synthesis and Characterization. 4-Methoxypolyethyleneoxyphthalonitrile (1). Finely ground K_2CO_3 (2.1 g, 15.2 mmol) was added to a solution of poly(ethylene glycol)monomethyl ether (4.5 g, 11.7 mmol) and 4-nitrophthalonitrile (2.0 g, 11.6 mmol) in DMF (30 mL) at 100°C . The mixture was stirred at this temperature for 24 h. After the mixture cooled, distilled water (200 mL) was added, and the medium was neutralized by a dilute aqueous solution of HCl. After extraction by CH_2Cl_2 (3 times, total volume 150 mL), drying over MgSO_4 , and solvent evaporation under vacuum, the residue was purified by chromatography on a silica gel column (70–230 mesh). The desired product was eluted by a mixture of dichloromethane/methanol (99/1 v/v) to give **1** (2.1 g, 35%) after solvent evaporation. It contained a small amount of unreacted poly(ethylene glycol)monomethyl ether but it was used in the preparation of compound **3** without further purification: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.8 \text{ Hz}$, 1H), 7.20 (d, $J = 2.4 \text{ Hz}$, 1H), 7.13 (dd, $J = 8.8, 2.4 \text{ Hz}$, 1H), 4.10 (t, $J = 4.5 \text{ Hz}$, 2H), 3.73 (t, $J = 4.5 \text{ Hz}$, 2H), 3.53 (t, $J = 4.5 \text{ Hz}$, 2H), 3.45–3.50 (br, xH), 3.37 (t, $J = 4.5 \text{ Hz}$, 2H), 3.18 (s, 3H); IR (KBr) 2228, 1253, 1105 cm^{-1} .

4-Dodecyloxyphthalonitrile (2). Compound **2** was synthesized in the same way as compound **1**, with 1-dodecanol (2.2 g, 11.8 mmol) instead of PEOH. The residue obtained after evaporation of the organic extracts was chromatographed on silica gel, the eluant being a mixture of toluene/hexane (80/20 v/v), to give **2** (1.1 g, 30%): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.70 (d, $J = 8.7 \text{ Hz}$, 1H), 7.25 (d, $J = 2.6 \text{ Hz}$, 1H), 7.17 (dd, $J = 8.7, 2.6 \text{ Hz}$, 1H), 4.04 (t, $J = 6.5 \text{ Hz}$, 2H), 1.83 (m, $J = 6.5 \text{ Hz}$, 2H), 1.26–1.45 (br, 18H), 0.88 (t, $J = 6.5 \text{ Hz}$, 3H); IR (KBr) 2230, 1250, 1095 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{ON}_2$: C, 76.88; H, 9.03; N, 8.97. Found: C, 76.97; H, 9.10; N, 8.92.

Metal-Free Tetrakis(methoxypolyethyleneoxy)phthalocyanine (3). Under an inert atmosphere, a large excess of lithium metal (0.28 g, 40.3 mmol) was added to a solution of **1** (2.1 g, 4.1 mmol) in dry pentanol (50 mL). After the lithium pentanolate formation, the mixture was refluxed for an additional 3 h. After it cooled, the solution was poured into acetic acid (100 mL) and heated at 100°C for 15 min. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane (100 mL). The organic phase was washed with acidified water and saturated brine solution, dried over MgSO_4 , and evaporated to give a green residue. The crude product, which contained the desired compound **3** and the unreacted poly(ethylene glycol)monomethyl ether, was purified by ultrafiltration through an Amicon YM1 membrane (cutoff 1000 Da) to afford **3** (0.9 g, 45%): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.70–8.50 (br, 4H), 8.15–7.90 (br, 4H), 7.55–7.35 (br, 4H), 4.60–4.50 (br, 8H), 4.30–4.20 (br, 8H), 4.00–3.50 (br, 104H), 3.40–3.35 (br, 12H); ESIMS m/z (rel intensity) 1537.8 (6), 1581.9 (7), 1625.9 (9), 1669.9 (16), 1713.8 (23), 1757.8 (27), 1801.8 (49), 1845.9 (68), 1889.9 (79), 1933.9 (95), 1977.9 (100), 2022.2 (98), 2066.1 (86), 2110.1 (58), 2154.1 (47), 2198.1 (38), 2242.0 (18), 2286.1 (12), 2330.1 (6), 2374.1 (3).

Metal-Free Tetrakis(dodecyloxy)phthalocyanine (4). Compound **2** (1.1 g, 3.5 mmol) reacted with lithium metal (0.24 g, 35 mmol) in pentanol (50 mL) to give **4**, following the same synthetic path used for **3**. At room temperature the metal-free phthalocyanine precipitated in the pentanol/acetic acid mixture. The green powder was isolated by filtration, and the impurities were removed by extraction with acetone (200 mL) in a Soxhlet apparatus. Compound **4** (0.35 g, 35%) was

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obtained as a green powder: ^1H NMR (300 MHz, CDCl_3) δ 8.25–8.00 (br, 4H), 7.70–7.40 (br, 4H), 7.20–7.00 (br, 4H), 4.30–4.10 (br, 8H), 2.10–2.00 (br, 8H), 1.80–1.30 (br, 72H), 1.00–0.90 (br, 12H). Anal. Calcd for $\text{C}_{80}\text{H}_{114}\text{O}_4\text{N}_8$: C, 76.76; H, 9.18; N, 8.95. Found: C, 76.58; H, 9.29; N, 8.87.

The dilithium phthalocyanines were synthesized according to Linstead's method with some modifications.^{23,27}

[Tetrakis(methoxypolyethyleneoxy)phthalocyanine] Lithium (5). Under an atmosphere of N_2 , to a stirred solution of compound **3** (0.9 g, 0.5 mmol) in methanol (50 mL) was added lithium metal (0.1 g, 14.4 mmol) at room temperature. Then, after 3 h of reflux, the solvent was removed under vacuum, and the green residue was separated from LiOH by extraction with acetone (200 mL) in a Soxhlet apparatus. The solution obtained was evaporated, and compound **5** (0.7 g, 80%) was isolated as a green paste after drying under vacuum during 24 h (50–100 °C): ^1H NMR (400 MHz, acetone- d_6) δ 9.25–9.15 (br, 4H), 9.00–8.80 (br, 4H), 7.60–7.50 (br, 4H), 4.60–3.45 (br, 120H), 3.30–3.20 (br, 12H).

[Tetrakis(dodecyloxy)phthalocyanine] Lithium (6). The same procedure was applied to compound **4** (0.35 g, 0.3 mmol), which reacted with lithium metal (0.06 g, 8.6 mmol) to give **6** in a good yield (0.30 g, 85%): ^1H NMR (300 MHz, acetone- d_6) δ 9.30–9.05 (br, 4H), 8.95–8.70 (br, 4H), 7.60–7.45 (br, 4H), 4.55–4.35 (br, 8H), 2.00–1.20 (br, 80 H), 0.95–0.85 (br, 12H).

Synthesis of the lutetium bisphthalocyanines 7–9. An excess of lutetium acetate tetrahydrate (0.014 g, 0.033 mmol) was added to a stirred mixture of **5** (0.050 g, 0.025 mmol) and **6** (0.032 g, 0.025 mmol) in freshly distilled quinoline (40 mL) at 240 °C under nitrogen. The mixture was left for 24 h at this temperature. After it cooled, the solution was poured on top of a silica gel column, and elution with pure dichloromethane separated compound **8** in association with quinoline. After evaporation of quinoline, **8** (0.015 g, 22%) was obtained pure. A second fraction eluted with dichloromethane/methanol (from 90/10 to 60/40 v/v) gave a mixture of compounds **7** and **9**. This mixture was chromatographed on a second silica gel column; the ternary mixture dichloromethane/ethyl acetate/methanol (60/30/10 v/v/v) gave desired compound **7** (0.038 g, 47%). Finally, compound **9** (0.025 g, 27%) was eluted from the column by dichloromethane/methanol (80/20 v/v).

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[Tetrakis(methoxypolyethyleneoxy)phthalocyanine]-[tetrakis(dodecyloxy)phthalocyanine] lutetium (7): ^1H NMR (400 MHz, DMF- d_7 + hydrazine monohydrate (1%)) δ 8.90–8.70 (br, 8H), 8.55–8.30 (br, 8H), 7.90–7.60 (br, 8H), 4.80–4.50 (br, 16H), 4.30–4.20 (br, 8H), 4.00–3.35 (br, xH), 3.30–3.20 (br, 12H), 2.30–1.25 (br, 80H), 0.90–0.85 (br, 12H); ESIMS m/z (rel intensity) 1535.3 (26), 1557.3 (28), 1579.3 (66), 1601.3 (68), 1623.3 (90), 1645.3 (100), 1667.3 (96), 1689.4 (90), 1711.4 (76), 1733.4 (64), 1755.4 (38), 1777.4 (26), 2959.5 (9), 3003.6 (15), 3047.6 (28), 3091.6 (49), 3135.7 (58), 3179.7 (65), 3223.8 (71), 3267.8 (56), 3311.8 (46), 3355.8 (35), 3399.8 (25), 3443.8 (17), 3487.9 (14); HRESIMS calcd for $[\text{C}_{168}\text{H}_{240}\text{N}_{16}\text{O}_{34}\text{Na}^{175}\text{Lu}]^+$ 3223.6848, found 3223.6897; HRESIMS calcd for $[\text{C}_{170}\text{H}_{244}\text{N}_{16}\text{O}_{35}\text{Na}^{175}\text{Lu}]^+$ 3267.7111, found 3267.7073; HRESIMS calcd for $[\text{C}_{172}\text{H}_{248}\text{N}_{16}\text{O}_{36}\text{Na}^{175}\text{Lu}]^+$ 3311.7373, found 3311.7415.

Bis[tetrakis(dodecyloxy)phthalocyanine] lutetium (8): ^1H NMR (300 MHz, DMF- d_7 + hydrazine monohydrate (1%)) δ 8.90–8.70 (br, 8H), 8.50–8.35 (br, 8H), 7.85–7.65 (br, 8H), 4.70–4.50 (br, 16H), 2.20–1.20 (br, 160H), 0.90–0.85 (br, 24H); HRESIMS calcd for $[\text{C}_{160}\text{H}_{224}\text{N}_{16}\text{O}_8^{175}\text{Lu}]^+$ 2672.7021, found 2672.7023.

Bis[tetrakis(methoxypolyethyleneoxy)phthalocyanine] lutetium (9): ^1H NMR (400 MHz, DMF- d_7 + hydrazine monohydrate (1%)) δ 8.95–8.80 (br, 8H), 8.60–8.50 (br, 8H), 8.00–7.80 (br, 8H), 4.60–3.40 (br, 208H), 3.30–3.20 (br, 24H); ESIMS m/z (rel intensity) 1236.6 (17), 1251.3 (20), 1265.9 (13), 1280.6 (18), 1295.3 (29), 1309.9 (34), 1324.6 (22), 1339.3 (19), 1353.9 (18), 1368.6 (20), 1383.3 (15), 1397.9 (10), 1667.2 (18), 1689.2 (25), 1711.2 (32), 1733.3 (41), 1755.3 (52), 1777.3 (48), 1799.3 (62), 1821.2 (68), 1843.3 (72), 1865.3 (90), 1887.3 (100), 1909.3 (84), 1931.4 (72), 1953.4 (80), 1975.3 (62), 1997.4 (44), 2019.4 (42), 2041.4 (40), 2063.4 (28), 2085.4 (16), 2107.5 (10); HRESIMS calcd for $[\text{C}_{170}\text{H}_{244}\text{N}_{16}\text{O}_{57}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1821.2945, found 1821.2798; HRESIMS calcd for $[\text{C}_{172}\text{H}_{248}\text{N}_{16}\text{O}_{58}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1843.3076, found 1843.3084; HRESIMS calcd for $[\text{C}_{174}\text{H}_{252}\text{N}_{16}\text{O}_{59}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1865.3207, found 1865.3255; HRESIMS calcd for $[\text{C}_{176}\text{H}_{256}\text{N}_{16}\text{O}_{60}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1887.3338, found 1887.3329; HRESIMS calcd for $[\text{C}_{178}\text{H}_{260}\text{N}_{16}\text{O}_{61}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1909.3469, found 1909.3340; HRESIMS calcd for $[\text{C}_{180}\text{H}_{264}\text{N}_{16}\text{O}_{62}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1931.3600, found 1931.3612; HRESIMS calcd for $[\text{C}_{182}\text{H}_{268}\text{N}_{16}\text{O}_{63}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1953.3731, found 1953.3693; HRESIMS calcd for $[\text{C}_{184}\text{H}_{272}\text{N}_{16}\text{O}_{64}\text{Na}_2^{175}\text{Lu}]^{2+}$ 1975.3862, found 1975.3825.

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