

Poly(oxyethylene)-Substituted Copper and Lutetium Phthalocyanines

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Received: February 19, 1996; In Final Form: April 25, 1996[⊗]

A new family of nonionic water-soluble lutetium bisphthalocyanines and a copper monophthalocyanine have been synthesized and characterized. Optical absorption determinations demonstrate aggregation processes in water. Optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction measurements have also been performed on the materials. The substituted copper complex yields a hexagonal columnar liquid crystal above 62 °C; this mesophase can incorporate up to 16% (w/w) of triethylene glycol without significant disturbance of the structure. One of the substituted lutetium bisphthalocyanines affords a tetragonal columnar mesophase; the other bisphthalocyanine derivatives show only highly ordered crystalline-like phases. Conductivity measurements have been carried out on thin films of the previous derivatives to determine the relative electronic and ionic conduction contributions.

Introduction

Unsubstituted lutetium bisphthalocyanine (Pc₂Lu) has been shown to be an intrinsic molecular semiconductor^{1,2} with thin film electronic conductivities of the order of $6 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$. In contrast, the dihydrogeno or metallic monophthalocyanine analogues yield insulating materials.³ The substitution of the Pc₂Lu subunit with various types of chains or macrocycles has been widely described.^{4–8}

Hydrophilic poly(oxyethylene) is, on the other hand, well-known to dissolve a large number of alkali salts^{9,10} (for instance M⁺CF₃SO₃⁻ with M = Li, Na, K, Rb, Cs). Above the melting point of poly(oxyethylene) (*M*_w = 6000, mp = 56–61 °C), which is well above the glass transition temperature (around –40 °C), fairly large ionic conductivities have been measured:¹⁰

$$\sigma = 5.6 \times 10^{-6} \Omega^{-1} \text{cm}^{-1} \text{ for } \text{H}(\text{O}-\text{CH}_2-\text{CH}_2)_n\text{OH} \cdot \text{Li}^+ \text{CF}_3\text{SO}_3^-$$

Comparable conductivities are obtained for Pc₂Lu and salt containing poly(oxyethylene) derivatives, although they derive from electronic or ionic charge carriers, respectively.

A phthalocyanine subunit octasubstituted with $-\text{[CH}_2\text{O(CH}_2\text{-CH}_2\text{O)}_2\text{CH}_3\text{]}$ side chains has already been shown to form hexagonal columnar mesophases in 1985.^{11,12} Approximately at the same time, the triphenylene subunit has been used for the same purpose.^{13,14} A polymeric derivative containing a substituted gallic subunit and poly(oxyethylene) chains has also been demonstrated to yield a columnar mesophase.¹⁵ More recently, the thermotropic mesomorphism of a mixture of position isomers of metal-free phthalocyanine tetrasubstituted with $-\text{O(CH}_2\text{CH}_2\text{O)}_n\text{CH}_3$ (*n* = 3 or 8)¹⁶ was reported. Dihydrogenophthalocyanines with both alkyl and poly(oxyethylene) side chains¹⁷ have also been synthesized. The thermotropic behavior of tetraphenylporphyrins with oligo(oxyethylene) side chains was reported.¹⁸ The antiaggregative properties in aqueous solutions of a hexadecasubstituted poly(oxyethylene) copper monophthalocyanine have also been demonstrated.¹⁹

One example of poly(oxyethylene)-substituted lutetium bisphthalocyanine has already been described by the present authors.⁵

Copper monophthalocyanine and lutetium bisphthalocyanine substituted with poly(oxyethylene) side chains have been synthesized in the present publication. The copper complex is expected to be an electronic insulator, whereas the lutetium derivative should be, as previously indicated, a molecular semiconductor. Supramolecular organization should occur, in the corresponding condensed phases, by segregation of the fragments of the same chemical nature²⁰ (Figure 1).

The aromatic central core should therefore provide electronic conduction properties, whereas linear poly(oxyethylene) side chains could afford an ionic conductivity after addition of salts. Both contributions are expected to have the same order of magnitude.

Synthesis

The lutetium complexes were synthesized in three steps using the chemical pathway shown in Scheme 1 starting from the suitable pyrocatechol derivatives.²¹

The bromination of the diethers **3** in the presence of a catalytic amount of iron and iodine gives the dibromo-derivatives **4** (yield: 55–75%). The corresponding dicyano-derivatives are obtained by reaction with CuCN following the Rosenmund–von Braun reaction (yield: 50–65%). The copper phthalocyanine complex **2_c** is obtained as a side product during this reaction. NMR studies show that a hydrate **2_c·6H₂O** is isolated. Reaction of the phthalonitrile derivatives **5_{a–d}** with Lu(OAc)₃·3H₂O and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in hexan-1-ol gives the lutetium complexes in approximately 5–10% yield.^{22,23} Purification was achieved by column chromatography (silica gel), preparative thin layer chromatography (neutral alumina), and reprecipitation from CH₂Cl₂/*n*-heptane mixtures.

For the first step (transformation of **3_{a–d}** into **4_{a–d}**) only a small excess of bromine (2.1 equiv) at 0 °C must be added to avoid partial demethylation of the poly(oxyethylene) side chains; this latter reaction is probably associated with the concomitant HBr release. The second step conditions were slightly modified as compared to standard ones.²⁴ Finally the reaction time of the last step was reduced to prevent side chain degradations (see the Experimental Section).

Compounds **1_{b–d}** and **2_c** are soluble in most organic solvents (CHCl₃, CH₂Cl₂, alcohols, acetone, ethylacetate, ether, DMF, etc.), soluble in water (up to 10⁻⁴ M for **1_d**), and insoluble in

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

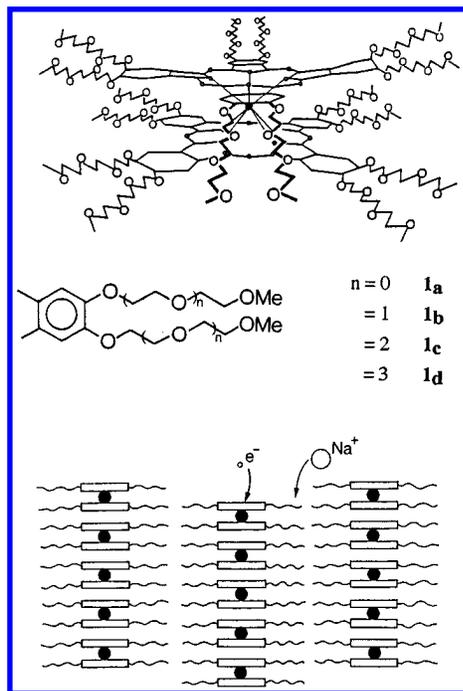
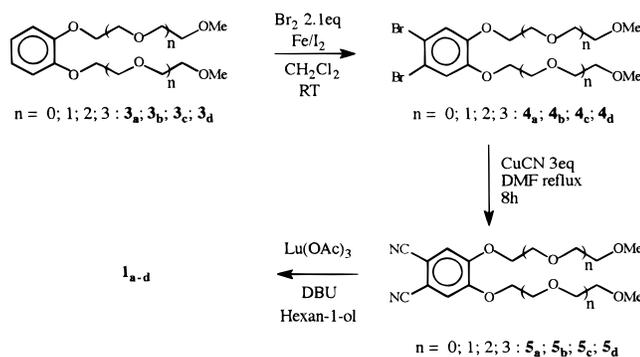


Figure 1. Schematic representation of one of the substituted lutetium bisphthalocyanines synthesized in the present study. The other side chains used have also been indicated.

SCHEME 1: Chemical Pathway Used To Synthesize the Lutetium Complexes 1_{a-d}



alkanes. **1_a** is soluble in low-polarity solvents, soluble in alcohols, and insoluble in water.

Mass Spectrometry Characterization

Mass spectrometry of compounds **1** has been carried out by the field desorption technique using solvents such as CHCl_3 or CH_2Cl_2 to deposit the products. Fast atom bombardment, which gives satisfactory results in the case of crown-ether-substituted homologues, gave only fragmentation peaks for the present compounds.

The most intense peak with the field desorption technique is due to the molecular ion (Table 1). The fragment ions correspond to the loss of oxyethylene moieties.

Aggregation in Various Solvents

We have studied the UV-visible changes of the Soret and Q bands of **1_c** and **2_c** as a function of the solvent.

A decrease of the extinction coefficient with a concomitant broadening of the Q band is noticed when the solvent polarity increases. This is accompanied by a small red shift of the maximum wavelength for **1_c** (Figure 2) and a strong blue shift for **2_c**.

TABLE 1: Mass Spectrometry Data of Compounds 1_a, 1_b, 1_c, 1_d, and 2_c

compound	formula	$[M]^+$ calc	$[M]^+$ found	
1_a	$\text{C}_{112}\text{H}_{128}\text{O}_{32}\text{N}_{16}\text{Lu}$	2385	2384.4	M^+
			2327.0	$\text{MH}^+ - \text{C}_2\text{H}_4\text{OMe}$
1_b	$\text{C}_{144}\text{H}_{192}\text{O}_{48}\text{N}_{16}\text{Lu}$	3090	3089.6	M^+
			2986.0	$\text{M}^+ - (\text{C}_2\text{H}_4\text{O})_2\text{Me}$
			2883.4	$\text{M}^+ - 2(\text{C}_2\text{H}_4\text{O})_2\text{Me}$
1_c	$\text{C}_{176}\text{H}_{256}\text{O}_{64}\text{N}_{16}\text{Lu}$	3795	3796.8	MH^+
			3650.0	$\text{MH}^+ - (\text{C}_2\text{H}_4\text{O})_3\text{Me}$
1_d	$\text{C}_{208}\text{H}_{320}\text{O}_{80}\text{N}_{16}\text{Lu}$	4500	4499.7	M^+
			4308.7	$\text{M}^+ - (\text{C}_2\text{H}_4\text{O})_4\text{Me}$
2_c	$\text{C}_{88}\text{H}_{128}\text{O}_{32}\text{N}_8\text{Cu}$	1871	1872	MH^+
			1726	$\text{M}^+ - (\text{C}_2\text{H}_4\text{O})_3\text{Me}$

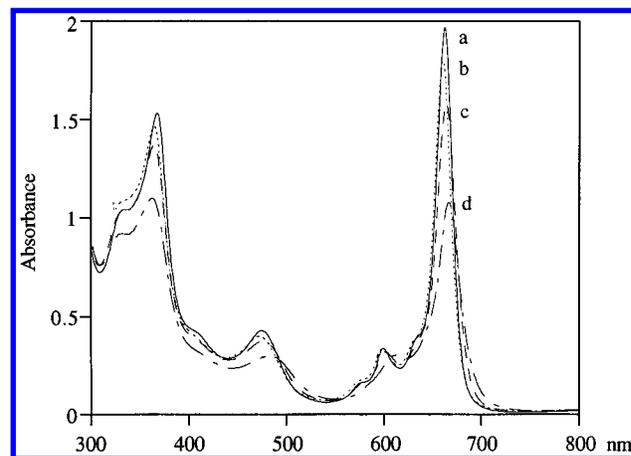


Figure 2. Visible absorption spectra of compounds **1_c** in various solvents: (a) dichloromethane; (b) acetone; (c) methanol; (d) water.

These phenomena have already been encountered^{5,19} and can be unambiguously ascribed to an aggregation process increasing in the order $\text{CH}_2\text{Cl}_2 < \text{acetone} < \text{methanol} < \text{water}$ for both **1_c** for **2_c**. This is consistent with the solvent polarity order.²⁵ The nature of the solvent does not change much the energy of the B and Q bands for the bisphthalocyanines **1**, contrarily to the monophthalocyanines derivatives **2**, as already found for crown-ether lutetium bisphthalocyanine.⁵

The spectroscopic characteristics of **1** in water are constant in the pH range 3–12.

It was also possible to determine the spectral properties of the oxidized and reduced forms of **1_d** in water and in CHCl_3 (Table 2).

The results are approximately the same for the other water-soluble compounds **1**. Aggregation causes a broadening of the absorption peaks and a correlative decrease of the absorption coefficients. In CHCl_3 , **1_d**, in its neutral form, is not aggregated. In comparison, the corresponding extinction coefficient in water is significantly smaller, indicating some aggregation. The monomeric form seems to be at least partly recovered after chemical reduction.

The same phenomenon is not observed for the oxidized species, which seem to remain aggregated in water.

Mesomorphic Properties

It has been previously shown that paraffinic-chain-substituted lutetium bisphthalocyanines exhibit liquid crystalline properties.⁴ However, the domain of stability of the mesophase is narrow compared to the monophthalocyanine derivatives.

Phase transitions of the compounds studied were investigated by polarizing microscopy from 25 to 300 °C and by differential scanning calorimetry (DSC) in the range –20 to 300 °C. In all cases, decomposition of the compounds started only around 250–270 °C.

TABLE 2: Visible Spectral Data of Reduced, Neutral, and Oxidized Forms of the Lutetium Bisphthalocyanine 1_a

			λ (nm) ($10^{-5} \epsilon$ in L mol ⁻¹ cm ⁻¹)					
1_a	CHCl ₃	reduced		358(1.79)		625(1.69)		700 (0.66)
		neutral	292(1.02)	367(1.44)	475(0.41)	602(0.32)	666(1.80)	
		oxidized		386(1.21)	498(0.84)			704(0.54)
	H ₂ O	reduced		359(1.67)		635(1.75)		704(0.54)
		neutral	291(1.10)	364(1.15)	480(0.31)	612(0.29)	670(1.10)	
		oxidized		379(0.95)	500(0.53)			703(0.35)

TABLE 3: Thermal Behavior and Structural Data for the Compounds 1_{a-d} and 2_c: T₁ First Transition, T₂ Clearing Point (°C); ΔH Enthalpy of the Transition (J g⁻¹); C, Crystal; M, Mesophase; I, Isotropic Phase

		T ₁ (ΔH)	T ₂ (ΔH)		
1_a			C	246(17.8)	I
1_b			C	138(13.3)	I
1_c	C	53(1.6)	M	57.6(6.4)	I
1_d					I
2_c	C	62(21)	M	260 ^a	I

^a Decomposition temperature.

2_c shows a reproducible phase transition at 62 °C, before its melting at 260 °C, which is accompanied by decomposition. X-ray diagrams have been performed at 20 and 75 °C. At room temperature, a crystalline state is observed. At 75 °C, a series of six Bragg reflections can be assigned to a hexagonal lattice with a parameter $a = 27.2$ Å. Halos are also visible at 4.2 and 3.37 Å. By addition of up to 16% (w/w) of triethylene glycol, the hexagonal structure is conserved with only a small decrease of the crystal to mesophase transition temperature (from 62 to 55 °C). At higher percentages of triethylene glycol, two phases are present.

The stability domain of the mesophase for the compounds **1** depends on the chain length (Table 3). X-ray diffraction indicates that the compounds **1_{a-b}** are crystalline in the whole temperature range before the clarification point. No halo was observed at large angles. The derivative **1_d**, on the contrary, exhibits an isotropic phase even at room temperature.

The behavior of **1_c** differs from other derivatives. The DSC thermogram shows the existence of several transitions (Table 3). However, the relative enthalpies indicate a fairly organized mesomorphic phase.

X-ray diffraction measurements on **1_c** indicate that the low-temperature phase is crystalline with an orthorhombic cell ($a = 25.4$ Å, $b = 19.2$ Å, $c = 13.75$ Å). The high-temperature phase affords a simpler pattern. It consists of a series of Bragg reflections corresponding to interplanar distances in the ratio $1:1/\sqrt{2}:1/2:1/2\sqrt{2}$. This is consistent with a two-dimensional square lattice ($a = 26.7$ Å). A halo is observed around 4.2 Å in both the isotropic and high-temperature birefringent phases. The derivative **1_c** therefore exhibits a disordered tetragonal mesophase between 53 and 57 °C (Figure 3).

A comparable mesophase has been reported for (2-ethylhexylo)₈PcH₂.²⁶

Conduction Properties

Preliminary conductivity experiments have been carried out on the previous poly(oxyethylene)-substituted phthalocyanine derivatives. Contributions from aromatic cores (electronic nature) or from the side chains (ionic nature) are expected. In this last case, water molecules and/or a minute amount of dissolved salts would be responsible for the conductivity. The intrinsic electronic conduction is, on the other hand, highly dependent on whether the copper or the lutetium complexes are used. The difference of redox potentials $\Delta E = E_{\text{ox}}^0 - E_{\text{red}}^0$ is about 1.82 eV for PcCu and only 0.4–0.5 eV for

Pc₂Lu^{2,6,27} (0.38 eV in DMF for **1_c**). This must lead to largely different conductivities since^{2,28}

$$\sigma = \sigma_0 \exp(-\Delta E/22T)$$

with $\sigma_0 = n_0 e \mu$, where n_0 = density of molecular units, e = charge of the electron (C), μ = mobility (cm²/V s), and k = Boltzmann's constant. It has been shown that $E_{\text{ox}}^0 - E_{\text{red}}^0$ is approximately equal to the thermal activation energy of conduction.²⁸

This is indeed experimentally found (Table 4).

TABLE 4: Conductivities Found at Room Temperature (Planar Configuration) for Thin Layers of Phthalocyanine Derivatives Deposited by Spin Coating (RH: Relative Humidity) (Interelectrode Spacing = 50 μm; Voltage = 10 V; Field = 2 × 10³ V/cm)

compound	σ (room temperature) ($\Omega^{-1} \text{cm}^{-1}$)	conditions
1_a	2.7×10^{-5}	10 ⁻⁶ Torr
1_b	4×10^{-6}	10 ⁻⁶ Torr
1_c	1.4×10^{-6}	10 ⁻⁶ Torr
2_c	1.5×10^{-7}	in air (50% RH)
	3×10^{-9}	10 ⁻⁶ Torr

The influence of the ambient on the conductivities is important, but it will not be detailed in the present paper. However, these studies on a closely related compound have been carried out.⁶ The samples **1_{a-c}** are measured under vacuum, where the major part of the water molecules present within the poly(oxyethylene) side chains have been eliminated. The presence of ambient air (relative humidity 50% or higher) significantly increases the conductivities of the thin films. The conductivity of **2_c** measured in air is 1 order of magnitude lower than the ones measured for the bisphthalocyanine lutetium derivatives. Under vacuum, a further 100-fold decrease in the conductivity of **2_c** is observed. The redox properties of the central rigid core therefore influences the conductivities of the materials in the expected way, independently of the ionic contribution, which is however significant. The values measured for **1_{a-c}** are of the same order of magnitude as those found for thin films of unsubstituted lutetium bisphthalocyanine.²

It has been checked in the case of **1_c** that an ohmic behavior is observed in the potential range 0–100 V (interelectrode spacing: 50 μm). This indicates that the mechanism involving charge injections from the electrodes is not effective. Further studies as a function of frequency and ambient are underway to precise the conduction processes.

Conclusion

The synthesis of new poly(oxyethylene)-substituted lutetium bisphthalocyanines is described, and the compounds are characterized by standard methods (¹H and ¹³C NMR, elemental analysis, FTIR, field desorption mass spectrometry). For comparison, one of the poly(oxyethylene) side chains was selected to prepare the corresponding copper complex.

The compounds prepared are soluble in most solvents from dichloromethane to water. They can form aggregates depending on the polarity of the solvent.

The derivative **1_c** forms a liquid crystalline phase with a

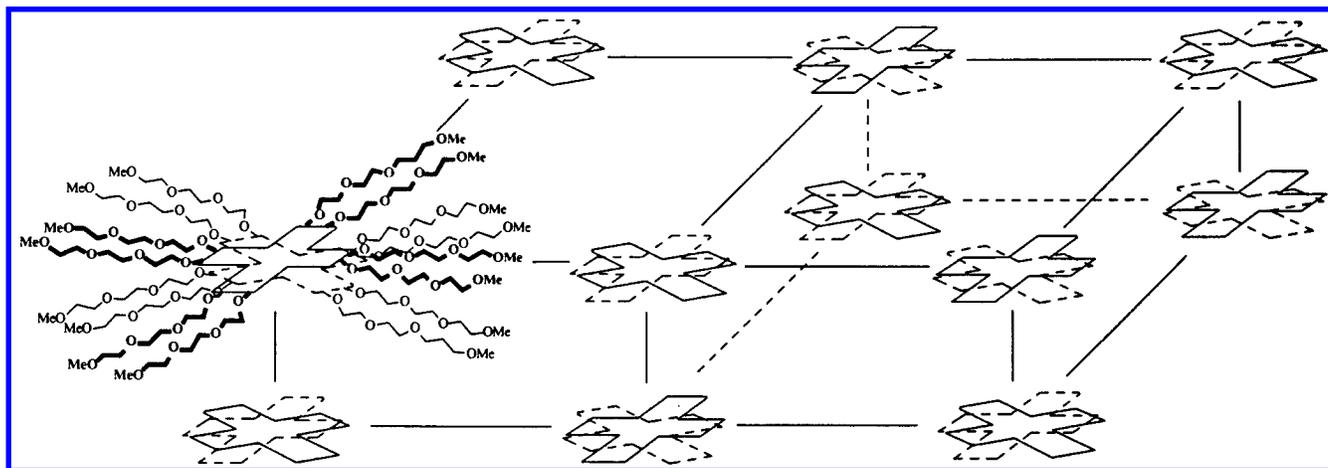


Figure 3. Schematic representation of the tetragonal columnar mesophase corresponding to **1c**.

square lattice ($a = 27.6 \text{ \AA}$), whereas the corresponding copper monophthalocyanine affords a hexagonal columnar liquid crystal.

Preliminary conductivity measurements have been carried out which demonstrate a 3 orders of magnitude difference in conductivity between the copper and the lutetium complexes. This difference can be predicted from a model derived from electrochemistry. It does not however correspond to the expected ratio of the densities of the intrinsic charge carriers, which must be significantly larger.

Experimental Section

The synthesis of **1c** has already been described.⁵ The diethers **3a** and **3b** were prepared by reacting pyrocatechol with the bromo-derivative of the corresponding ethylene glycol monomethyl ether in the presence of Cs_2CO_3 (92% yield). Compound **3a** was obtained by reacting 1,2-bis(hydroxyethoxy)benzene²⁹ with 1-chloro-8-methoxy-3,6-dioxaoctane in the presence of NaOH (yield 30%).

The purity of **3**, **4**, and **5** was checked by a gas chromatography–mass spectrometry apparatus (GCMS) (Hewlett-Packard). IR spectra were performed with a Perkin-Elmer 1600 FTIR spectrometer and UV–visible spectra with a UVIKON 860 spectrophotometer. NMR spectra were recorded in CDCl_3 using a Bruker AM300 apparatus. Field desorption mass spectrometry measurements were carried out at the “Institut für Organische Chemie II” at Tübingen. Elemental analyses were performed at ICS-Strasbourg. Calorimetric measurements were made with a Perkin-Elmer DSC-7 at $5 \text{ }^\circ\text{C}/\text{min}$. X-ray diffraction patterns were recorded under vacuum, with monochromatic ($\text{Cu K}\alpha$) X-ray radiation.

Synthesis. 1,2-Bis(12-methoxy-1,4,7,10-tetraoxadecanyl)-4,5-dibromobenzene, **4a**. In a 500 mL three-necked flask containing 130 mL of CH_2Cl_2 , 5 g (0.01 mol) of compound **3a**, 100 mg of iron powder, and a catalytic amount of iodine was added dropwise a solution of 3.42 g (0.0215 mol) of bromine in 50 mL of CH_2Cl_2 in 2 h at $0 \text{ }^\circ\text{C}$. After warming to room temperature, the solution was stirred for 20 h. The mixture was treated with an aqueous solution of sodium hyposulfite and sodium hydroxide until complete decoloration. The organic layer was washed with distilled water (three times), dried (MgSO_4), and evaporated under reduced pressure. The obtained crude oil was purified by column chromatography on silica gel (eluent: $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{EtOH}$, 70:27:3 (v/v)), yielding 5 g of a pale yellow oil (76%). $R_f = 0.45$ (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{EtOH}$, 70:25:5 (v/v)).

Elemental analysis for $\text{C}_{24}\text{H}_{40}\text{O}_{10}\text{Br}_2$ ($M_w = 648$). Calc: C, 44.46; H, 6.22; Br, 24.65. Found: C, 44.35; H, 6.32; Br, 24.45.

Mass spectrometry (GCMS) m/z : 650, 648, 646 (M^+), 460, 458, 456 ($\text{MH}^+ - (\text{C}_2\text{H}_4\text{O})_4\text{Me}$), 323, 321, 319 ($\text{MH}^+ - (\text{C}_2\text{H}_4\text{O})_4\text{Me} - \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{Me}$), 296, 294, 292 ($M^+ - (\text{C}_2\text{H}_4\text{O})_4\text{Me} - \text{O}(\text{C}_2\text{H}_4\text{O})_3\text{Me}$), 281, 279, 277 ($\text{MH}^+ - (\text{C}_2\text{H}_4\text{O})_4\text{Me} - \text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{Me}$). ^1H (300 MHz, CDCl_3) δ ppm: 3.34 (s, 6H, OCH_3), 3.51 (t, 4H, $J = 4.78 \text{ Hz}$), 3.63 (m, 16H), 3.67 (m, 4H), 3.81 (t, 4H, $J = 4.78 \text{ Hz}$), 4.10 (t, 4H, $J = 4.96 \text{ Hz}$), 7.11 (s, 2H, aromatic protons). ^{13}C (75 MHz, CDCl_3) δ ppm: 58.90, 69.15, 69.42, 70.38, 70.47, 70.52, 70.74, 71.78, 115.15, 118.92, 148.72. IR (KBr): 2876, 1582, 1497, 1452, 1350, 1327, 1297, 1251 (val. asym. $\text{C}_{\text{ar}}-\text{O}-\text{C}_{\text{al}}$), 1200, 1108 (val. asym. $\text{C}_{\text{al}}-\text{O}-\text{C}_{\text{al}}$), 1053 (val. sym. $\text{C}_{\text{ar}}-\text{O}-\text{C}_{\text{al}}$), 949, 854, 651 (C–Br) cm^{-1} .

1,2-Bis(6-methoxy-1,4-dioxahexyl)-4,5-dibromobenzene, **4b**. The same procedure as for **4a** is used. Twelve grams (0.038 mol) of **3b** were reacted with 15.26 g (0.095 mol) of bromine in CH_2Cl_2 (250 mL) in the presence of 300 mg of iron powder and a catalytic amount of iodine. Purification: column chromatography on silica gel (elution gradient: $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ from 100:0 to 50:50 (v/v)). Yield: 10.39 g (58%), yellow oil, $R_f = 0.33$ (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 8:2 (v/v)).

Elemental analysis for $\text{C}_{16}\text{H}_{24}\text{O}_6\text{Br}_2$ ($M_w = 472$). Calc: C, 40.70; H, 5.12, Br, 20.33. Found: C, 40.64; H, 5.19; Br, 20.39. Mass spectrometry (GCMS) m/z : 474, 472, 470 (M^+), 296, 294, 292 ($M^+ - 2(\text{CH}_2\text{OC}_2\text{H}_4\text{OMe})$). ^1H (300 MHz, CDCl_3) δ ppm: 3.35 (s, 6H, OCH_3), 3.52 (t, 4H, $J = 4.59 \text{ Hz}$), 3.68 (t, 4H, $J = 4.59 \text{ Hz}$), 3.81 (t, 4H, $J = 4.89 \text{ Hz}$), 4.11 (t, 4H, $J = 4.89 \text{ Hz}$), 7.11 (s, 2H, aromatic protons). ^{13}C (75 MHz, CDCl_3) δ ppm: 58.90, 69.12, 69.47, 70.63, 71.79, 115.13, 118.85, 148.66. IR (KBr): 3081, 2924, 2876, 2823, 1582, 1497, 1452, 1350, 1328, 1296, 1251 (val. asym. $\text{C}_{\text{ar}}-\text{O}-\text{C}_{\text{al}}$), 1201, 1110 (val. asym. $\text{C}_{\text{al}}-\text{O}-\text{C}_{\text{al}}$), 1055 (val. sym. $\text{C}_{\text{ar}}-\text{O}-\text{C}_{\text{al}}$), 944, 853, 652 (C–Br) cm^{-1} .

1,2-Bis(3-methoxy-1-oxapropyl)-4,5-dibromobenzene, **4a**.

The same procedure as for **4a** is used with the following quantities: 10 g (0.044 mol) of **3a**, 15.51 g (0.097 mol) of bromine in CH_2Cl_2 (250 mL), 100 mg of iron powder, a catalytic amount of iodine. Purification: column chromatography on silica gel (elution gradient: $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ from 100:0 to 93:7 (v/v)). Yield: 10.83 g (64%), yellow oil, $R_f = 0.39$ (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 95:5 (v/v)).

Elemental analysis for $\text{C}_{12}\text{H}_{16}\text{O}_4\text{Br}_2$ ($M_w = 384$). Calc: C, 37.53; H, 4.20, Br, 41.60. Found: C, 37.42; H, 4.26; Br, 41.56. Mass spectrometry (GCMS) m/z : 386, 384, 382 (M^+), 296, 294, 292 ($M^+ - \text{C}_2\text{H}_4\text{OMe} - \text{OMe}$). ^1H (300 MHz, CDCl_3) δ ppm: 3.43 (s, 6H, OCH_3), 3.74 (t, 4H, $J = 4.74 \text{ Hz}$), 4.11 (t, 4H, $J = 4.74 \text{ Hz}$), 7.13 (s, 2H, aromatic protons). ^{13}C (75 MHz, CDCl_3) δ ppm: 59.17, 69.16, 70.76, 115.34, 118.95, 148.95. IR (KBr): 3081, 2981, 2927, 2881, 2820, 1582, 1498, 1451,

1370, 1351, 1327, 1296, 1252 (val. asym. C_{ar}-O-C_{al}), 1203, 1126 (val. asym. C_{al}-O-C_{al}), 1055 (val. sym. C_{ar}-O-C_{al}), 928, 864, 652 (C-Br) cm⁻¹.

1,2-Bis(12-methoxy-1,4,7,10-tetraoxadodecanyl)-4,5-dicyanobenzene, 5_d. A mixture of 5 g (7.71 mmol) of **4_d**, 2.07 g (23.1 mmol) of CuCN, and 39 mL of freshly distilled DMF was refluxed under nitrogen for 8 h. After cooling and evaporation of the solvent, the crude product, dissolved in dichloromethane, was treated with 200 mL of aqueous NH₄OH (25%); air was then passed through the solution for 24 h. The aqueous solution became dark blue. A similar treatment was made with 200 mL of ethylene diamine (25%). The organic layer was washed with distilled water, dried (MgSO₄), filtered, and concentrated under reduced pressure. The green-brownish oil was chromatographed on silica gel (elution gradient: CH₂Cl₂/ethyl acetate/EtOH from 100:0:0 to 70:26:4 (v/v)), and a colorless oil was obtained in 61% yield (2.7 g). *R_f* = 0.45 (SiO₂, CH₂Cl₂/ethyl acetate/EtOH, 70:26:4 (v/v)).

Elemental analysis for C₂₆H₄₀O₁₀N₂ (*M_w* = 540). Calc: C, 57.76; H, 7.46; N, 5.18. Found: C, 56.82; H, 7.66; N, 4.91. Mass spectrometry (GCMS) *m/z*: 495 (M⁺ - CH₂OCH₃), 451 (M⁺ - CH₂OCH₂CH₂OCH₃), 407 (M⁺ - CH₂(OCH₂CH₂)₂-OCH₃), 363 (M⁺ - CH₂(OCH₂CH₂)₃OCH₃), 171 (MH⁺ - ((OC₂H₄)₄OMe) - ((C₂H₄O)₃OMe)). ¹H (300 MHz, CDCl₃) δ ppm: 3.32 (s, 6H, OCH₃), 3.49 (t, 4H, *J* = 4.59 Hz), 3.60 (m, 20H), 3.84 (t, 4H, *J* = 4.59 Hz), 4.21 (t, 4H, *J* = 4.6 Hz), 7.23 (s, 2H, aromatic protons). ¹³C (75 MHz, CDCl₃) δ ppm: 58.78, 69.13, 69.22, 70.25, 70.35, 70.37, 70.41, 70.74, 71.68, 108.49, 115.63, 116.85, 152.18. IR (KBr): 3056, 2876, 2229 (C≡N), 1590, 1563, 1518, 1452, 1408, 1351, 1290 (val. asym. C_{ar}-O-C_{al}), 1230, 1108 (val. asym. C_{al}-O-C_{al}), 1040 (val. sym. C_{ar}-O-C_{al}), 949, 890 cm⁻¹.

1,2-Bis(6-methoxy-1,4-dioxahexyl)-4,5-dicyanobenzene, 5_b. The same procedure as for **5_d** was used. Quantities: 8 g (0.017 mol) of **4_b**, 4.54 g (0.051 mol) of CuCN in DMF (70 mL), reflux for 6 h. Purification: column chromatography on silica gel (elution gradient: CH₂Cl₂/ethyl acetate from 100:0 to 80:20, then CH₂Cl₂/EtOH from 98:2 to 80:20 (v/v) and recrystallization in a toluene/*n*-heptane (2:1 v/v) mixture. Yield: 3.23 g (55%), white crystals. *R_f* = 0.30 (SiO₂, CH₂Cl₂/EtOH, 97:3 v/v).

Elemental analysis for C₁₈H₂₄O₆N₂ (*M_w* = 364). Calc: C, 59.33; H, 6.64; N, 7.69. Found: C, 59.02; H, 6.61; N, 7.55. Mass spectrometry (GCMS) *m/z*: 364 (M⁺), 306 (MH⁺ - CH₂-CH₂OCH₃), 262 (MH⁺ - (CH₂CH₂O)₂CH₃), 186 (M⁺ - OCH₂-CH₂OCH₃ - (CH₂CH₂O)₂CH₃), 171 (M⁺ - (OCH₂CH₂OCH₃) - (O(CH₂CH₂O)₂CH₃)). ¹H (300 MHz, CDCl₃) δ ppm: 3.42 (s, 6H, OCH₃), 3.59 (t, 4H, *J* = 4.53 Hz), 3.75 (t, 4H, *J* = 4.54 Hz), 3.94 (t, 4H, *J* = 4.64 Hz), 4.30 (t, 4H, *J* = 4.64 Hz), 7.30 (s, 2H, aromatic protons). ¹³C (75 MHz, CDCl₃) δ ppm: 58.92, 69.19, 69.31, 70.76, 71.76, 108.60, 115.67, 116.95, 152.25. IR (KBr): 3060, 2940, 2884, 2228 (C≡N), 1588, 1566, 1525, 1456, 1408, 1354, 1294 (val. asym. C_{ar}-O-C_{al}), 1232, 1144, 1124, 1107 (val. asym. C_{al}-O-C₁₁), 1088, 1048 (val. sym. C_{ar}-O-C_{al}), 955, 890 cm⁻¹.

1,2-Bis(3-methoxy-1-oxapropyl)-4,5-dicyanobenzene, 5_a. The same procedure as for **5_d** was used. Quantities: 10 g (0.026 mol) of **4_a**, 7 g (0.078 mol) of CuCN in DMF (131 mL), reflux for 8 h. Purification: column chromatography on silica gel (elution gradient: CH₂Cl₂/ethyl acetate from 100:0 to 8:2, v/v) and recrystallization in a toluene/*n*-heptane (10:0.5 v/v) mixture. Yield: 4.72 g (66%), white crystals. *R_f* = 0.43 (SiO₂, CH₂Cl₂/ethyl acetate, 8:2 (v/v)).

Elemental analysis for C₁₄H₁₆O₄N₂ (*M_w* = 276). Calc: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.79; H, 5.74; N, 10.04. Mass spectrometry (GCMS) *m/z*: 276 (M⁺), 244 (MH⁺ -

OCH₃), 231 (M⁺ - CH₂OCH₃), 218 (MH⁺ - CH₂CH₂OCH₃), 201 (MH⁺ - (CH₂CH₂OCH₃) - (CH₃)), 186 (M⁺ - (CH₂-CH₂OCH₃) - (OCH₃)), 171 (MH⁺ - (CH₂CH₂OCH₃) - (CH₂-OCH₃)). ¹H (300 MHz, CDCl₃) δ ppm: 3.42 (s, 6H, OCH₃), 3.78 (t, 4H, *J* = 4.51 Hz), 4.22 (t, 4H, *J* = 4.60 Hz), 7.30 (s, 2H, aromatic protons). ¹³C (75 MHz, CDCl₃) δ ppm: 59.14, 69.22, 70.39, 108.67, 115.71, 116.75, 152.27. IR (KBr): 3061, 2991, 2930, 2815, 2228 (C≡N), 1588, 1566, 1525, 1448, 1404, 1366, 1296 (val. asym. C_{ar}-O-C_{al}), 1230, 1132 (val. asym. C_{al}-O-C_{al}), 1085 (val. sym. C_{ar}-O-C_{al}), 891 cm⁻¹.

Bis[4,5,4',5',4'',5'',4''',5'''-octakis(12-methoxy-1,4,7,10-tetraoxadodecanyl)phthalocyanine] Lutetium(III), 1_d. A round-bottomed flask fitted with a condenser was degassed and flame-dried under dry argon. The flask was charged under argon with the dinitrile derivative **5_d** (1 g, 1.85 mmol), Lu(OAc)₃·3H₂O (81.5 mg, 0.231 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (185 μL, 1.23 mmol), and 4.5 mL of hexan-1-ol; the mixture was refluxed for 8 h. The crude product was deposited on Celite and successively washed with cooled and warmed *n*-heptane (500 mL) and finally with a mixture of *n*-heptane:CH₂Cl₂ (20:1, v/v) (200 mL). The remaining solids were put in a thimble of a Soxhlet apparatus and extracted with *n*-heptane for 3 days to remove organic impurities. Phthalocyanines were recovered by extracting the solid residue with chloroform. Purification was achieved by (i) column chromatography over silica gel (CHCl₃/ethyl acetate/EtOH, 80:15:5 (v/v)), then CHCl₃/MeOH, 95:5 (v/v); (ii) two successive preparative thin layer chromatographies (neutral alumina; eluent CHCl₃/ethyl acetate/propan-2-ol, 60:37:3 (v/v); *R_f* = 0.41). A precipitation from a CH₂Cl₂/*n*-heptane (1:5 (v/v)) mixture led to 70 mg (yield: 6.5%) of a viscous paste.

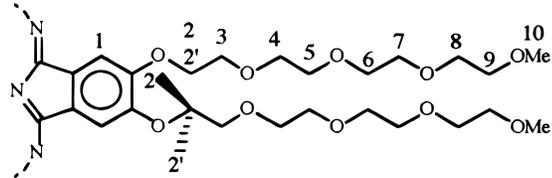
Elemental analysis for C₂₀₈H₃₂₀O₈₀N₁₆Lu (*M_w* = 4500). Calc: C, 55.52; H, 7.17; N, 4.98; Lu, 3.89. Found: C, 55.16; H, 7.21; N, 4.88; Lu, 4.06. IR (KBr): 2879, 1599, 1500, 1458, 1363, 1277, 1200, 1107, 1062, 948, 858 cm⁻¹. UV-visible (CHCl₃): ε₂₉₂ 102 000, ε₃₆₇ 144 000, ε₄₇₅ 41 000, ε₆₀₂ 32 000, ε₆₆₆ 180 000.

Bis[4,5,4',5',4'',5'',4''',5'''-octakis(6-methoxy-1,4-dioxahexyl)phthalocyanine] Lutetium(III), 1_b. The same procedure as for **1_d** was used. Quantities: 1 g (2.74 mmol) of **5_b**, 120.6 mg (0.343 mmol) of Lu(OAc)₃·3H₂O, 205 μL (1.37 mmol) of DBU in hexan-1-ol (7 mL), reflux for 18 h. Purification: column chromatography on silica gel (elution gradient CHCl₃/EtOH from 100:0 to 90:10 (v/v)), preparative thin layer chromatography (neutral alumina; eluent CHCl₃/ethyl acetate/propan-2-ol, 60:36.5:3.5 (v/v); *R_f* = 0.5), and reprecipitation in a CH₂Cl₂/*n*-heptane (2:5) mixture. Yield: 67 mg (6%), green powder, mp = 138 °C.

Elemental analysis for C₁₄₄H₁₉₂O₄₈N₁₆Lu (*M_w* = 3090). Calc: C, 55.97; H, 6.26; N, 7.26; Lu, 5.66. Found: C, 55.58; H, 6.20; N, 7.11; Lu, 5.55. IR (KBr): 3071, 2924, 2875, 1597, 1500, 1451, 1386, 1354, 1322, 1278, 1204, 1124, 1063, 938, 859, 757 cm⁻¹. UV-visible (CHCl₃): ε₂₉₁ 109 000, ε₃₆₇ 149 000, ε₄₇₅ 42 000, ε₆₀₂ 32 000, ε₆₆₅ 185 000.

Bis[4,5,4',5',4'',5'',4''',5'''-octakis(3-methoxy-1-oxapropyl)phthalocyanine] Lutetium(III), 1_a. The same procedure as for **1_d** was used. Quantities: 1 g (3.61 mmol) of **5_a**, 159 mg (0.452 mmol) of Lu(OAc)₃·3H₂O, 270 μL (1.81 mmol) of DBU, hexan-1-ol (12 mL), reflux for 22 h. Purification: column chromatography on silica gel (elution gradient CHCl₃/EtOH from 100:0 to 96:4 (v/v)), preparative thin layer chromatography (neutral alumina; eluent CHCl₃/ethyl acetate/propan-2-ol, 60:36:3 (v/v); *R_f* = 0.6), and reprecipitation in a CH₂Cl₂/*n*-heptane (2:3) mixture. Yield: 116 mg (12%), green powder. mp = 246 °C.

Elemental analysis for C₁₁₂H₁₂₈O₃₂N₁₆Lu (*M_w* = 2385).

TABLE 5: ^1H Chemical Shifts (δ in ppm Downfield from TMS), Number of Protons, and Assignments for Oxidized, Neutral, and Reduced Form of 1_{d} (t, triplet)


oxidized form ^a		neutral form ^b		reduced form ^c	
δ	atom	δ	atom	δ	atom
7.44 (16H)	1			8.53 (16H)	1
4.43 (32H)	2			4.79 (16H)	2 or 2'
				4.66 (16H)	2 or 2'
4.07 (32H)	3	4.22 (32H)	3	4.32 (32H)	3
3.83 (32H)	4	3.95 (32H)	4	3.98 (32H, t, 5.15 Hz)	4
3.71 ^e	5	3.78 (32H)	5	3.82 (32H, t, 5.15 Hz)	5
		3.69 (64H)	6, 7	3.73 (32H, t) ^d	6
3.63 ^e	6,7,8			3.65 (32H, t)	7
		3.64 (32H)	8	3.59 (32H, t, 4.90 Hz)	8
3.50 ^e	9	3.53 (32H)	9	3.46 (32H, t, 4.96 Hz)	9
3.30 (48H)	10	3.35 (48H)	10	3.28 (48H, s)	10

^a $\text{CDCl}_3/\text{CD}_3\text{OD}$, 5:1. ^b CDCl_3 . ^c DMF. ^d Overlap with H_2O signal. ^e Solvent peak overlap.

Calc: C, 56.30; H, 5.41; N, 9.40; Lu, 7.33. Found: C, 56.11; H, 5.34; N, 9.21; Lu, 7.58. IR (KBr): 2925, 2878, 2815, 1601, 1500, 1452, 1392, 1366, 1324, 1278, 1200, 1125, 1104, 1082, 1060, 925, 862, 813, 755 cm^{-1} . UV-visible (CHCl_3): ϵ_{292} 115 000, ϵ_{367} 156 000, ϵ_{476} 45 000, ϵ_{602} 34 000, ϵ_{665} 201 000.

4,5,4',5',4'',5'',4''',5'''-Octakis(9-methoxy-1,4,7-trioxanonyl) Copper Phthalocyanine, **2e**. This compound is a side product of the reaction with CuCN , yielding **5c**. A partly purified product was obtained after column chromatography giving **5c**. It is isolated *via* preparative thin layer chromatography over neutral alumina (eluent: $\text{CHCl}_3/\text{AcOEt}/\text{MeOH}$, 60:36:4), followed by precipitation in a $\text{CH}_2\text{Cl}_2/n$ -heptane mixture (2:10).

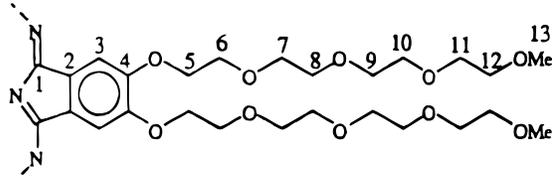
Elemental analysis for $\text{C}_{88}\text{H}_{128}\text{O}_{32}\text{N}_8\text{Cu}$ ($M_w = 1873.5$). Calc: C, 56.41; H, 6.88; N, 5.98, Cu, 3.39. Found: C, 56.06; H, 6.93; N, 5.78; Cu, 3.05. Mass spectrometry (field desorption) m/z : 1872 (MH^+), 1726 ($\text{M}^+ - (\text{C}_2\text{H}_4\text{O})_3\text{CH}_3$). ^1H (300 MHz, CDCl_3) δ ppm: 3.39 (s, 24H, OCH_3), 3.60 (bs, 16H), 3.73 (bs, 16H), 3.81 (bs, 16H), 3.96 (bs, 16H), 4.19 (bs, 16H). UV-visible (CHCl_3): ϵ_{341} 82 000, ϵ_{412} 31 000, ϵ_{610} 43 000, ϵ_{630} 21 000, ϵ_{677} 250 000.

^1H NMR Spectroscopy. The experimental methods of oxidation and reduction allowing the obtainment of the NMR spectra of the ionized molecular units were previously described.⁵

The chemical shifts and tentative assignments of the different redox forms of 1_{d} are given in Table 5. For all neutral forms, the paramagnetism of the Pc_2Lu perturbs the proton signals situated in the vicinity of the aromatic core. In the case of the side chains, the protons have been assigned following their proximity to the central aromatic core.

The reduction or the oxidation of the macrocycle yields a diamagnetic anion or cation, respectively. In the reduced form of 1_{d} , a peak at 8.5 ppm appears. In the $-\text{OCH}_2-$ region, nine different peaks are observed, among them six well-defined triplets at the highest fields. The integration (32H) and the chemical shift allow the approximate assignment of the 4, 5, 6, 7, and 8 positions.

By oxidation of 1_{d} with bromine, a resonance at 7.4 ppm is detected; it is significantly shifted compared to that of the reduced form (8.5 ppm). In the $\text{O}-\text{CH}_2$ region, the peaks are broad and unresolved.

TABLE 6: ^{13}C Chemical Shifts (δ in ppm Downfield from TMS) and Assignments for the Neutral and Reduced Forms of 1_{d}


neutral form ^a		reduced form ^b	
δ	atom	δ	atom
		158.0	1
		151.2	4
		132.2	3
		106.6	2
71.93	12	72.30	12
71.13	11	71.37	11
70.77	10	71.12	10
70.65	9, 8	70.97	9
		70.89	8
70.59	7	70.67	7
69.92	6	70.40	6
		70.20	5
		58.89	13

^a CDCl_3 . ^b DMF.

^{13}C NMR Spectroscopy. Spectral data and assignments for 1_{d} are gathered in Table 6. The carbon atoms close to the central aromatic core are not observed in the neutral forms but appear after reduction.

The carbon 1 has been assigned following ref 30. The chemical shift of carbon 4 has been calculated.³¹

Peak 5 has been assigned by postulating it is the closest to the paramagnetic center in the neutral form; this yields to its absence in the spectrum. The other signals have been classified following their proximity to the aromatic core.

Acknowledgment. D. Lelièvre and L. Bosio are thanked for the X-ray experiments. C. Jallabert is acknowledged for her assistance for NMR determinations. Field desorption mass spectrometry has been carried out at the University of Tübingen by R. Polley.

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JP960504C