Water-Soluble Phtalocyanines Containing Aza-Crown Ether Substituents☆

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Received May 13, 1991

Key Words: Aza-crown ethers / Phthalocyanines, amphiphilic / Quaternary lutetium bis(phthalocyaninates) / Quaternerization of acetyl amines / Lutetium complexes

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A straightforward and generalizable synthesis of metal-free and metal (Ni, Pb, Lu) derivatives of symmetrically tetrasubstituted phthalocyanines derived from 15,16-dibromo- or -dicyano-2,3,6,7,8,9,11,12-octahydro-5*H*-benzo[e][1,4,7,13]tetroxazacyclopentadecine (**1**) is described. Quaternarization of the *N*-acetyl derivatives **7** in a chloroform/dimethyl sulfate mixture gives phthalocyanines **9** soluble in the pH range of 1 – 13. The electronic spectra of the phthalocyanines in buffered solutions (pH 4, 7, and 10) are examined. Furthermore, the electronic spectra of lutetium bis(phthalocyaninate) **9d** in water and in DMSO are compared for the first time.

One of the important aims of research on the chemistry of phthalocyanines (Pc) is to enhance their solubility in various solvents. While peripheral substitution with bulky groups[1] or long alkyl chains[2] leads to Pc derivatives soluble in common organic solvents, the introduction of sulfonyl[3], carboxyl[4], or amino[5] groups results water-soluble products. However, the solubility in water can be accomplished only within certain pH ranges with these substituents. Quaternarized ammonium groups are especially useful to achieve solubility within a wide pH range, and there are only a few papers describing phthalocyanines bearing quaternary ammonium substituents[6,7].

α,β,γ,δ-Tetrakis(benzo-15-crown-5)porphyrin and its metal-substituted derivatives, synthesized by Thanabal and Krishnan[8], are the first examples of supermolecular systems in which dimerization is induced by alkali or alkali earth cations.

We have previously synthesized for the first time crown ether-substituted phtahlocyanines which are soluble in most common organic solvents and which are capable of binding alkali metal salts[9-11]. In an endeavour to extend the range of available soluble substituted phthalocyanines we have recently reported on the preparation of a phthalocyanine containing four tetraazamacrocycles which enables the coordination of additional four metal ions[12].

The high absorptivity of phthalocyanines at long wavelengths of the visible spectrum has received considerable attention as a probe for photodynamic therapy of tumors by laser[13]. For this application, the most important point is the solubility in water at different pH values. Also the polar substituent (e.g. ammonium group) should be sufficiently far away from the phthalocyanine core, since peripheral substitution causes shifts in the Q bands[14]; this can be accomplished by using flexible polyether chains of sufficient length between the polar group and the phthalocyanine core.

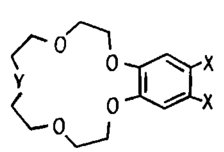
In the present paper, we describe water-soluble phthalocyanines carrying quaternarized symmetrical monoazabenzo-15-crown-5 units. In these compounds the quaternary ammonium groups are bound to phthalocyanines by two ethylene oxide chains. A first example of this group of phthalocyanines obtained directly by cyclotetramerization of quaternarized dibromomonoaza-15-crown-5 with CuCN has been reported as a note[15]. In this paper we report on a generalizable procedure for the synthesis of various quaternarized monoaza-crown ether-substituted water-soluble phthalocyanines.

Results and Discussion

Starting from monoazabenzo-15-crown-5 (**1**), we have illustrated the general route for the synthesis of new water soluble phthalocyanines in Scheme 1. Although there are some reports on the synthesis and reactions of monoazabenzo-15-crown-5, no experimental details and spectral data have been given so far[16–18]. Therefore, its synthesis is also reported here for completeness and the spectral data are included for the structural characterization. Bromination of **1** in acetic acid gives **2**, which is treated either with dimethyl sulfate in acetonitrile in the presence of sodium carbonate to obtain the quaternary ammonium salt **3** or with acetic anhydride to protect the amino group in the phthalocyanine reaction (**4**). The bromo substituents in **3** and **4** are converted into dicyano groups in derivatives **5** and **6** resp., by the Rosenmund-von-Braun reaction. In order to obtain the water-soluble phthalocyanines **9**, dinitrile **5** is directly treated with suitable metal salts, but the yields obtained are rather low and the workup conditions are cumbersome. A more practical way to isolate compound **9a** is to start the cyclotetramerization reaction from the *N*-acetyl compound **6** to obtain **7a** which can be hydrolyzed in conc. H$_2$SO$_4$ at 125 – 130°C to yield **8a**. Methylation of **8a** with dimethyl sulfate in various solvents (e.g. DMSO, DMF, acetonitrile)

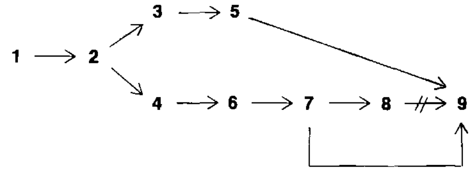
Chem. Ber. **124** (1991) 2531 – 2536 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009 – 2940/91/1111 – 2531 $ 3.50+.25/0

affords no appreciable amount of quaternarized end product **9a**. However, an efficient and easy method for the preparation of **9a** is to carry out the quaternarization directly by treating *N*-acetylphthalocyanine **7a** with excess dimethyl sulfate in chloroform. In this non-aqueous medium, the acetyl group is split of without any hydrolysis, and methylation accurs simultaneously.

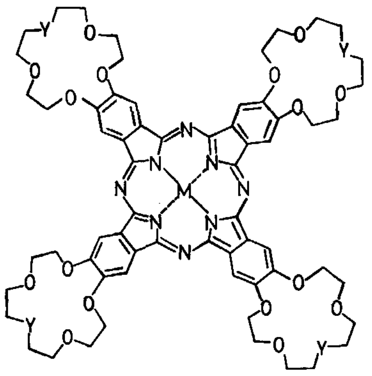


	X	Y		X	Y
1	H	NH	**4**	Br	$NCOCH_3$
2	Br	NH	**5**	CN	$N^+(CH_3)_2 \cdot CH_3SO_4^-$
3	Br	$N^+(CH_3)_2 \cdot CH_3SO_4^-$	**6**	CN	$NCOCH_3$

Scheme 1



The obvious difference among the IR spectra of aza-unsubstituted (**8**) and -quaternarized (**9**) phthalocyanines are NH vibrations of the macrocyclic ring appearing at 3400 cm^{-1} for **8** and the SO_2 vibrations of the methyl sulfate anion around 1300–1200 cm^{-1} for **9**. These differences are evident especially when the spectra of **8a** and **9a** are compared.



	M	Y		M	Y
7a	2H	$NCOCH_3$	**9a**	2H	$N^+(CH_3)_2 \cdot CH_3SO_4^-$
b	Ni	$NCOCH_3$	**b**	Ni	$N^+(CH_3)_2 \cdot CH_3SO_4^-$
c	Pb	$NCOCH_3$	**c**	Pb	$N^+(CH_3)_2 \cdot CH_3SO_4^-$
8a	2H	NH			
b	Ni	NH			
c	Pb	NH			

The ^1H-NMR data of *N*-acetylphthalocyanines **7** in chloroform exhibit the typical absorptions of monoazacrown ether and phthalocyanine moieties. Strong shielding of the protons in the phthalocyanine core of **7a** is manifested by a broad and weak absorption at $\delta = -3.43$. In the case of **9a**, the solubility of the compound in $[D_6]DMSO$ is not sufficient to observe the weak NH proton signals of the cavity. When D_2O is used as the solvent, these protons are replaced by deuterium. Also in D_2O, the absorptions are rather broad when compared with those of **7a** in chloroform, and these absorptions are the result of aggregation in polar solvents. By increasing the polarity of the solvent, the more hydrophobic moieties of amphiphile approach each other and form dimers[6]. The compounds **9** are the first examples of phthalocyanines soluble in pH range of 1–13. The UV-Vis spectra of these compounds in water at different pH values maintained by phosphate buffers are given in Table 2 (cf. also Table 1). There is almost no appreciable change in the spectra of **9a–c** with varying pH values. A single intense Q band for the metal-free phthalocyanine is interesting, while D_{2h} symmetry of these compounds is expected give rise to the formation of two bands in the low-energy region. However, aggregation of phthalocyanine molecules exhibit spectra similar to those for **9a**. Metal-free phthalocyanine sulfonates are reported to give a single broad absorption around 630 nm in water as a result of dimerization or tetramerization[19]. The solvent dependence of aggregation is also verified for **9a** since a double Q band spectrum is obtained with DMSO (Figure 1).

Table 1. Electronic spectra of phthalocyanines **7–9**

	λ/nm (10^{-4} $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)							
7a[a)]	225 (8)	291 (8)	344 (11.4)	422 (4.86)	600 (3.5)	659 (15.8)	697 (19.84)	
7b[a)]	217 (6.08)	241 (5.08)	286 (7.54)	308 (6.7)	413[b)] (2.88)	615 (3.04)	641[b)] (3.92)	665 (17.44)
7c[a)]	232 (8.4)	291 (8.44)	339 (10.26)	409[b)] (4.22)	600 (4.6)		672 (20.4)	
7d[a)]		292 (8.28)	339 (9.78)	422[b)] (4.16)		616 (4.72)	686 (27.78)	
9a[c)]		280 (4.4)	320 (4.05)	400[b)] (1.65)		600 (3.2)		
9b[c)]	228 (3.53)	273 (4.61)		397[b)] (1.23)		603 (2.37)		
9c[c)]		280 (4.15)	320 (3.7)	400[b)] (1.62)	600 (2.9)			
9d[c)]	200 (4.36)	280 (5.35)		393[b)] (1.9)		610 (3.75)	670 (3.5)	

[a)] In chloroform. – [b)] Shoulder. – [c)] In H_2O, **c** $= A/\varepsilon \cdot l$, $l = 1$ cm.

Recently, the bis(phthalocyaninato)lutetium(III) derivatives are receiving considerable interest for their electrochemical properties and they are the first known intrinsic molecular semiconductors[20,21]. While the neutral Pc_2Lu molecule is green, the one electron-oxidized cation Pc_2Lu^+ is orange and the one electron-reduced anion Pc_2Lu^- is blue.

Table 2. Electronic spectra of phthalocyanines **9a**−**d** in aqueous solutions at different pH values

		λ/nm ($10^{-4}\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)				
9a	pH 4		320(3.92)	400(1.55)	603(3.12)	
	pH 7	280(4.8)	320(3.92)	402(1.57)	604(3.10)	
	pH 10	280(4.75)	320(4.15)	400(1.67)	602(3.27)	
9b	pH 4	292(3.01)		397(1.37)	603(2.27)	
	pH 7	273(3.81)		397(1.11)	602(1.99)	
	pH 10	273(4.85)		396(1.24)	603(2.38)	
9c	pH 4		320(3.81)	400(1.61)	600(2.80)	
	pH 7	280(4.92)	328(3.5)	400(1.46)	600(2.5)	
	pH 10	280(4.8)	320(3.89)	400(1.42)	600(2.96)	
9d	pH 4		320(4.9)	400(1.98)	620(3.96)	670(3.05)
	pH 7	280(6.37)	323(6.21)	400(1.85)	610(4.24)	670(3.71)
	pH 10	280(4.76)	320(4.91)	400(1.98)	610(4.43)	670(4.1)

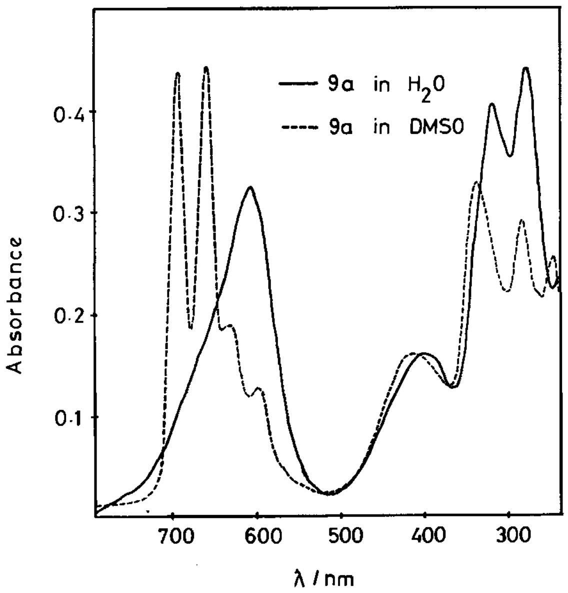
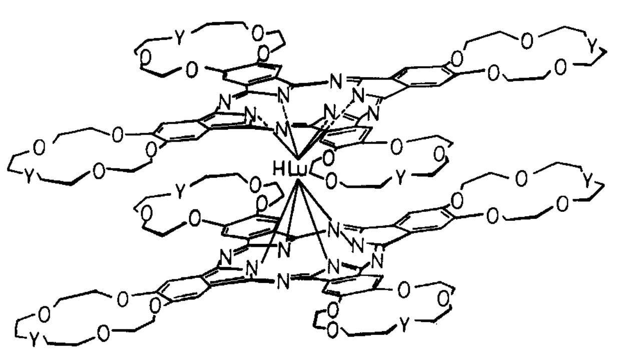


Figure 1. Electronic spectra of **9a** in water and in DMSO



7d: Y = $NCOCH_3$ **8d**: Y = NH

9d: Y = $N^+(CH_3)_2 \cdot CH_3SO_4^-$

Although there have been some reports on the UV-Vis spectra of lutetium bis(phthalocyaninate) derivatives, these are measured either as solutions in organic solvents[22] or as thin films[23,24]. In the present work, quaternarization of the monoaza function of the macrocyle **7d** has enabled the synthesis of **9d**, the first water-soluble lutetium bis(phthalocyaninate).

The color of the solutions of these bis(phthalocyaninato)lutetium(III) compounds (**7d** in chloroform, **8d** and **9d** in water) is green indicating that these products are in neutral form.

The electronic spectra of **9d** in water and in DMSO are given in Figure 2. In the Q band region two intense absorptions are present around 670 and 610 nm. The intensities of these two bands are about the same as in water, but the higher energy band is more intense in DMSO.

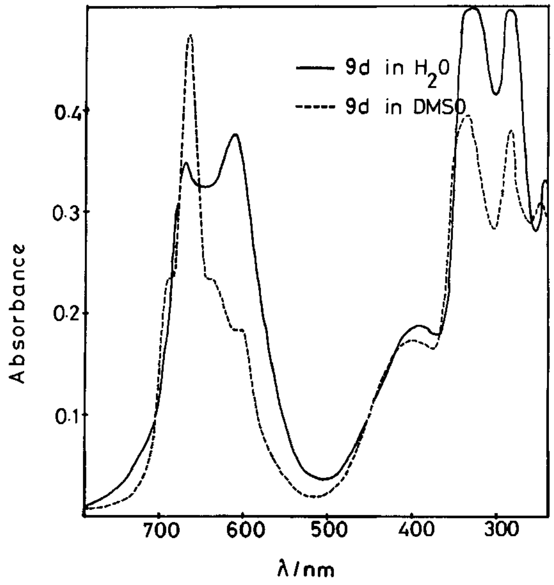


Figure 2. Electronic spectra of **9d** in water and in DMSO

The optical spectra have been repeated in the presence of a mild reductant (hydrazine hydrate) and a mild oxidant (sodium chlorate) in order to avoid the presence of mixtures of oxidized and reduced forms, but in all cases the resulting spectra are identical which confirms the presence of only one neutral form. Q bands show some difference according to the pH of the aqueous solution (Table 2): At low pH values (e.g. pH 4) there is an intense absorption at 620 nm with a shoulder at around 660 nm. In neutral or basic solutions two absorptions of equal intensity are present in the spectra.

Experimental

IR: Perkin-Elmer 983 spectrophotometer, KBr pellets. — ^1H and off resonance-decoupled ^{13}C NMR: Bruker 200-MHz spectrometer. — UV/Vis: Varian DMS 90 spectrophotometer. — Elemental analyses: Instrumental Analysis Laboratory of TÜBİTAK Marmara Research center.

1,2-Bis(2-hydroxyethoxy)benzene[25], 1,2-bis[2-(tosyloxy)ethoxy]-benzene[26] and the quaternary ammonium salt of dibromomonoazabenzo-15-crown-5 (**3**)[15] were prepared according to reported procedures.

2,3,6,7,8,9,11,12-Octahydro-5H-benzo[e][1,4,7,10,13]tetroxazacyclopentadecine (monoazabenzo-15-crown-5) (**1**): Diethanolamine (5.26 g, 4.82 ml, 0.05 mol) and metallic sodium (2.76 g, 0.12 mol) were dissolved in *tert*-butyl alcohol (700 ml) under argon. Then a solution of 1,2-bis[2-(tosyloxy)ethoxy]benzene (25.33 g, 0.05 mol) in 1,4-dioxane (300 ml) was added dropwise for 3 h. The mixture was refluxed for 17 h. After it was filtered to remove the sodium tosylate the filtrate was evaporated to dryness, and a yellowish-orange oily crude product was obtained. Extraction of this oily material with *n*-heptane gave light-yellow bright crystals. Yield: 5.3 g (40%), m.p. 143–145°C. – IR (KBr): $\tilde{\nu}$ = 3320 cm^{-1}, 2930, 2850, 2800, 1590, 1500, 1450, 1330, 1260–1220, 1120, 1080, 1050, 950, 930, 920, 735. – ^1H NMR ($CDCl_3$): δ = 6.74–6.90 (m, 4H), 4.34–3.84 (m, 12H), 3.73–2.76 (m, 4H), 2.52 (s, 1H). – ^{13}C NMR [D_6]DMSO: δ = 148.04, 120.43, 112.15, 69.47, 68.05, 66.94, 48.51.

$C_{14}H_{21}NO_4$ (267.3) Calcd. C 62.90 H 7.92 N 5.24
Found C 62.59 H 7.96 N 5.59

15,16-Dibromo-2,3,6,7,8,9,11,12-octahydro-5H-benzo[e][1,4,7,10,13]tetroxazacyclopentadecine (**2**): Compound **1** (13.37 g, 0.05 mol) was dissolved in acetic acid (37.5 ml), and a solution of bromine (5.2 ml, 0.1 mol) in acetic acid (26.5 mol) was added dropwise to this solution at room temp. in 4 h. After stirring for 24 h, the mixture was diluted with water (100 ml) and neutralized with a solution of sodium hydrogencarbonate and then extracted with dichloromethane. The organic layer was dried with sodium sulfate and the solvent evaporated. The remaining reddish oily product was precipitated with acetone to yield light yellow crystalls, 10.1 g (47.5%), m.p. 142–144°C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2950, 2920, 2850, 2830, 1570, 1490, 1440, 1350, 1250–1210, 1130, 1070, 1040, 960, 850, 830, 800, 645. – ^1H NMR ($CDCl_3$): δ = 7.01 (s, 2H), 4.08–3.70 (m, 12H), 2.83–2.78 (m, 4H), 2.37 (s, 1H). – ^{13}C NMR ($CDCl_3$): δ = 148.5, 116.63, 114.48, 70.18, 68.45, 67.86, 48.99.

$C_{14}H_{19}Br_2NO_4$ (425.1) Calcd. C 39.55 H 4.50 N 3.29
Found C 39.53 H 4.56 N 3.21

7-Acetyl-15,16-dibromo-2,3,6,7,8,9,11,12-octahydro-5H-benzo[e][1,4,7,10,13]tetroxazacyclopentadecine (**4**): A solution of **2** (2.0 g 4.7 mmol) in a mixture of acetic acid (2 ml) and acetic anhydride (2 ml) was refluxed for 3 h. After cooling, the reaction mixture was poured into icewater and extracted with dichloromethane. The extract was dried with Na_2SO_4 and concentrated. The resulting yellowish-brown oily product was extracted with *n*-heptane to give bright white crystals. Yield: 1.5 g (69%), m.p. 104–106°C. – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2920, 2860, 1630, 1500, 1440, 1405, 1360, 1330, 1300, 1250–1205, 1140, 1090, 1060, 1020, 930, 880, 830, 650. – ^1H NMR ($CDCl_3$): δ = 7.06 (s, 2H), 4.11–3.53 (m, 12H), 3.13–3.07 (m, 4H), 2.22 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 170.97, 148.61, 117.71, 114.53, 71.03, 70.36, 69.68, 51.32, 21.58.

$C_{16}H_{21}Br_2NO_5$ (467.35) Calcd. C 41.12 H 4.53 N 3.00
Found C 41.32 H 4.77 N 3.68

Synthesis of the Quaternary Ammonium Salt **5** *of Dicyanomonoazabenzo-15-crown-5:* A Schlenk tube was charged with **3** (0.5 g, 0.892 mmol), CuCN (0.238 g, 2.65 mmol), and dry pyridine (3.65 ml) under argon and then sealed. The reaction was held at 175–180°C for 8 h. After the brown mixture was cooled, it was diluted with absol. EtOH (5–6 ml), filtered to remove the inorganic impurities, and the filtrate was concentrated. The obtained crude oily product was purified by column chromatography (neutral Al_2O_3; CH_2Cl_2/EtOH, 5:1). Yield: 0.12 g (30%), m.p. 215–217°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 2225, 1605, 1530, 1480, 1370, 1300, 1280–1240, 1180, 1140, 1100, 965, 900, 540. – ^1H NMR [D_6]DMSO: δ = 7.75 (s, 2H), 4.25–3.72 (m, 11H), 3.62–3.36 (m, 8H), 3.35 (s, 6H). – ^{13}C NMR ([D_6]DMSO): δ = 151.93, 117, 113.07, 107.5, 68.60, 68.47, 68.25, 64.07, 63.74, 51.58.

$C_{19}H_{27}N_3O_8S$ (457.5) Calcd. C 49.88 H 5.94 N 9.18
Found C 49.97 H 5.97 N 8.85

7-Acetyl-15,16-dicyano-2,3,6,7,8,9,11,12-octahydro-5H-benzo[e][1,4,7,10,13]tetroxazacyclopentadecine (**6**): A round-bottomed flask fitted with a condenser was evacuated and refilled with argon three times and flamed under vacuum. Under argon the flask was charged with CuCN (0.288 g, 3.21 mmol), **4** (0.5 g, 1.07 mmol) and anhydrous tetramethylurea (4.5 ml), and this mixture was heated to 165–170°C. It was held at this temp. for 16 h. During this time the solution became dark green-brown. After cooling it was mixed with aqueous NH_4OH (15 ml, 25%), and air was passed through the solution for 24 h. The solution became dark blue and a greenish-yellow precipitate formed. This precipitate was isolated by filtration and washed with water until the filtrate was neutral. The precipitate was then dried and extracted with acetone. After reduction of the volume of the acetone extract yellowish-white crystals were obtained. Yield: 0.20 g (52%), m.p. 194–196°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2900, 2220, 1640, 1580, 1520, 1480, 1425, 1360, 1350, 1290–1230, 1130, 1090, 1030, 930, 900, 880, 540. – ^1H NMR ($CDCl_3$): δ = 7.05 (s, 2H), 4.15–3.69 (m, 12H), 3.60–3.53 (m, 4H), 2.13 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 171.03, 148.65, 115.62, 112.43, 104.0, 71.30, 70.20, 68.87, 51.35, 21.57.

$C_{18}H_{21}N_3O_5$ (359.4) Calcd. C 60.16 H 5.89 N 11.69
Found C 60.65 H 5.88 N 11.65

Metal-free N,N',N'',N'''-Tetraacetylphthalocyanine Derivative **7a**: A mixture of **6** (0.50 g, 1.39 mmol) and hydroquinone (0.153 g, 1.39 mmol) (purified by sublimation) was fused in a glass tube under argon by gentle heating and then cooled. The tube was sealed and heated at 200°C for 7 h. After cooling the dark green product was dissolved in 50 ml of chloroform/ethanol (4:1) and precipitated with warm ethyl acetate (100 ml). The resulting dark green precipitate was filtered off, washed with warm ethyl acetate, and then dried with diethyl ether. Yield: 0.135 g (27%). – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2920, 2880, 1620, 1480, 1450, 1280–1210, 1100, 1030, 930, 745. – ^1H NMR ($CDCl_3$ + CD_3OD): δ = 7.76 (s, 8H), 4.10–3.73 (m, 64H), 2.27 (s, 12H), –3.43 (s, broad, 2H). – ^{13}C NMR ($CDCl_3$ + CD_3OD): δ = 171.59, 150.54, 147.61, 128.5, 103.82, 71.19, 69.98, 68.70, 51.36, 21.42.

$C_{72}H_{86}N_{12}O_{20}$ (1439.5) Calcd. C 60.07 H 6.02 N 11.67
Found C 59.71 H 6.15 N 11.27

(N,N',N'',N'''-Tetraacetylphthalocyaninato)nickel(II) Complex **7b**: A mixture of **6** (1 g, 2.78 mmol), $NiCl_2 \cdot 6\,H_2O$ (0.17 g, 0.715 mmol), and dry quinoline (2.1 ml) was heated to 200–205°C with stirring under argon and held at this temp. for 6.5 h. After cooling, the green product was diluted with 10 ml of ethanol and filtered. From the filtrate the product was precipitated with warm ethyl acetate, then washed with diethyl ether and dried. Yield: 0.45 g (43%). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 2880, 1650, 1500, 1470, 1440, 1380, 1305, 1230, 1130, 1085, 960, 765. – ^1H NMR ($CDCl_3$ + CD_3OD): δ = 7.74 (s, 8H), 4.11–3.53 (m, 64H), 2.25 (s, 12H). – ^{13}C NMR ($CDCl_3$ + CD_3OD): δ = 171.60, 149.95, 142.98, 129.24, 102.58, 71.16, 69.89, 68.57, 51.28, 21.36.

$C_{72}H_{84}N_{12}NiO_{20}$ (1496.2) Calcd. C 57.79 H 5.66 N 11.23
Found C 58.02 H 5.31 N 11.27

(N,N',N'',N'''-Tetraacetylphthalocyaninato)lead(II) Complex **7c**: **6** (1.0 g, 2.78 mmol) was heated to 200°C under argon, and PbO (0.185 g, 0.829 mmol) was added portionwise for 2 h. The reaction

was continued at 200°C for 6 h. After cooling to room temp., the green crude product formed was dissolved in 75 ml of $CHCl_3$/EtOH (4:1) and filtered to remove unreacted PbO. The filtrate was added dropwise to warm ethyl acetate (140 ml) and the resulting green precipitate filtered off, washed with warm ethyl acetate, and then dried with diethyl ether. Yield: 0.20 g (17.5%). – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 2880, 1620, 1470, 1450, 1410, 1350, 1280, 1205, 1100, 1080, 1025, 930, 745. – ^1H NMR ($CDCl_3$ + CD_3OD): δ = 7.99 (s, 8H), 4.05–3.70 (m, 64H), 2.25 (s, 12H). – ^{13}C NMR ($CDCl_3$ + CD_3OD): δ = 171.60, 152.90, 146.53, 131.85, 104.29, 71.17, 69.87, 68.73, 51.18, 21.43.

$C_{72}H_{84}N_{12}O_{20}Pb$ (1644.7) Calcd. C 52.58 H 5.15 N 10.22
Found C 52.32 H 5.39 N 10.26

Bis[N,N',N'',N'''-tetraacetylphthalocyaninato]hydrogenlutetium(III) (**7d**): Compound **6** (0.25 g, 0.696 mmol), $Lu(OAc)_3 \cdot 3\,H_2O$ (0.036 g, 0.0888 mmol), DBU (51.9 µl), and *n*-hexanol (1.8 ml) were heated to 170–175°C under argon for 22 h. After cooling the mixture was evaporated to dryness under vacuum, and the remaining green precipitate was dissolved in $CHCl_3$/EtOH (4:1, 40 ml). The obtained solution was added dropwise to warm ethyl acetate (90 ml). A green product precipitated, which was washed with warm ethyl acetate and dried with diethyl ether. Yield: 0.07 g (26.%). – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 2870, 1620, 1480, 1450, 1350, 1280, 1205, 1130, 1090, 1060, 1030, 935, 750. – ^1H NMR ($CDCl_3$ + CD_3OD): δ = 7.39 (s, 16H), 4.05–3.7 (m, 128H), 2.25 (s, 24H). – ^{13}C NMR ($CDCl_3$ + CD_3OD): δ = 171.86, 155.30, 150.9, 132.50, 105.55, 71.22, 70.19, 69.97, 51.59, 21.55.

$C_{144}H_{169}LuN_{24}O_{40}$ (3051.05) Calcd. C 56.69 H 5.58 N 11.02
Found C 56.17 H 5.73 N 10.79

Deacetylation of the Phthalocyanines with conc. H_2SO_4

8a · 2 H_2SO_4: **7a** (0.25 g, 0.174 mmol) was treated with conc. H_2SO_4 (5 ml) at 125–130°C for 5 h. After cooling the mixture was poured into ethanol (50 ml) and centrifuged and the residue dried with diethyl ether. Yield: 0.12 g (47%). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 1600, 1470, 1420, 1370, 1280, 1190, 1060, 1040, 910, 640.

$C_{64}H_{82}N_{12}O_{24}S_2$ (1467.5) Calcd. C 52.38 H 5.63 N 11.45
Found C 52.94 H 5.95 N 10.85

8b · 2 H_2SO_4 was prepared according to the same procedure as described for the preparation of **8a**·2H_2SO_4 by starting from **7b** (0.25 g, 0.167 mmol). Yield: 0.12 g (47%). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 1600, 1480, 1420, 1380, 1290, 1260, 1220, 1180, 1060, 910, 750, 580.

$C_{64}H_{80}N_{12}NiO_{24}S_2$ (1524.2) Calcd. C 50.43 H 5.29 N 11.02
Found C 50.02 H 5.42 N 10.45

8c · 2 H_2SO_4 was prepared according to the same procedure as described for the preparation of **8a**·2H_2SO_4 by starting from **7c** (0.25 g, 0.152 mmol). Yield: 0.13 g (51%). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 1605, 1475, 1410, 1370, 1290, 1260, 1220, 1180, 1050, 900, 750.

$C_{64}H_{80}N_{12}O_{24}PbS_2$ (1672.7) Calcd. C 45.95 H 4.82 N 10.04
Found C 45.26 H 4.96 N 9.87

8d · 4 H_2SO_4 was prepared according to the same procedure as described for the preparation of **8a**·2H_2SO_4 by starting from **7d** (0.25 g, 0.082 mmol). Yield: 0.07 g (27.5%). – IR (KBt): $\tilde{\nu}$ = 2920 cm^{-1}, 2880, 1590, 1470, 1415, 1370, 1285, 1160, 910, 705, 645.

$C_{128}H_{161}LuN_{24}O_{48}S_4$ (3107.0) Calcd. C 49.48 H 5.22 N 10.82
Found C 50.29 H 4.43 N 10.35

Quaternarization of the Phthalocyanines

9a: **7a** (0.05 g, 0.035 mmol) was dissolved in a mixture of dry chloroform (15 ml) and absol. EtOH (1 ml), and excess dimethyl sulfate (0.1 ml, 1.05 mmol) was added to this solution, which was refluxed for 24 h. The green precipitate formed was centrifuged, washed with dry chloroform, and dried with diethyl ether. Yield: 0.039 g (61%). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 1620, 1510, 1460, 1300, 1220, 1110, 1060, 940, 740, 600. – ^1H NMR (D_2O): δ = 7.85 (s, br, 8H), 4.07 (s, br, 60H), 3.55 (s, br, 40H).

$C_{76}H_{110}N_{12}O_{32}S_4$ (1832.0) Calcd. C 49.82 H 6.05 N 9.17
Found C 49.51 H 5.82 N 9.69

9b was prepared according to the same procedure as described for the preparation of **9a** by starting from **7b** (0.03 g, 0.02 mmol). Yield: 0.012 g (31.5%). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 2880, 1600, 1480, 1430, 1360, 1290, 1220, 1120, 1060, 940, 870, 750, 590. – ^1H NMR (D_2O): δ = 7.80 (s, br, 8H), 4.20 (s, br, 60H), 3.82 (s, br, 40H).

$C_{76}H_{108}N_{12}NiO_{32}S_4$ (1888.7) Calcd. C 48.33 H 5.76 N 8.89
Found C 48.98 H 5.57 N 8.39

9c was prepared according to the same procedure as described for the preparation of **9a** by starting from **7c** (0.05 g, 0.03 mmol). Yield: 0.33 g (53%). – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 2880, 1660, 1600, 1480, 1450, 1280, 1210, 1020, 930, 770, 740, 580.

$C_{76}H_{108}N_{12}O_{32}PbS_4$ (2037.2) Calcd. C 44.81 H 5.34 N 8.25
Found C 44.30 H 5.19 N 7.75

9d was prepared according to the same procedure as described for the preparation of **9a** by starting from **7d** (0.065 g, 0.0213 mmol). Yield: 0.050 g (61%). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2880, 1610, 1460, 1410, 1300, 1220, 1140, 1060, 940, 780, 660, 590.

$C_{152}H_{217}LuN_{24}O_{64}S_8$ (3836.0) Calcd. C 47.59 H 5.70 N 8.76
Found C 47.02 H 5.77 N 8.66

CAS Registry Numbers

1: 54533-83-4 / **2**: 119877-79-1 / **3**: 119877-81-5 / **4**: 135733-25-4 / **5**: 135760-38-2 / **6**: 135733-26-5 / **7a**: 135733-27-6 / **7b**: 135760-41-7 / **7c**: 135760-42-8 / **7d**: 135789-08-1 / **8a** · 2 H_2SO_4: 135733-29-8 / **8b** · 2 H_2SO_4: 135760-44-0 / **8c** · 2 H_2SO_4: 135760-46-2 / **8d** · 2 H_2SO_4: 135912-58-2 / **9a**: 135760-40-6 / **9b**: 135760-48-4 / **9c**: 135760-50-8 / **9d**: 135877-61-1 / 1,2-bis[2-(tosyloxy)ethoxy]-benzene: 54535-06-7 / diethanolamine: 111-42-2

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[*] Dedicated to Professor *Michael Hanack* on the occasion of his 60th birthday.

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