Synthesis and characterization of new soluble phthalocyanines substituted with four tetrathiamacrocycles through oxy bridges and their complexes with silver(I) and palladium(II) ions

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Received (in Montpellier, France) 9th July 2001, Accepted 21st August 2001
First published as an Advance Article on the web

The synthesis of a metal-free phthalocyanine (**3**) and metal phthalocyanines [**4**–**7**; M = Ni(II), Co(II), Cu(II) and Zn(II)] with four tetrathiamacrocycles obtained from 4-({3,6,10,13-tetrathiacyclotetradecyl}oxy)phthalonitrile (**2**) in the presence of dimethylaminoethanol or the corresponding anhydrous metal salts is described. The new soluble compounds have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, MS and UV-Visible spectra. The thermal stabilities have been determined by thermogravimetric analyses. Complexation of the tetrathiamacrocycles of **4** with silver(I) or palladium(II) yields forms pentanuclear compounds.

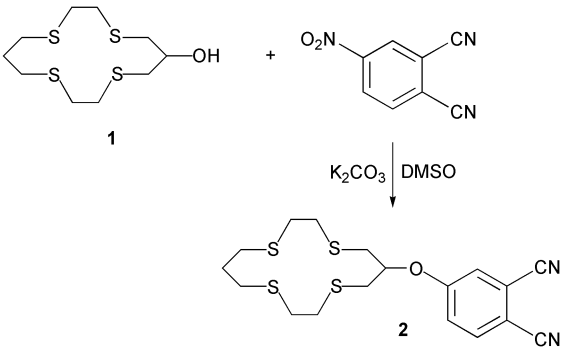
Although phthalocyanines (pcs) have found widespread industrial application as dyes and pigments, some derivatives have been extensively studied because of their interesting conductivity, catalytic, photovoltaic and electrochromic properties.[1–4] For a broad range of applications, the stable phthalocyanine core should be amenable to modifications that can be accomplished either by changing the central metal ion or by adding functional groups on the periphery.[5] In recent years a large number of derivatives have been prepared to facilitate the exploitation of these properties in gas sensors, electrography, fuel cells, solar energy conversion, non-linear optics and the photodynamic therapy of cancer.[4] Due to intermolecular interactions between the macrocycles, peripherally unsubstituted metallophthalocyanines are practically insoluble in common organic solvents, thereby minimizing their usefulness in applications. The solubility of phthalocyanines can be improved by introducing substituents on the periphery that increase the distance between the planar macrocycle rings carrying the π-electron and making solvation easier. Starting from simple mono-functional substituents, more complex structures such as crown ethers,[6,7] tetraaza,[8,9] diazatrioxa,[10] diazadioxa,[11] and tetraaza-crown ether double layers[12] and crown ethers with methyleneoxy[13] or sulfanyl bridges[14] have been introduced onto the periphery of the phthalocyanine nucleus. These structures are capable of binding alkali metal ions and provide donor sites for binding transition metal ions, leading to homo- and heteronuclear complexes. As donors, thioether moieties can be placed between oxa and aza groups for their tendency to complex with alkali and transition metal ions.[15]

Although pcs with N- and O-donor substituents are frequently encountered, those with thioether moieties are rather rare.[16,17] The latter group essentially contains products obtained by the cyclotetramerization of thioether-substituted phthalonitriles, which themselves have been derived from nucleophilic displacement reactions of dinitriles. A literature survey[18a–g] shows that most of the recent work on thioether-substituted phthalocyanines has been patented for applications as IR absorbers.[18h,i]

Our group previously reported the synthesis of metal-free and metallophthalocyanines (M = Co, Ni, Zn) fused to four 13-membered tetrathiamacrocycles on the periphery and their complexation through sulfur donor groups to Ag(I) and Pd(II).[19] The present paper describes the preparation of new soluble metal-free and metallophthalocyanines carrying four 14-membered tetrathiamacrocycles with oxy bridges and their complexation with Ag(I) and Pd(II) ions.

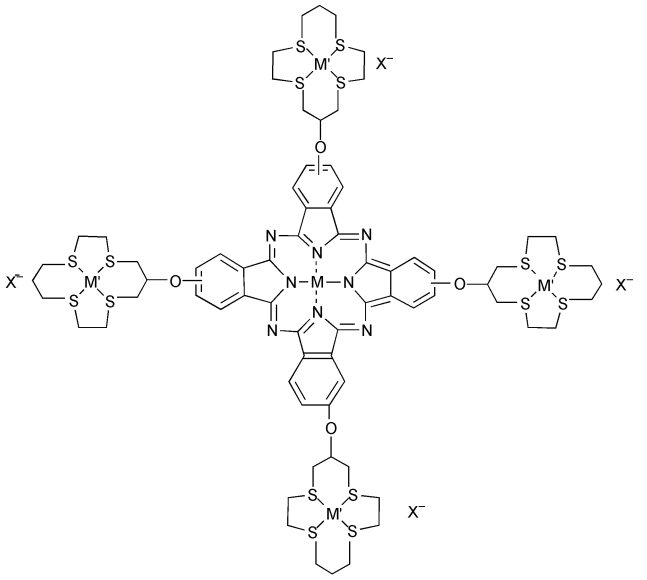
Results and discussion

As a first step, 3,6,10,13-tetrathiacyclotetradecan-1-ol ([14]ane S_4-ol) (**1**) was used to prepare 4-({3,6,10,13-tetrathiacyclotetradecyl}oxy)phthalonitrile (**2**) through base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile (Scheme 1). The reaction was carried out in dimethylsulfoxide at room temperature and the yield was reasonably high (*ca.* 85%).



Scheme 1

Cyclotetramerization of the phthalonitrile derivative **2** to the metal-free phthalocyanine **3** was accomplished in 2-dimethylaminoethanol at reflux temperature. The metal pcs (**4**–**7**) were obtained by using the anhydrous metal salts [$NiCl_2$, $CoCl_2$,



Compound	M	M'	X^-
3	2H	-	-
4	Ni	-	-
5	Co	-	-
6	Cu	-	-
7	Zn	-	-
8	Ni	Ag	NO_3
9	Ni	Pd	$2(CH_3COO)$

Fig. 1 The structure of the phthalocyanines **3**–**7** and Ag(I) and Pd(II) complexes of **4** (**8** and **9**).

$CuCl_2$ or $Zn(O_2CMe)_2$] (Fig. 1). **2** was cyclotetramerized to Ni(II) (**4**) or Co(II) (**5**) phthalocyanines in hexanol at reflux temperature in the presence of a strong organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). In the case of the Cu(II) derivative (**6**), pentanol was used as the solvent. Quinoline was the solvent of choice for the preparation of phthalocyaninatozinc(II) (**7**). Column chromatography with silica gel was employed to obtain the pure products from the reaction mixtures. The intense green products are very soluble in a number of solvents such as chloroform, dimethylformamide and tetrahydrofuran. Tetrasubstituted phthalocyanines obtained from 4′-substituted phthalonitriles are naturally a mixture of isomers. The yields of these reactions were rather low, as encountered for phthalocyanines with other bulky groups.[10,20] An exceptional feature of the phthalocyanines **3**–**7**, in contrast to the tetrathiamacrocycle substituted analog, is their solubility in common solvents. However, the complexes of a vicinal-dioxime ligand carrying a similar 13-membered tetrathiamacrocycle are also insoluble in common organic solvents,[21] in contrast to soluble oxa or aza analogs.[22,23] Therefore, the solubility of the newly synthesized phthalocyanines can be attributed to the tetrathiamacrocycles containing oxy bridges. The good solubility also allowed us to investigate the complexation properties of the phthalocyanines. Thus, we could isolate Pd(II) and Ag(I) complexes of NiPc, all having one metal ion for each tetrathiamacrocycle.[24]

The complexation of silver(I) and palladium(II) ions with the thioether macrocycles of the phthalocyanine leads to a phthalocyanine : metal ratio of 1 : 4. They can be easily differentiated from the free phthalocyanines by their bluish tone

Table 1 Proton NMR spectral data for the starting compound and the phthalocyanines in $CDCl_3$ (ppm)

Compound	CH_2	SCH_2	CH	Ar–H
2	1.89–2.03 (p, 2H)	2.70–3.19 (m, 16H)	4.67–4.79 (p, 1H)	7.26–7.30 (dd, $J=3$ Hz, 1H) 7.39–7.40 (d, $J=3$Hz, 1H) 7.70–7.74 (d, $J=9$ Hz, 1H)
3[a]	2.10 (br s, 8H)	2.85–3.43 (m, 64H)	5.09 (br s, 4H)	7.17–8.56 (m, 12H)
4	2.14 (br s, 8H)	2.89–3.41 (m, 64H)	5.01 (br s, 4H)	7.13–7.87 (m, 12H)
7	2.09 (br s, 8H)	2.86–3.28 (m, 64H)	4.99 (br s, 4H)	7.25–7.78 (m, 12H)

[a] There is also a peak at -4.14 ppm assigned to the internal NH.

and lower solubility in common organic solvents, especially in the case of the palladium derivative. All new compounds were characterized by their ^{1}H NMR (Table 1), ^{13}C NMR (Table 2) and MS spectra, and elemental analyses (Table 3).

In the IR spectrum of **2**, the intense absorption band at 2220 cm^{-1} corresponding to the C≡N groups, disappears after conversion into the phthalocyanines. The IR spectra of metal-free **3** and metallo (**4**–**7**) pcs are very similar. Another significant difference is the presence of ν(NH) vibrations of the inner phthalocyanine core, which are assigned to a weak band at 3280 cm^{-1} in the metal-free derivative. These protons are also very well characterized by the ^{1}H NMR spectrum, which shows a peak at -4.14 ppm as a result of the 18π-electron system of the phthalocyanine ring.[7,25] In addition, the nitrate is observed as a strong band at 1380 cm^{-1} for [NiPc-$(AgNO_3)_4$] (**8**).

A common feature of the ^{1}H NMR spectra of nickel(II) and zinc(II) phthalocyanines is the broad peaks. Tetrasubstituted phthalocyanines obtained from 4′-substituted phthalonitriles are a mixture of isomers, which is a primary reason for the broadness of the peaks.[4,26] Aggregation of the planar phthalocyanine molecules, however, is also expected to contribute to the broadening. In the NMR analysis of starting compound **2** in $CDCl_3$, the aromatic protons appear as doublets at 7.74, 7.40 and 7.30 ppm (dd). The CH proton, which is linked to the aromatic ring by an oxy bridge appears as a pentet at 4.67–4.79 ppm. Aliphatic SCH_2 protons of the tetrathia moiety are observed at 3.09–2.70 ppm as a multiplet and at 1.89–2.03 ppm as a pentet. The ^{13}C NMR spectrum of **2** shows six different signals for aromatic carbons between 161.09 and 107.91 ppm, two arising from C≡CN (115.19 and 115.57 ppm), and also gives five different signals for the aliphatic carbons between

Table 2 ^{13}C NMR spectral data for the starting material and phthalocyanines in $CDCl_3$ (ppm)

Compound	CH_2	SCH_2	CH	Ar–C
2[a]	30.19	30.68, 32.51, 33.53, 35.14	79.62	107.91, 117.59, 120.54, 121.02, 135.43, 161.09
3	30.72	30.97, 32.61, 33.62, 35.27	78.45	106.67, 116.96, 123.65, 136.77, 146.92, 159.12
4	30.80	30.98, 32.63, 33.83, 35.20	79.20	107.12, 118.49, 122.52, 136.28, 141.49, 158.21
7	31.00	31.12, 32.64, 33.77, 35.12	78.76	109.44, 119.78, 124.44, 140.68, 152.83, 159.35

[a] Peaks at 115.19 and 115.57 are assigned to C≡N.

Table 3 Analytical data found and (calculated) for the starting material and the phthalocyanines

Compound	Formula	C (%)	H (%)	N (%)	M (%)	M′ (%)
2	$C_{18}H_{22}N_2OS_4$	(52.65)	(5.40)	(6.82)		
		52.26	5.26	7.11		
3	$C_{72}H_{90}N_8O_4S_{16}$	(52.59)	(5.52)	(6.81)		
		52.26	6.01	7.04		
4	$C_{72}H_{88}N_8NiO_4S_{16}$	(50.84)	(5.21)	(6.58)	(3.45)	
		50.92	5.50	6.67	3.12	
5	$C_{72}H_{88}CoN_8O_4S_{16}$	(50.83)	(5.21)	(6.58)	(3.46)	
		50.42	5.78	6.12	3.36	
6	$C_{72}H_{88}CuN_8O_4S_{16}$	(50.69)	(5.20)	(6.57)	(3.72)	
		51.07	5.69	7.01	3.42	
7	$C_{72}H_{88}N_8O_4S_{16}Zn$	(50.64)	(5.19)	(6.56)	(3.83)	
		50.17	5.38	6.32	3.46	
8	$C_{72}H_{88}Ag_4N_{12}NiO_{16}S_{16}$	(36.32)	(3.72)	(7.06)	(2.46)	(18.12)
		35.72	3.33	6.87	2.17	17.78
9	$C_{88}H_{112}N_8NiO_{20}Pd_4S_{16}$	(40.66)	(4.34)	(4.31)	(2.26)	(16.37)
		39.74	4.12	4.22	1.98	16.02

Table 4 Electronic spectra of the phthalocyanines in $CHCl_3$ at 25 °C

Compound	λ/nm (10^{-4} ε/L mol^{-1} cm^{-1})							
3	240 (8.79)	287 (8.54)	340 (15.5)	385 sh (8.44)	600 (7.13)	637 sh (11.30)	670 (24.62)	700 (28.64)
4	220 (5.00)	297 (5.00)	328 (5.15)		607 sh (3.93)		674 (16.48)	
5	222 (5.00)	293 (5.00)	330 (4.83)		608 sh (3.22)		675 (11.48)	
6	232 (9.14)	282 (8.85)	334 (8.57)		610 sh (2.85)		680 (22.85)	
7	240 (5.14)	280 (3.31)	332 (5.71)		612 (2.28)		680 (11.88)	

35.14–30.19 ppm. The ^{1}H and ^{13}C NMR spectra of the phthalocyanines are in excellent agreement with the proposed structures of **2**, **3**, **4** and **7**. Due to the paramagnetic properties of Cu and CoPcs, NMR spectra could not be recorded. The molecular ion peaks at m/z 1707 and 1702 for Cu and CoPcs identified the expected structures. The insolubility of complexes **8** and **9** did not allow us to obtain their NMR and MS spectra.

In addition to the elemental analysis results, the mass spectral analysis also reveals the structures of the newly synthesized compounds. The molecular ion peak at m/z 410 has been found for **2**, together with the corresponding leaving groups, by the EI technique. The mass spectra of the phthalocyanines obtained by the FAB technique show relatively intense molecular ion peaks. The metal-free phthalocyanine **3** gives the M peak at m/z 1643.1. The metallo-phthalocyanines also give molecular ion peaks at 1701, 1702, 1707 and 1706 for NiPc, CoPc, ZnPc and CuPc, respectively.

The thermal stability of the pcs was confirmed by thermogravimetric analysis, decompositions occur above 300 °C. In [NiPc$(AgNO_3)_4$] (**8**), the nitrate groups are lost at 225 °C, but the phthalocyanine itself decomposes above 300 °C. In the case of [NiPc{Pd$(CH_3COO)_2$}$_4$] (**9**), the decomposition starts above 300 °C.

The electronic spectra of the phthalocyanines **3**–**7** (Table 4) show the characteristic Q band absorptions as a single peak around 674–680 nm with a shoulder around 607–612 nm, and as two intense peaks at 700 and 670 nm in H_2Pc. The characteristic Q band has been considered as a probe in discussing the self-assembly features of phthalocyanines in solution.[27] While monomeric species with D_{2h} symmetry (*e.g.*, the metal-free derivative) show two intense absorptions of comparable intensity around 700 nm, those having D_{4h} symmetry give only a single band in this region. Any increase in the concentration results in the aggregation of phthalocyanine molecules, accompanied by a blue shift of the Q band with some decrease in intensity.[6,7,25–30]

The complexation of NiPc with a palladium(II) salt has been followed spectrophotometrically by addition of small amounts of Pd$(CH_3COO)_2$ to a solution of NiPc in THF (Fig. 2). The gradual change in the spectrum upon the addition of Pd(II) can be easily observed. Similar experiments carried out with a 10^{-3} mol dm^{-3} solution of silver nitrate in a water–THF mixture (0.2 : 7) is shown in Fig. 3. Since $AgNO_3$ can dissolves in water, a possible solvent effect needs to be taken into account. In order to evaluate its importance, the spectra of NiPc alone in the corresponding solvent mixtures were obtained and these indicated that any solvent effect can be safely neglected. A limiting spectrum is reached at an Ag(I) : NiPc ratio of *ca.* 4 : 1. (Fig. 3). When the interaction of **4** in THF with Ag(I) ion was followed spectrophotometrically, two completely different coupling patterns between phthalocyanine units were observed, according to the changes in the Q band region. Addition of small amounts of Ag(I) leads to gradual disappearance of the monomeric species, which show an absorption at 673.4 nm, and simultaneously enhances the intensity of aggregated species absorbing around 622.2 nm. In

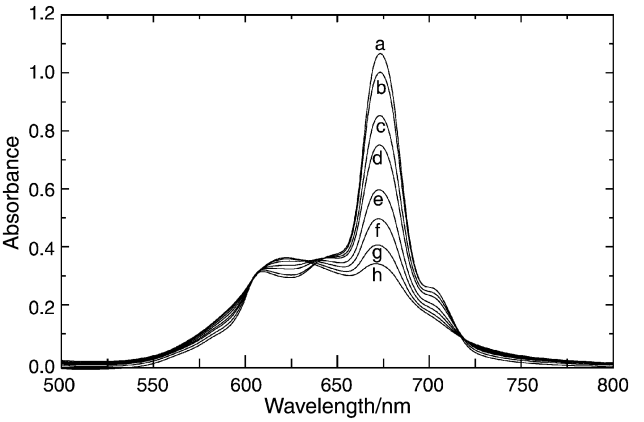


Fig. 2 Spectral changes occurring in the Q band of a 10^{-5} mol dm^{-3} THF solution of complex **4** (3 mL) in the presence of increasing amounts of palladium(II) solution (10^{-3} mol dm^{-3}): (a) 10, (b) 20, (c) 30, (d) 40, (e) 60, (f) 80, (g) 100, (h) 120 μL.

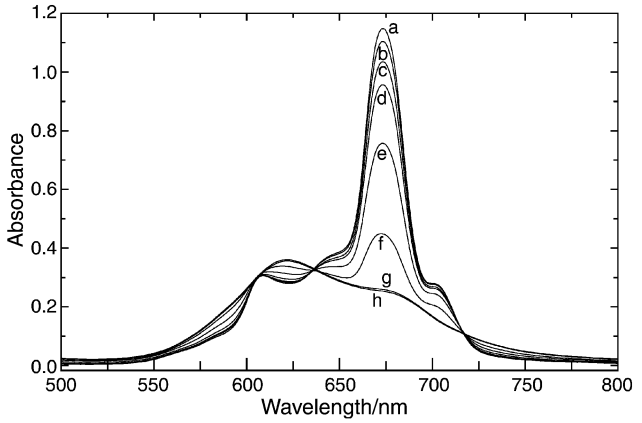


Fig. 3 Spectral changes occurring in the Q band of a 10^{-5} mol dm^{-3} solution of complex **4** (3 mL) in the presence of increasing amounts of $AgNO_3$ solution (10^{-3} mol dm^{-3}): (a) 10, (b) 20, (c) 30, (d) 40, (e) 60, (f) 80, (g) 100, (h) 120 μL.

the case of portionwise addition of Pd(II) ions, similar results are observed. A new absorption band appears at 622.3 nm, which reaches a higher intensity than that of the original Q band. Thus we could isolate Pd(II) and Ag(I) complexes of nickel(II) phthalocyanine, each having one metal ion per tetrathiamacrocycle.

Experimental

General methods

Routine IR spectra were recorded on a Perkin Elmer 983 spectrophotometer from KBr pellets. Electronic spectra in the UV-Visible region were recorded with a Schimadzu 2001 UV PC using 1 cm pathlength cuvettes at room temperature. Elemental analysis was performed at the TUBITAK Marmara Research Center. Thermogravimetric analyses were run on a DuPont differential thermoinstrument type 990 at 10 °C min^{-1} in a nitrogen flow (10 mL min^{-1}). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Mass spectra were recorded on a VG ZAB-SPEC spectrometer. 1,3-Dichloro-2-propanol,[31] 1,4,8,11-tetrathiaundecane (TTU),[32] 3,6,10,13-tetrathiacyclotetradecan-1-ol ([14]aneS$_4$-ol **1**)[33] and 4-nitrophthalonitrile[34] were synthesized according to the reported procedures.

Syntheses

4-({3,6,10,13-Tetrathiacyclotetradecyl}oxy)phthalonitrile (2). **1** (2.5 g, 8.78 mmol) was dissolved in anhydrous dimethylsulfoxide (50 mL) under argon and 4-nitrophthalonitrile (1.53 g, 8.78 mmol) was added. After stirring for 15 min. at room temperature, dry fine-powdered potassium carbonate (5 g, 36.23 mmol) was added portionwise over 1 h with efficient stirring. The reaction mixture was stirred under argon at room temperature overnight. The reddish-brown mixture was extracted with dichloromethane (20 mL). The organic layer was seperated, washed with water and then dried over Na_2SO_4. After evaporation of the solvent the product was crystallized from EtOH as pale yellow crystals. This compound is soluble in chloroform, tetrahydrofuran and dimethylformamide. Yield: 3.08 g (85%), m.p. 100–102 °C; IR ν_{max}/cm^{-1} (KBr): 2920–2840, 2220, 1590, 1560, 1480, 1420, 1250, 1010, 830, 730, 520; MS (EI) m/z (%): 410 (100) $[M]^+$, 382 (13) $[M - 2\ (CH_2)]^+$, 275 (37), $[M - \{2\ (SCH_2) + 3\ (CH_2)\}]^+$, 248 (43) $[M - \{2\ (SCH_2) + 5\ (CH_2)\}]^+$, 144 (33) $[M$ – tetrathiamacrocycle$]^+$, 119 (19), 106 (94), 87 (20), 73 (55), 61 (34).

Metal-free phthalocyanine (3). Compound **2** (0.5 g, 1.22 mmol) was refluxed at 135 °C in dimethylaminoethanol (2 mL) under argon with stirring for 6 h. After cooling the dark-green product was filtered off and washed successively with hot acetone. This procedure was repeated until no more impurities were observed in the filtrate (TLC). The pure product was obtained after column chromatography (silica gel, eluent 100 : 1 CH_2Cl_2–MeOH) and dried *in vacuo* at 100 °C. The product is soluble in chloroform, tetrahydrofuran and dimethylformamide. Yield: 0.14 g (28%); IR ν_{max}/cm^{-1} (KBr): 3280, 2920–2840, 1600, 1470, 1420, 1220, 1090, 1000, 740; MS (FAB) m/z (%): 1643.1 (25) $[M]^+$, 1376.7 (15) $[M$ – tetrathiamacrocycle$]^+$, 851.3 (54), 766.1 (48), 613 (100).

Nickel(II) phthalocyanine (4). A mixture of **2** (0.6 g, 1.46 mmol) and anhydrous $NiCl_2$ (0.05 g, 0.385 mmol) was refluxed at 160 °C in *n*-hexanol (5 mL) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU 0.15 mL, 1 mmol) with stirring for 8 h under argon. (When the reaction temperature was brought to 160 °C in 1 h, the color changed from dark brown to green.) After cooling, the green product was filtered off and washed with hot MeOH several times. The crude product was purified by means of column chromatography (silica gel, eluent chloroform). The metal-free phthalocyanine is soluble in chloroform, tetrahydrofuran and dimethylformamide. Yield: 0.141 g (23%); IR ν_{max}/cm^{-1} (KBr): 2920– 2850, 1600, 1470, 1410, 1230, 1120, 1090, 1000, 750; MS (FAB) m/z (%): 1701 (13) $[M + 1]^+$, 1643 (6) $[M - Ni]^+$, 1434 (8) $[M$ – tetrathiamacrocycle$]^+$, 1354 (8), 1254 (10), 1153 (7), 1106 (6) $[M - (Ni + 2$ tetrathiamacrocycle)$]^+$, 1062 (7), 944 (8), 806 (10), 670 (7), 621 (11), 462 (8), 403 (7), 327 (17), 281 (100).

Cobalt(II) phthalocyanine (5). **5** was prepared according to the procedure described for **4** by starting from **2** (0.5 g, 1.22 mmol), andhydrous $CoCl_2$ (0.04 g, 0.304 mmol), DBU (0.12 mL, 0.8 mmol) and *n*-hexanol (5 mL). Yield: 0.27 g (52%); IR ν_{max}/cm^{-1} (KBr): 2920–2850, 1600, 1470, 1400, 1220, 1100, 1060, 750; MS (FAB) m/z (%): 1702 (25) $[M + 1]^+$, 1462.6 (7), 1193.3 (8), 1084.3 (7), 992.7 (7), 920.2 (12), 749.1 (26), 701.2 (33), 595.1 (31), 486.1 (17), 443.2 (67), 308.3 (55), 154.3 (28).

Copper(II) phthalocyanine (6). **6** was prepared according to the procedure described for **4** by starting from **2** (0.5 g, 1.22 mmol), anhydrous $CuCl_2$ (0.047 g, 0.345 mmol), DBU (0.19 mL, 1.26 mmol) and *n*-pentanol (7 mL). Yield: 0.32 g (61.5%); IR ν_{max}/cm^{-1} (KBr): 2920–2850, 1600, 1490, 1400, 1220, 1080, 1050, 740; MS (FAB) m/z (%): 1706 (30) $[M + 1]^+$, 1626.3 (15), 1556.8 (25), 1462.6 (19), 1394.7 (12), 1368.6 (16), 1344.8 (20), 1279.7 (17), 1250.5 (18), 1222.2 (22), 1148.6 (17), 1105.5 (27), 1073.3 (35), 966.5 (75), 920.4 (100).

Zinc(II) phthalocyanine (7). A mixture of compound **2** (0.5 g, 1.22 mmol), anhydrous zinc acetate (0.011 g, 0.057 mmol) and quinoline (1.5 mL) was heated and stirred at 190 °C for 6 h under argon. After cooling to room temperature, dichloromethane (8 mL) was added in order to dissolve the crude product, which was then precipitated with acetone. The dark-green product was filtered off and washed with hot acetone (3×20 mL). The new product was isolated on a silica gel column with chloroform as the eluent. Yield: 0.102 g (19.7%); IR ν_{max}/cm^{-1} (KBr): 2920–2840, 1600, 1480, 1220, 1080, 1040, 740; MS (FAB) m/z (%): 1707 (25) $[M + 1]^+$, 1632.5 (12), 1552 (8), 1434 (15), 1352 (8), 1239.2 (18), 1137.3 (22), 1102.3 (10), 979.6 (11), 910.3 (8).

Silver(I) complex of 4 (8). **4** (0.08 g, 0.047 mmol) was dissolved in a tetrahydrofuran–water mixture (5.1 + 0.1 mL); silver nitrate (0.064 g, 0.376 mmol) in the same solvent mixture (5.1 + 0.1 mL) was added. The mixture was refluxed for 2 h

and a bluish-green product formed. The product was filtered off and washed with hot water, hot ethanol and then dried with diethyl ether. Yield: 0.072 g (64.4%); IR ν_{max}/cm^{-1} (KBr): 2920, 1610, 1460, 1380, 1240, 1130, 1100, 1070, 1020, 840, 760.

Palladium(II) complex of 4 (9). The metallophthalocyanine **4** (0.05 g, 0.0293 mmol) was dissolved in tetrahydrofuran (5 mL) and a solution of $Pd(CH_3COO)_2$ (0.0526 g, 0.234 mmol) in THF (5 mL) was added. The color became bluish-green while refluxing for 2 h and precipitation occurred. The product was separated by centrifuging and washed several times successively with hot water, hot ethanol and then with diethyl ether. The bluish-green product was filtered off. Yield: 0.043 g (56.5%); IR ν_{max}/cm^{-1} (KBr): 2920, 1620, 1500, 1460, 1400, 1320, 1220, 1110, 1090, 1045, 1000, 740.

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