147. Synthesis and Characterization of New Phthalocyanines Peripherally Fused to Four 13-Membered Tetrathiamacrocycles

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The new metal-free phthalocyanine **5** and phthalocyaninatometals **6–8** (M=Co, Ni, or Zn) fused in peripheral positions with four 13-membered tetrathiamacrocycles were prepared by cyclotetramerization of 2,3,6,7,9,10-hexahydro-5*H*-[1,4,8,11]benzotetrathiacyclotridecine-13,14-dicarbonitrile in the presence of a suitable metal salt or a strong organic base. In contrast to the aza- or oxamacrocycle-fused analogs, the solubility of these phthalocyanines is very low. Complexation of the tetrathiamacrocycles of **7** and **8** with Pd^{II} or Ag^{I} to form pentanuclear products was accomplished from their suspensions.

Introduction. – In the last decade, the synthesis and study of new phthalocyanines with functional substituents has grown impressively, particularly in the light of the possibility of achieving wide application of these colored compounds in non-traditional fields of technology which include fuel cells, chemical sensors, solar cells, electrophotography, and the photodynamic therapy of cancer [1–3]. A common prerequisite for the materials for each field is solubility in practical solvents [4]. Additional factors such as wavelength of the Q-band absorption, thermal stability, electrical conductivity, and redox potentials are accomplished by purpose-designed substitution patterns [5] [6].

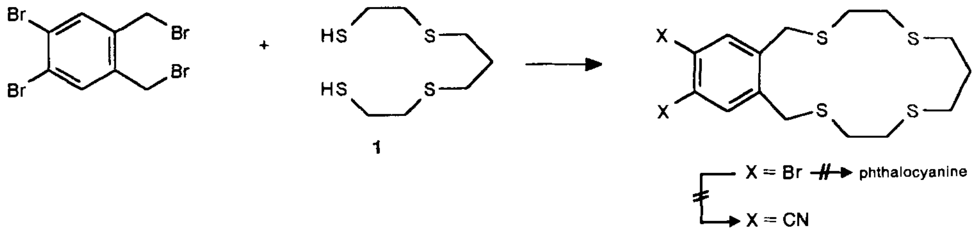
We described for the first time the synthesis of novel soluble phthalocyanines where crown-ether moieties are integral parts on the periphery [7–9]. They have been shown to be capable of binding alkali-metal cations. Another success of this approach was demonstrated by the fact that these molecules lead to ion channels for alkali ions in the condensed phase and form discotic mesophases [10]. Additionally, its bis(phthalocyaninato)lutetium derivative was a starting point for a completely new field of iono-electronics [11–13].

The second important step in combining heteromacrocycles with phthalocyanines was the synthesis of phthalocyanines fused to four 14- or 15-membered tetraazamacrocycles which allowed the preparation of pentanuclear complexes with transition-metal ions [14] [15]. Tetraoxamonoaza- [16], trioxadiaza- [17], and dioxadiazamacrocycles [18] were also fused to the phthalocyanine core, but their interactions with alkali and transition-metal ions were negligible. Even a two-fold macrocycle fusion on the phthalocyanine core was accomplished by starting with a dicyano compound carrying a [15]crown-5 moiety together with a 14-membered tetraazamacrocycle [19].

As donors, thioether moieties can be placed between oxa and aza groups for their tendency to complex with alkali and transition-metal ions [20]. Thioether groups on the benzene rings of phthalocyanine were also proven to be effective, as shown by relatively few communications reporting alkylthio-substituted derivatives to shift the Q-band absorption of the phthalocyanine to a lower-energy region [21–23]. We report now on a new group of phthalocyanines fused to four 13-membered tetrathiamacrocycles on the periphery as a further step of the series on macrocycle-fused phthalocyanines.

Results and Discussion. – As in the case of all other fused phthalocyanines, a new derivative with tetrathiamacrocyclic components requires a phthalic-acid derivative carrying this component from the beginning. Our first aim was to prepare a benzo-fused 15-membered tetrathiamacrocycle with 1,2-dibromo substitution on the benzene moiety, by a procedure similar to those reported earlier for the condensation of 1,2-dibromo-4,5-bis(bromomethyl)benzene with 2,2′-[(propane-1,3-diyl)bis(thio)]bis(ethanethiol) (**1**) [24]. The dibromo derivative would then be converted into a dicarbonitrile by a *Rosenmund-von Braun* reaction. However, all efforts to accomplish these reactions failed in the second step, no carbonitriles could be observed (*Scheme 1*). Similarly, no phthalocyanatocopper was detected in a number of trials to convert the dibromo compound directly in high-boiling solvents such as quinoline, or DMF at reflux temperature or in pyridine in a sealed tube.

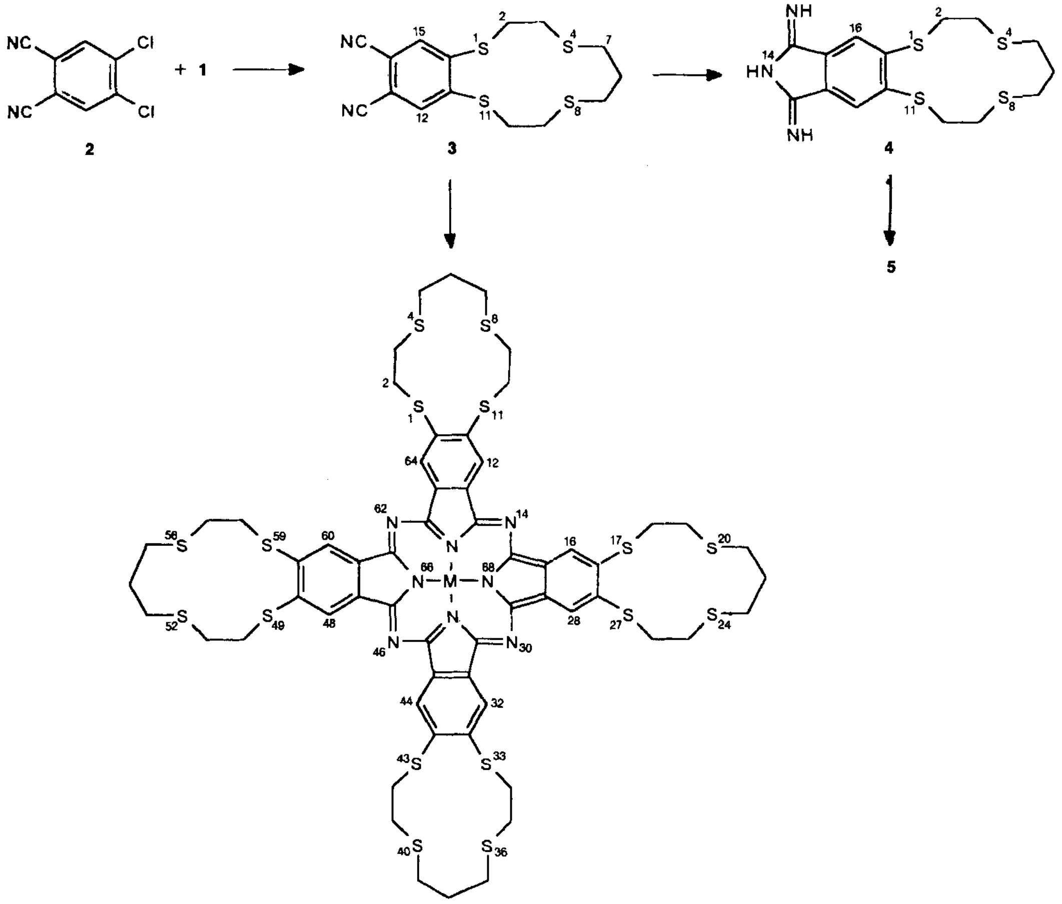
Scheme 1



To overcome these difficulties, a new macrocycle was designed which would carry the phthalonitrile unit from the beginning. We used the nucleophilic displacement reaction of 4,5-dichlorophthalonitrile (**2**) with dithiol **1** in the presence of excess Na_2CO_3, a procedure reported recently for the preparation of some bis(alkylthio)- or bis(alkoxy)phthalonitrile derivatives [25–27] (*Scheme 2*). Of course, it was necessary to use equivalent amounts of the two reagents to promote a 1:1 condensation, but some 2:2 condensation products and other by-products were unavoidable, so the yield of the desired compound **3** was only 21% after chromatographic isolation. Isoindoline-diimine **4** was then obtained by bubbling ammonia through a solution of **3** in MeOH/BuOH in the presence of NaOMe [28].

The usual synthetic routes were applied to obtain the metal-free phthalocyanine **5** and the phthalocyaninatometals **6**–**8**. Thus, either **4** was heated to its melting point and kept at this temperature for *ca.* 0.5 h to give **5** or, more precisely, **3** was cyclotetramerized to **5** in pentanol at reflux temperature in the presence of a strong organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). As a high-boiling aprotic solvent, quinoline was the solvent of choice for the preparation of phthalocyaninatonickel(II) **7** and -zinc(II) **8**, whereas cyclotetramerization of **3** to the Co^{II} derivative **6** was carried out in ethylene glycol with better yields. Many attempts to obtain phthalocyaninatocopper(II), including the reaction of acetylacetonatocopper(II) and **4** in 2-(dimethylamino)ethanol, led to

Scheme 2



5 M = 2H
6 M = Co
7 M = Ni
8 M = Zn

intensly coloured products. But the latter did not give satisfactory elemental analysis, probably due to metallic contamination on the tetrathiamacrocycles which could not be eliminated.

A common feature of the phthalocyanines **5**–**8**, in contrast to the tetraazamacrocycle- or crownether-substituted analogues, is their insolubility in the usual solvents. Only **6** and **8** are soluble to a certain extent, in donor solvents such as pyridine. Since phthalocyanines with bulky peripheral substituents (*e.g.* long alkyl or alkoxy chains, *tert*-butyl or neopentoxy groups, crown ethers, *etc.*) [7–9] [29] are known to be soluble in common organic solvents, the solubility behaviour of **5**–**8** is exceptional. However, the complexes of a vicinal-dioxime ligand carrying a similar 13-membered tetrathiamacrocycle are also insoluble in common solvents [30], in contrast to soluble oxa or aza analogs [31] [32]. Therefore, the insolubility of **5**–**8** is due to the tetrathiamacrocycle which does not lie in the plane of the phthalocyanine core according to molecular models. The solubility of **6** and **8** in pyridine is a consequence of the binding of the solvent as axial ligands in Co^{II} and Zn^{II} complexes.

The low solubility of the new phthalocyanines is an obstacle to investigate the interaction of the thia donor groups with metal ions under similar conditions as in the case of their tetraoxa or tetraazaanalogs. However, it is possible to study such complexation using phthalocyanine suspensions. Thus, we could isolate Pd^{II} complexes of phthalocyanines **7** and **8** and an Ag^{I} complex of **8**, all having one metal ion for each tetrathiamacrocycle. The solubility of these pentanuclear products is even lower than that of the parent phthalocyanines, and their complexes through the thia groups decompose on treatment with solvents of high donor capacity such as pyridine.

All new compounds were characterized by their spectra and their elemental analyses (see *Table*).

Table. *Elemental Analyses of Precursors* **3** *and* **4**, *Phthalocyanines* **5–8**, *and Complexes of* **7** *and* **8**

	Formula	Calc. [%]						Found [%]					
		C	H	N	S	M	Pd or Ag	C	H	N	S	M	Pd or Ag
3	$C_{15}H_{16}N_2S_4$	51.10	4.57	7.95	36.38	–	–	51.05	4.40	7.85	36.35		–
4	$C_{15}H_{20}N_3S_4$	48.61	5.44	11.34	34.61	–	–	48.52	5.33	10.84	34.01	–	–
5	$C_{60}H_{66}N_8S_{16}$	51.03	4.71	7.93	36.33	–	–	50.91	4.68	7.25	36.15	–	–
6	$C_{60}H_{64}N_8NiS_{16}$	49.06	4.39	7.63	34.92	4.00	–	49.34	4.28	7.61	34.78	3.98	–
7	$C_{60}H_{64}CoN_8S_{16}$	49.05	4.39	7.63	34.92	4.01	–	48.95	4.29	7.56	34.85	3.96	–
8	$C_{60}H_{64}N_8S_{16}Zn$	48.84	4.37	7.59	34.77	4.43	–	48.66	4.46	7.37	34.59	4.24	–
7·$4PdCl_2$	$C_{60}H_{64}Cl_8N_8NiPd_4S_{16}$	33.08	2.96	5.14	23.55	2.69	19.54	32.95	2.58	5.01	22.99	2.50	19.30
8·$4PdCl_2$	$C_{60}H_{64}Cl_8N_8Pd_4S_{16}Zn$	32.98	2.95	5.13	23.48	2.99	19.48	32.55	2.85	4.95	23.01	2.65	19.10
8·$4AgNO_3$	$C_{60}H_{64}Ag_4N_{12}O_{12}S_{16}Zn$	33.44	2.99	7.80	23.81	3.03	20.02	33.25	2.86	7.40	23.22	2.98	19.85

The IR spectrum of **3** clearly indicates the presence of alkyl and CN groups by the intense stretching bands at 2960–2920 (C–H) and 2220 cm^{-1} (CN). The latter disappeared after conversion of **3** to isoindoline-diimine **4** which shows absorption at 3405 and 3220 cm^{-1} for the NH groups. The IR spectra of the phthalocyanine **5–8** are very similar, with the exception of the metal-free **5** showing a NH stretching band at 3270 cm^{-1} due to the inner core.

In the ^1H-NMR spectrum (D_6)DMSO of **3**, the aromatic protons appear as a *s* at 8.14 ppm and the aliphatic protons as 3 *t*'s and 1 *quint.* at 3.44–1.56 ppm as expected. The ^{13}C-NMR spectrum of **3** shows 4 different signals for the unsaturated C-atoms, one arising from C≡N (115.46 ppm). As a consequence of the symmetric structure, the aliphatic C-atoms also give 4 different signals between 32.21 and 28.76 ppm. The only soluble phthalocyanine, **8**, shows signals for 4 aromatic and 3 aliphatic C-atoms, the aliphatic atoms C(3) and C(5) with relatively similar chemical environment having the same chemical shift.

The VIS spectra of the phthalocyanines **6** and **8** in pyridine show the intense Q-band absorptions at 680 and 714 nm (*Fig. 1*). There is also a shoulder at slightly higher energy side for both products. The longer wavelength encountered for the intense band of phthalocyaninatozinc(II) **8** is especially noteworthy, the shift of this band to the near-IR region is a result of S-substitution with respect to the unsubstituted or N- or O-substituted phthalocyanines.

A close investigation of the mass spectra of the phthalonitrile derivative **3** and phthalocyaninatozinc(II) **8** confirmed the proposed structures. In the case of **3**, in addition to the M^+ peak at 352, fragment ions corresponding to the loss of CH_2CH_2 ($[M-28]^+$), $CH_2CH_2SCH_2CH_2CH_2SCH_2$ ($[M-149]^+$), and $CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2$ ($[M-162]^+$) were easily identified. The spectrum of **8** was obtained by the FAB technique using a HCOOH and glycerine matrix; the region of the molecular ion (*m/z* 1476) and of the other bigger fragment ions is shown in *Fig. 2*, together with the corresponding leaving groups. The fragmentation pattern closely follows that of **3** indicating the high stability of the phthalocyanine core.

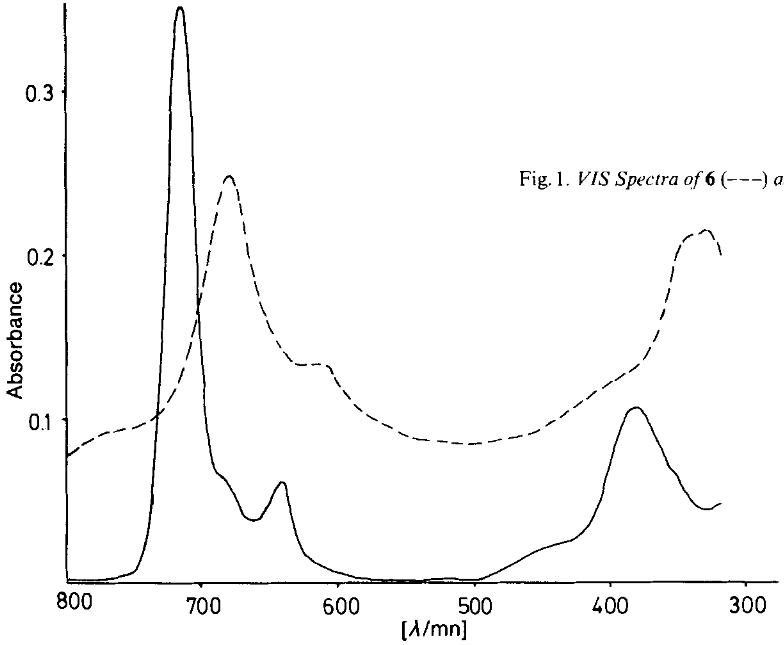


Fig. 1. *VIS Spectra of* **6** *(– – –) and* **8** *(——) in pyridine*

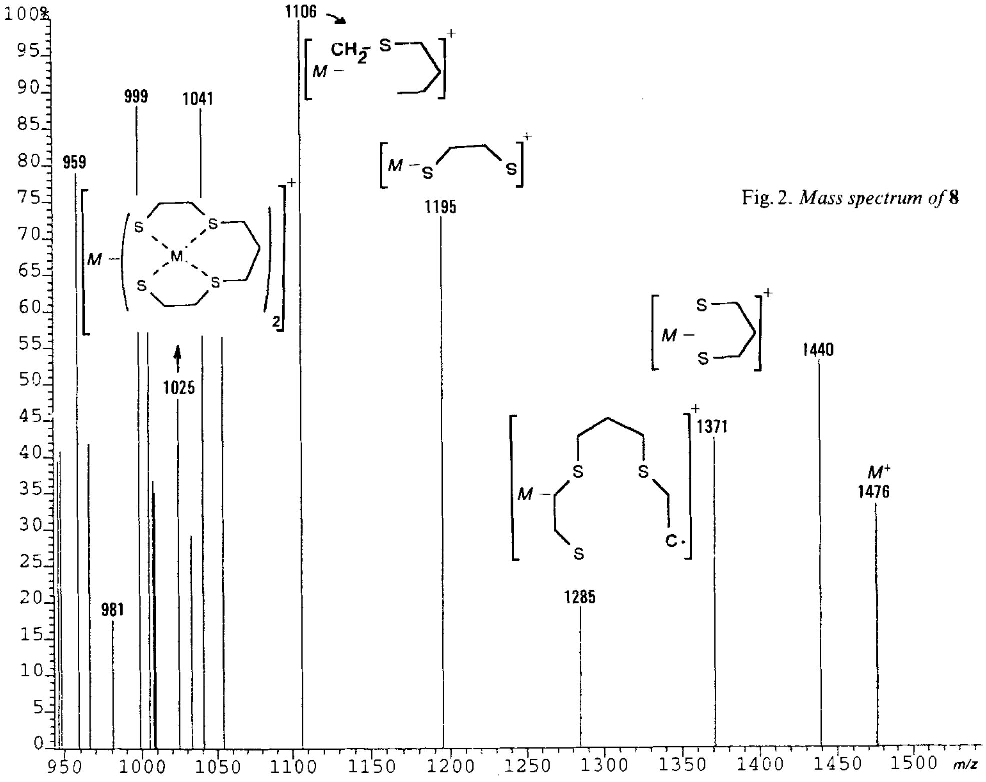


Fig. 2. *Mass spectrum of* **8**

Experimental Part

General. The 2,2′-[(propane-1,3-diyl)bis(thio)]bis(ethanethiol) (**1**) [24] and 4,5-dichlorobenzene-1,2-dicarbonitrile (**2**) [25] were prepared by reported procedures. UV/VIS: *Varian-DMS-90* spectrophotometer. IR Spectra: *Perkin-Elmer-983* spectrophotometer (KBr pellets). ^{1}H- and ^{13}C-NMR Spectra: *Bruker-200-MHz* spectrometer. MS: *VG ZAB Spec.* Elemental analyses were performed by the Instrumental Analysis Laboratory of *TÜBİTAK Gebze Research Center.* The metal contents of the complexes were determined by a *Hitachi-180-80* atomic-absorption spectrophotometer in solns. prepared by decomposing the compounds in conc. $HClO_4$ and conc. HNO_3 soln. and then digesting in conc. HCl soln.

*2,3,6,7,9,10-Hexahydro-5*H*-1,4,8,11-benzotetrathiacyclotridecine-13,14-dicarbonitrile* (**3**). Dry DMSO (150 ml) containing Na_2CO_3 (10 g, 94 mmol) was heated and stirred at 40° under Ar. To this soln., a soln. of **2** (3.96 g, 20 mmol) and **1** (4.59 g, 20 mmol) in dry DMSO (200 ml) was gradually added over 6 h and the reaction continued for over 48 h. After evaporation, H_2O (100 ml) was added to the residue, the aq. layer extracted with $CHCl_3$ (50 ml each) several times, the combined org. layer dried (Na_2SO_4) and evaporated, and the white residue purified by column chromatography (silica gel, $CHCl_3$): pure **3** (1.5 g, 21%). M.p. 223–225°. IR (KBr): 2960–2920 (CH_2), 2220 ($C{\equiv}N$), 1570, 1530, 1460, 1440, 1420, 1345, 1265, 1225, 1210, 1120, 900, 860, 830, 760, 730, 710, 690, 530. ^{1}H-NMR ((D_6)DMSO): 8.14 (*s*, 2 H arom.); 3.44 (*t*, 4 H, Ar-SCH_2); 2.73 (*t*, 4 H, Ar-SC–CH_2); 2.57 (*t*, 4 H, SCH_2); 1.56 (*quint.*, 2 H, SC–CH_2–CS). ^{13}C-NMR ((D_6)DMSO): 143.15 (C(11a), C(15a)); 133.26 (C(12), C(15)); 115.46 (CN); 111.56 (C(13), C(14)); 32.21 (C(2), C(10)); 30.23 (C(3), C(9)); 29.80 (C(5), C(7)); 28.76 (C(6)). EI-MS (70 eV): 352 (68, M^+), 203 (25), 190 (28), 133 (52).

*2,3,6,7,9,10-Hexahydro-5*H*,13*H*-[1,4,8,11]benzotetrathiacyclotridecino[13,14-*c*]pyrrole-13,15(14*H*)-diimine* (**4**). To a soln. of **3** (1 g, 2.84 mmol) in dry BuOH/MeOH 4:1 (100 ml) under Ar, NaOMe (0.12 g, 2.2 mmol) in dry BuOH (10 ml) was added. Anh. NH_3 was bubbled through the mixture for 8 h at reflux temp. after which time the reaction was complete (TLC). The NH_3 inlet was stoppered and the volume of the soln. reduced to 30 ml under reduced pressure. From BuOH/Et_2O 1:5 (*v*/*v*), **4** was obtained as pale yellowish-green crystals (1 g, 95%). M.p. 215° (dec.). IR (KBr): 3405 (NH), 3220 (NH), 2980–2960 (CH_2), 1640 (NH bending), 1520, 1420, 1380, 1300, 1280, 1200, 1180, 1140, 1080, 910, 870, 760, 680. ^{1}H-NMR ((D_6)DMSO): 8.59 (br. *s*, NH); 7.90 (*s*, 2 arom. H); 3.34 (*t*, 4 H, Ar-SCH_2); 2.73 (*t*, 4 H, Ar–SC–CH); 2.58 (*t*, 4 H, SCH_2); 1.59 (*quint.*, 2 H, SC–CH_2–CS). ^{13}C-NMR ((D_6)DMSO): 138.31 (C(11a), C(16a)); 122.54 (C(12), C(16)); 111.53 (C(12a), C(15a)); 104.83 (C(13), C(15)); 31.71 (C(2), C(10)); 29.67 (C(3), C(9)); 29.59 (C(5), C(7)); 28.55 (C(6)).

*2,3,6,7,9,10,18,19,22,23,25,26,34,35,38,39,41,42,50,51,54,55,57,58-Tetracosahydro-5*H*,21*H*,37*H*,53*H*,66*H*,68*H*-tetrakis[1,4,8,10]tetrathiacyclotridecino[5,6-*b*:5′,6′-*k*:5″,6″-*t*:5‴,6‴-c_1]phthalocyanine* (**5**). Compound **3** (0.450 g, 1.275 mmol) was refluxed for 18 h under stirring and Ar in pentanol (45 ml) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.21 ml, 1.4 mmol). After the hot mixture was filtered, the dark green precipitate was washed with hot EtOH (3 × 10 ml). The precipitate was then treated at 60–70° with DMF (3 × 20 ml), filtered off, then washed with hot EtOH and Et_2O, and dried *in vacuo*: green **5** (0.178 g, 40%). IR (KBr): 3270 (NH), 2970–2940 (CH_2), 1610, 1510, 1420, 1400, 1370, 1340, 1290, 1210, 1190, 1130, 1080, 1020, 940, 870, 760, 690.

Phthalocyaninatocobalt(II) **6**. A mixture of **3** (0.60 g, 1.70 mmol), anh. $CoCl_2$ (0.056 g, 0.43 mmol), and dry ethylene glycol (34 ml) was heated and stirred at 200° for 4 h under Ar. After the hot mixture was filtered and the precipitate refluxed 4 times with EtOH to remove unreacted org. materials, the solid was heated at 60° with DMF (2 × 20 ml) and DMSO (2 × 20 ml) and filtered off. Finally, pure dark green **6** (0.165 g, 26%) was obtained by washing with hot EtOH and Et_2O. This compound was soluble in pyridine. IR (KBr): 2980–2940 (CH_2), 1620, 1530, 1420, 1390, 1350, 1290, 1205, 1130, 100, 1080, 970, 860, 780, 760, 705.

Phthalocyaninatonickel(II) **7**. A mixture of **3** (0.503 g, 1.43 mmol), anh. $NiCl_2$ (0.052 g, 0.40 mmol), and quinoline (1 ml) was heated and stirred at 190° for 4 h under Ar. After cooling to r.t., the dark green mixture was diluted with EtOH (5 ml) and the crude product precipitated. This was filtered off and washed with hot EtOH to remove unreacted org. materials. The precipitate was then heated at 80° with DMF (3 × 20 ml) and DMSO (3 × 20 ml) and filtered off. The dark green product was washed with hot EtOH and Et_2O and dried *in vacuo*: (0.270 g, 51%). IR (KBr): 2970–2940 (CH_2), 1610, 1540, 1420, 1390, 1260, 1205, 1130, 1100, 1080, 975, 860, 780, 760, 705.

Phthalocyaninatozinc(II) **8**. A mixture of **3** (0.60 g, 1.70 mmol), anh. zinc(II) acetate (0.079 g, 0.43 mmol), and quinoline (1.4 ml) was heated and stirred at 185–190° for 5 h under Ar. After cooling to r.t., the dark green mixture was diluted with EtOH (5 ml) and filtered off. The dark green precipitate was refluxed with EtOH (2 × 20 ml), $CHCl_3$ (2 × 20 ml), and DMF (2 × 20 ml) and filtered off. Pure **8** (0.410 g, 65%) was obtained by washing with hot EtOH and Et_2O. This compound was soluble in pyridine. IR (KBr): 2980–2940 (CH_2), 1620, 1500, 1420, 1380, 1350, 1290, 1205, 1130, 1100, 1080, 950, 780, 750, 700. ^{1}H-NMR ((D_6)DMSO): 9.47 (*s*, 8 arom. H); 3.83 (*t*, 16 H, Ar–SCH_2); 2.88 (*t*, 16 H, Ar–SC–CH_2); 2.55 (*t*, 16 H, SCH_2); 1.47 (*quint.*, 8 H, SC–CH_2–CS). ^{13}C-NMR

((D_6DMSO; '*etc*'. stands for the corresponding C's of the 3 remaining identical moieties): 152.75 (C(11a), C(64a), *etc.*); 139.16 (C(12), C(64), *etc.*); 137.05 (C(12a), C(63a), *etc.*); 125.16 (C(13), C(63), *etc.*); 33.45 (C(2), (C(10), *etc.*); 30.35 (C(3), C(5), C(7), C(9), *etc.*); 29.02 (C(6), *etc.* FAB-MS (HCOOH/glycerine): 1476 (M^+).

(μ_5-Phthalocyaninato)cobalt(II)tetrapalladium(II) Octachloride (**7** · $PdCl_2$) *and (μ_5-Phthalocyaninato)tetrapalladium(II)zinc(II) Octachloride* (**8** · $PdCl_2$). A suspension of **7** (0.10 g, 0.068 mmol) or **8** (0.101 g, 0.068 mmol) in EtOH (30 ml) was treated with excess $Na_2[PdCl_4] \cdot 3 H_2O$ (0.189 g, 0.544 mmol) in EtOH (30 ml) and refluxed for 16 h under stirring. The dark green precipitate was filtered off, washed with H_2O, EtOH, and Et_2O, and dried *in vacuo*.

7 · 4$PdCl_2$: Yield 0.120 g (81%). IR (KBr): 2970–2950 (CH_2), 1610, 1540, 1420, 1390, 1360, 1260, 1205, 1110, 1080, 970, 850, 785, 750, 705.

8 · 4$PdCl_2$: Yield 0.135 g (91%). IR (KBr): 2990–2950 (CH_2), 1610, 1500, 1420, 1380, 1360, 1300, 1205, 1100, 1075, 950, 840, 780, 750, 700.

(μ_5-Phthalocyaninato)tetrasilver(I)zinc(II) Tetranitrate **8** · 4 $AgNO_3$. As described above, with **8** (0.067 g, 0.045 mmol), EtOH (30 ml), $AgNO_3$ (0.046 g, 0.272 mmol), and EtOH (10 ml; 6 h reflux): 0.070 g (72%) of **8** · 4$AgNO_3$. IR (KBr): 2980–2960 (CH_2), 1600, 1480, 1400–1380 (NO_3), 1340, 1280, 1120, 1090, 950, 840, 780, 750, 700.

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