Synthesis and Characterization of Novel Phthalocyanines with Four 16-Membered Diazadithia Macrocycles

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Metal phthalocyanines (M = Cu, Ni, Co) **3**–**5** bearing four 16-membered diazadithia macrocycles at the peripheral positions were prepared. Detosylation with concentrated sulfuric acid afforded products containing both sulfonated groups on the aromatic rings of the macrocyclic substituents which are excellently soluble in water and donor sites for binding four Cu^{II} ions to give a pentanuclear complex.

Phthalocyanines are widely used as pigments and dyes. Various other properties for new applications were investigated in the last decade: Photodynamic activity in the photodynamic cancer therapy, photosensitization in solution, electrocatalysts for dioxygen reduction in fuel cells, electrochromic processes as thin films, photoreductions or photooxidations in photo electrochemical cells, materials for electrophotography, optical information storage systems, catalysts for mercaptan oxidations and use as sensors[1–4]. A common prerequisite for most of these above mentioned applications is the solubility of the products in conventional solvents[5]. By generation of purpose-designed substitution patterns materials with additional properties such as thermal stability, electrical conductivity, and wavelength of the Q-band absorption were obtained[6,7]. Minor changes in the position of the side groups or alteration of the size of the groups or of the central metal atom have been found to affect appreciably the physical and the chemical properties of phthalocyanines[6,8]. Starting from simple mono-functional substituents, more complex structures such as crown ethers[9,10], tetraaza[11,12], diazatrioxa[13], diazadioxa[14], tetraaza-crown ether double layer[15], and tetrathia macrocycles[16], which are capable of binding alkali metal ions and provide donor sites for binding transition metal ions leading to homo- and heteropentanuclear complexes, have been introduced into the periphery of the phthalocyanines nucleus.

There are rather few phthalocyanines bearing sulfur donors[17,18]. Our research group synthesized octakis(alkylthio)-substituted phthalocyanines and phthalocyanines peripherally fused to four 13-membered tetrathiamacrocycles which undergo complexation with Ag^I and Pd^{II} to form heteronuclear products from their suspensions[16,19].

The introduction of water-soluble groups into the peripheral sites of the phthalocyanine gives rise to lyotropic liquid crystallinity attributed to the formation of columnar aggregates in concentrated aqueous solution[20].

In this present paper, we report for the first time on the preparation and characterization of a 16-membered symmetrical tetrabenzodiazadithia macrocycle and metal phthalocyanines (M = Cu, Ni, Co) derived from this macrocycles, which carry sulfo groups generated by the sulfonation of the aromatic rings of the macrocycles of the phthalocyanines during the detosylation reaction. As expected from the combination of diaza and dithia donor groups, the result is the coordination of transition metal ions, i.e. new heteropolynuclear compounds are highly coordinated by metal ions to the macrocyclic substituents.

Results and Discussion

Starting from 2-aminothiophenol, we illustrate the general route for the synthesis of new phthalocyanines in Scheme 1. 1,2-Bis(2′-aminophenylthiamethyl)benzene **1a** was obtained in 71% yield by reaction of 2-aminothiophenol with 1,2-bis(bromomethyl)benzene in the presence of a 40% NaOH solution in ethanol. The amino groups of **1a** were protected by tosylation with *p*-toluene sulfonylchloride in pyridine at 0°C for subsequent reactions. 1,2-Bis(2′-*p*-tolylsulfonylaminophenylthiamethyl)benzene **1b** was allowed to react with 1,2-dibromo-4,5-bis(bromomethyl)benzene in the presence of potassium carbonate as a base conditions in DMF to form the 16-membered symmetrical tetrabenzodiazadithia macrocycle **2a**. The yield of this ring-closure reaction between two bifunctional reactants is relatively high[21]. Of course, it was necessary to use equivalent amounts of the two reactants to promote a 1:1 condensation, but no 2:2 condensation products or other by-products were detected although molecular models revealed no steric constraints imposed on this compound.

Diazadithiamacrocycle **2a** was directly converted into the copper(II) phthalocyanine derivative **3** by the reaction with CuCN in tetramethylurea (TMU). The yield of the crude product was rather low and the purification steps were tedious and required a final column chromatography on silica gel[14]. The dicyano derivative **2b** was isolated under mild

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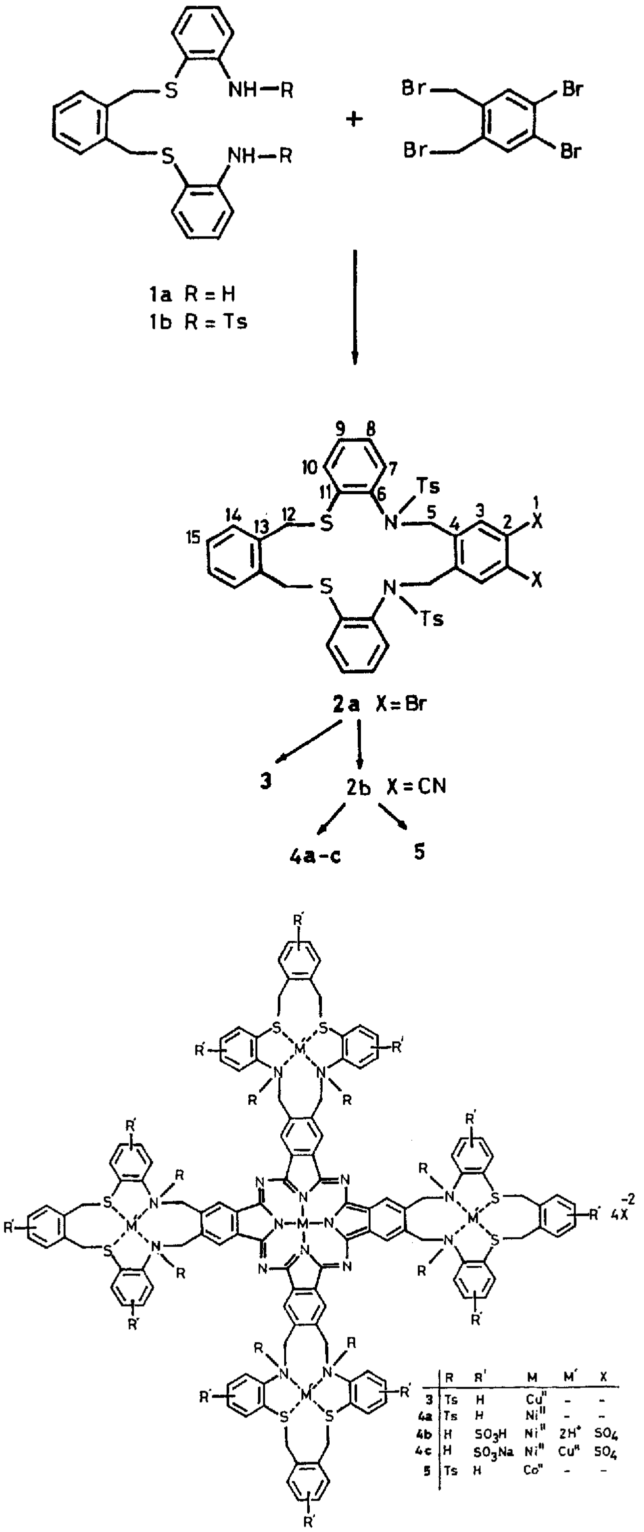

	R	R'	M	M'	X
3	Ts	H	Cu"	-	-
4a	Ts	H	Ni"	-	-
4b	H	SO_3H	Ni"	$2H^+$	SO_4
4c	H	SO_3Na	Ni"	Cu"	SO_4
5	Ts	H	Co"	-	-

conditions according to the Rosenmund von Braun procedure which might be considered as an intermediate step in the phthalocyanine formation. The reaction of **2b** in a high-boiling aprotic solvents such as quinoline with the appropriate metal salts gave the monomeric phthalocyanines **4**–**5** (M = Ni^{II}, Co^{II}). The yields of the products were very low as encountered for phthalocyanines with other bulky groups[13,22].

The most characteristic feature of complexes **3**, **4**, and **5** is their high solubility in common organic solvents, e.g. chloroform, dichloromethane, THF, DMSO, *N*,*N*-dimethylformamide (DMF). Complexation experiments with phthalocyanines containing four 16-membered diazadithia macrocycles were carried out with both transition and alkali metal ions, but no binding was indicated in the case of *N*-tosylated phthalocyanines which do not provide appropriate donor groups on the macrocycles[13,14].

Detosylation of complex **4a** was accomplished only in concentrated sulfuric acid at 125 °C for 5 h, although other detosylation methods under milder conditions had been attempted. Moreover, longer reaction times and higher temperatures resulted in decomposition of the phthalocyanine derivatives. However, detosylation with sulfuric acid leads to a product with sulfonyl groups on the aromatic rings of the macrocycle which consists of a mixture of regioisomers[13]. All attempts to separate these isomers by chromatographic techniques failed, but their presence could be verified by the slight broadening of the absorption bands in the ^{1}H-NMR and electronic spectra when compared with those of octasubstituted phthalocyanines composed of a single isomer[23,24]. The elemental analytical results indicate the presence of twelve sulfo groups for each phthalocyanine along with four sulfuric acid groups bound to the aza functions (Table 1). Addition of these polar groups gave phthalocyanines which are extremely soluble in water. Neutralization of the four sulfuric acid groups bound to the aza functions and a complexation experiment of the four diazadithiamacrocycles to obtain a pentanuclear complex were simultaneously accomplished by reaction of the phthalocyanine-substituted sulfonyl groups on the aromatic ring of macrocycle **4b** with $CuCl_2$ in an aqueous 2 M NaOH solution at reflux temperature. The dark blue product obtained was shown by elemental analysis to contain Cu^{II} and Pc in a ratio of 4:1 as a consequence of encapsulation of one metal ion by each diazadithia macrocycle. In this pentanuclear complexes, their highly ionic character was clearly indicated by their solubility in water.

Elemental analytical results and the spectral data (^{1}H- and ^{13}C-decoupled NMR, IR, and UV-VIS) of all the new products are consistent with the assigned formulations.

Comparison of the IR spectral data of **2a** and **2b** clearly indicate the conversion of the aromatic bromo substituents into cyano groups by the disappearance of the C–Br band at 640 cm^{-1} in **2a**, the appearance of a new C≡N band at 2220 cm^{-1} in **2b**. The rest of the spectrum of **2a** is closely similar to that of **2b** including the characteristic vibrations of tosyl groups. Detosylation is revealed by changes in the SO_2 stretching vibrations at 1370 and 1150 cm^{-1} for the tosylated compounds and 1100, 1220 cm^{-1} for the sulfonated products. The band at 3250 cm^{-1} for **4c** can be attributed to the NH stretching frequency[13]. In addition, the characteristic absorption of the sulfate anion can be differentiated between **4a** and **4b** (1100, 1220 cm^{-1}). In the pentanuclear complex **4c**, intense absorptions due to this anion at 1100–1220 cm^{-1} are observed.

Table 1. Elemental analysis results

Compound	Formula (Mol.mass)	C	H	N	S	Br	M	M′
		Analysis Calcd. (Found)						
1a	$C_{20}H_{20}N_2S_2$	68.14	5.72	7.94	18.19	–	–	–
	(352.5)	(67.94)	(5.60)	(7.68)	(18.01)	–	–	–
1b	$C_{34}H_{32}N_2O_4S_4$	61.79	4.88	4.23	19.41	–	–	–
	(660.8)	(61.61)	(4.81)	(4.10)	(19.25)	–	–	–
2a	$C_{42}H_{36}Br_2N_2O_4S_4$	54.78	3.94	3.04	13.93	17.36	–	–
	(920.8)	(54.06)	(3.90)	(2.81)	(13.45)	(17.07)	–	–
2b	$C_{44}H_{36}N_4S_4O_4$	65.00	4.46	6.89	15.78	–	–	–
	(813.01)	(65.01)	(4.40)	(6.80)	(15.55)	–	–	–
3	$C_{176}H_{144}CuN_{16}O_{16}S_{16}$	63.76	4.37	6.76	15.47	–	1.92	–
	(3315.6)	(64.05)	(4.49)	(6.62)	(15.14)	–	(1.76)	
4a	$C_{178}H_{144}N_{16}NiO_{16}S_{16}$	63.85	4.39	6.77	15.49	–	1.77	–
	(3310.8)	(63.65)	(4.43)	(6.32)	(15.32)	–	(1.68)	–
4b	$C_{120}H_{104}N_{16}NiO_{52}S_{24}$	42.01	3.07	6.53	23.43	–	1.49	–
	(3430.5)	(41.25)	(3.09)	(6.40)	(23.01)	–	(1.24)	–
4c	$C_{120}H_{84}Cu_4N_{16}Na_{12}NiO_{52}S_{24}$	36.58	2.13	5.69	19.53	–	1.49	6.45
	(3939.7)	(35.47)	(2.31)	(5.39)	(19.39)	–	(1.37)	(6.33)
5	$C_{176}H_{144}CoN_{16}O_{16}S_{16}$	63.08	4.38	6.77	15.49	–	1.78	–
	(3311.0)	(63.02)	(4.45)	(6.35)	(15.40)	–	(1.67)	–

Table 2. UV/Vis data for phthalocyanines **3–5**

Compound	λ/nm (10^{-4} ε/dm^{3}mol^{-1}cm^{-1}				
3[a]	692 (14.58)	660 (3.33)	625 (3.41)	345 (6.92)	260 (11.72)
4a[a]	684 (14.17)	656 (2.75)	616 (2.58)	339 (4.17)	250 (10.23)
4b[b]	640 (8.12)			320 (5.41)	240 (6.15)
4c[c]	638 (7.82)			345 (3.20)	250 (4.20)
5[a]	691 (5.83)	640 (3.20)	621(2.75)	325 (14.25)	265 (6.75)

[a] In chloroform. – [b] In water.

The ^{1}H-NMR spectra are also consistent with the proposed structures. In addition to the aromatic protons in diazadithiamacrocycles **2a–b**, CH_2-N and CH_2-S protons appear at δ = 4.35, 4.15, respectively. ^{1}H-NMR investigations of metal phthalocyanines **4a** and **4b** provided the characteristic chemical shifts for the structures expected. A common feature of the ^{1}H-NMR spectra of **4a** and **4b** is the broad absorption caused probably by the aggregation of Pc which is frequently encountered at the concentrations used for NMR. The only difference between **4a** and **4b** are the polar ammonium and sulfonyl groups on **4b** which probably enhance the broadening. ^{1}H-NMR measurements were precluded owing to the paramagnetic nature of the copper(II) phthalocyanine **3**, the cobalt(II) phthalocyanine **5**, and pentanuclear complex **4c**[1,9,13].

Phthalocyanines containing the 16-membered diazadithia macrocycles **3–5** show typical electronic spectra with two strong absorption regions, one in the visible region at 600–700 nm (Q band) attributed to the π-π* transition from the HOMO (Highest Occupied Molecular Orbital) to the LUMO (Lowest Unoccupied Molecular Orbital) of the Pc^{2-} ring and the other in the UV region at 300–350 nm (B band) arising from the deeper π levels $\rightarrow$ LUMO transition (Table 2). In extremely dilute solution (ca. 10^{-6} mol dm^{-3}), the molecules are present as monomers in dichloromethane. An increase in the concentration leads to aggregation, which is easily monitored by the position of the Q band which is shifted to shorter wavelengths, and to a decrease in the molar absorption coefficient. The sulfonated product obtained after detosylation shows aggregation even at very low concentrations. The Q bands are shifted 40–45 nm to higher energy from **4a** to **4b** and **4c**. This is consistent with the result obtained previously for similar phthalocyanines with sulfonated 17-membered diazatrioxa macrocycles[13]. Of course, the solvent effect should also be taken into account, while **4b** and **4c** are soluble in water. Complexation of four diazadithia macrocycles with Cu^{II} did not lead to appreciable changes in the Q band region in water, as expected from the low-intensity d-d transition[15].

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Experimental

FTIR (KBr): ATI Unicom-Mattson 1000 spectrophotometer. – UV/VIS: Varian DMS 90 (Table 2). – Elemental analysis (Table 1). – ^{1}H and decoupled ^{13}C NMR: Bruker (200 MHz) Spectrometer. – MS: EI and FAB on VG Zabspec GS-MS Spectrometer. – The metal contents of the complex were determined with a Hitachi-180-80 atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in conc. $HClO_4$ and conc. HNO_3 solution followed by digestion in conc. HCl solution. – The homogeneity of the products were tested in each step by TLC (SiO_2, chloroform).

1,2-Bis(2′-aminophenylthiomethyl)benzene (**1a**): 2-Aminothiophenol (10.0 g, 80 mmol) was dissolved in ethanol (30 ml) under nitrogen. A solution of 40% NaOH (8 ml) was added and the mixture was stirred and heated at reflux for 10 min. A solution of 1,2-bis(bromomethyl)benzene (10.56 g, 40 mmol) in ethanol (20 ml) was added dropwise over a period of 1 h. After the reaction mixture had been refluxed for 2 h, the solvent was distilled off, the yellow residue was dissolved in chloroform (50 ml) and the solution was filtered. The filtrate was washed with water (3 × 50) to separate any inorganic residues, dried with sodium sulfate, filtered and evaporated to dryness. The yellowish residue was crystallized from hexane. This compound is soluble in chloroform, dichloromethane, diethyl ether, ethanol, DMSO, and DMF. Yield of **1a** 10 g (71%); m.p. 98 °C. – IR (KBr): ṽ = 3450–3350 cm^{-1}, 3020, 2920–2840, 1610, 1475, 750. – ^1H NMR ([D_6]DMSO): δ = 7.21–6.42 (m, 12H, aromatic H), 5.21 (s, 4H, Ar-NH_2), 4.00 (s, 4H, Ar-CH_2S). – EI-MS (70 eV), *m/z* (%): 352 (75) [M^+].

1,2-Bis(2'-p-tolylsulfonylaminophenylthiomethyl)benzene (**1b**): Compound **1a** (3.52 g, 10 mmol) was dissolved in pyridine (10 ml) under N_2 and a solution of *p*-toluenesulfonyl chloride (3.81 g, 20 mmol) in pyridine (10 ml) was added dropwise over a period of 2 h to the stirred and ice-cooled solution. The reaction mixture was stirred at room temp. overnight. Then the solution was poured slowly into a stirred mixture of concentrated HCl (25 ml) and ice (200 g). The precipitated ditosylate was filtered off and washed with water (300 cm^3), ethanol, and diethyl ether. The creamy colored ditosylate is crystallized from acetone. This compound is soluble in chloroform, dichloromethane, THF, DMSO, and DMF. Yield of **1b** 5.8 g (88%); m.p. 149 °C. – IR (KBr): ṽ = 3250 cm^{-1}, 3020, 2910–2820, 1590, 1475, 1370–1150, 660, 575. – ^1H NMR ([D_6]DMSO): δ = 9.18 (s, 2H, aromatic-NH), 7.65–7.10 (m, 20H, ArH), 4.15 (s, 4H, Ar-CH_2S), 2.25 (s, 6H, Ar-CH_3). – EI-MS (70 eV), *m/z* (%): 661 (54) [M^+].

Diazadithia Macrocycle (**2a**): Compound **1b** (1.20 g, 1.80 mmol) was dissolved in dry DMF (35 ml) containing finely ground anhydrous K_2CO_3 (0.50 g, 3.6 mmol) and the solution was stirred at 40 °C for 1 h. A solution of 1,2-dibromo-4,5-bis(bromomethyl)benzene (0.76 g, 1.80 mmol) in dry DMF (25 ml) was added dropwise over 8 h and the mixture was stirred at the same temperature for 48 h. It was then poured onto ice water (250 g) and stirred for 1 h. The precipitate was filtered off, washed with water until the filtrate was neutral, then washed with ethanol and diethyl ether. Recrystallization from THF (20 ml) gave the pure macrocyclic compound. This compound is soluble in chloroform, dichloromethane, DMSO, DMF. Yield of **2a** 0.5 g (30%); m.p. 303 °C (dec.). – IR (KBr): ṽ = 3020 cm^{-1}, 2920, 2840, 1475, 1370–1150, 660, 640, 575. – ^1H NMR ($CDCl_3$): δ = 7.55–6.42 (m, 22H, aromatic H), 4.35 (s, 4H, Ar-CH_2N), 4.15 (s, 4H, Ar-CH_2S), 2.30 (s, 6H, Ar-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 142.01 (C-6), 141.90 (Ts-Ar), 139.92 (Ts-Ar), 138.20 (C-4), 137.03 (C-13), 136.05 (Ts-Ar), 134.09 (C-3), 131.08 (Ts-Ar), 130.04 (C-14), 129.90 (C-15), 128.25 (C-2), 127.64 (C-8), 126.85 (C-10), 125.85 (C-11), 124.08 (C-7), 123.52 (C-9), 47.10 (C-5), 38.20 (C-12), 21.62 (Ar-CH_3). – EI-MS (70 eV), *m/z* (%): 921 (24) [M^+].

Diazadithia Macrocycle (**2b**): A round-bottom flask fitted with a condenser was evacuated, refilled three times with N_2 and flame-dried in vacuo. Under nitrogen the flask was charged with CuCN (0.27 g, 3.0 mmol), **2a** (0.92 g, 1.0 mmol), and anhydrous dimethylformamide (DMF) (10 ml), and the mixture was heated to 160–165 °C. It was kept at this temperature for 10 h. During this time the resulting solution became dark brown. After cooling, it was mixed with aqueous NH_4OH (25%, 100 ml), and air was passed through the solution for 12 h. The solution became dark blue and a brown precipitate formed. This precipitate was filtered and washed with water until the filtrate was neutral and then washed with ethanol and diethyl ether. The brown precipitate was recrystallized from a mixture of acetonitrile water (20:10). This compound is soluble in chloroform, dichloromethane, THF, acetonitrile, DMSO, DMF. Yield of **2b** 0.4 g (50%); m.p. >300 °C. – IR (KBr): ṽ = 3020 cm^{-1}, 2920–2840, 2220, 1475, 1370–1150, 660, 570. – ^1H NMR ([D_6]DMSO): δ = 7.61–6.72 (m, 22H, aromatic H), 4.25 (s, 4H, Ar-CH_2N), 4.10 (s, 4H, Ar-CH_2S), 2.41 (s, 6H, Ar-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 143.20 (C-6), 140.25 (Ts-Ar), 139.20 (Ts-Ar), 139.10 (C-4), 138.20 (C-13), 137.80 (Ts-Ar), 133.85 (C-3), 132.28 (Ts-Ar), 130.85 (C-14), 128.80 (C-15), 128.20 (C-8), 126.25 (C-10), 126.01 (C-11), 124.80 (C-7), 122.50 (C-9), 118.25 (C-2), 115.94 (C-1), 47.25 (C-5), 38.22 (C-12), 21.62 (Ar-CH_3). – EI-MS (70 eV), *m/z* (%): 813 (15) [M^+].

[Octakis(N-p-tosyl)tetrakis(macrocycle)phthalocyaninato]copper(II) (**3**): A mixture of **2a** (0.15 g, 0.18 mmol), CuCN (0.05 g, 0.50 mmol), and dry TMU (0.5 ml) was heated and stirred at 190–195 °C in a sealed glass tube for 3 h under N_2. After cooling to room temp., the dark green mixture was diluted with ethanol (5 ml), and the crude product precipitated. This product was filtered off and washed with hot ethanol to remove unreacted organic materials. It was then refluxed four times with a solution of NaCN in water ethanol (1:2) to remove excess CuCN which subsequently was filtered off. The greenish blue powder was washed with water, ethanol, and diethyl ether. This product was then chromatographed (silica gel, chloroform) to afford 0.03 g (20%) of **3**. The compound is soluble in chloroform, dichloromethane, THF, DMSO, DMF. – IR (KBr): ṽ = 3020 cm^{-1}, 2920–2860, 1600, 1470, 1370–1150, 660, 570. – MS (FAB), *m/z*: 3315 [M^+].

[Octakis(N-p-tosyl)tetrakis(macrocycle)phthalocyaninato]nickel(II) (**4a**): A mixture of **2b** (0.40, 0.49 mmol), anhydrous $NiCl_2$ (0.016 g, 0.12 mmol), and dry quinoline (1 ml) was heated and stirred at 210 °C for 6 h and N_2 in a round-bottomed flask. After cooling to room temp., the dark blue mixture was diluted with ethanol until the crude product precipitated. It was filtered off and washed with hot ethanol. The precipitate was dissolved in chloroform (10 ml) and filtered off, reprecipitated from the solution with ethanol in order to remove unreacted organic materials, and finally the product was obtained by chromatography (silica gel, chloroform). Yield of **4a** 0.15 g (37%). The compound is soluble in chloroform, dichloromethane, THF, DMSO, DMF. – IR (KBr): ṽ = 3020 cm^{-1}, 2920–2860, 1600, 1470, 1370–1150, 660, 570. – ^1H NMR ([D_6]DMSO): δ = 7.81–6.72 (m, 88H, aromatic-H), 4.30 (s, 16H, Ar-CH_2N), 4.15 (s, 16H, Ar-CH_2S), 2.34 (s, 24H, Ar-CH_3). – ^{13}C NMR ([D_6]DMSO): δ = 147.22 (C-1), 144.22 (C-6), 142.50 (Ts-Ar), 142.25 (Ts-Ar), 135.65 (C-4), 134.35 (C-13), 134.02 (Ts-Ar), 132.01 (Ts-Ar), 131.05 (C-14), 130.20 (C-15), 129.85 (C-2), 129.20 (C-8), 128.10 (C-10), 128.11 (C-11), 126.25 (C-7), 123.80 (C-9), 123.50 (C-3), 48.20 (C-5), 38.20 (C-12), 21.60 (Ar-CH_3). – MS (FAB), *m/z*: 3310 [M^+].

[Tetrakis(macrocycle)phthalocyaninato]nickel(II) (**4b**) *(Detosylation of* **4a** *with H_2SO_4)*: Compound **4a** (0.15 g, 0.045 mmol) was treated with concentrated H_2SO_4 (10 ml) at 125 °C for 5 h. After cooling to room temp., the mixture was poured into cold ethanol (100 ml) and centrifuged. The blue precipitate was stirred in ethanol to remove excess H_2SO_4 and centrifuged. After dissolution in a minimum amount of water (ca. 5 ml), the product was reprecipitated from the blue solution by addition of ethanol (30 ml) and isolated by centrifugation. The product was dried with diethyl ether. Yield of **4b** 0.08 g (47%). The compound is soluble in water and DMSO. – IR (KBr): ṽ = 3020 cm^{-1}, 2920–2860, 1600, 1470, 1220–1100, 640. – ^1H NMR ([D_6]DMSO): δ = 12.11 (s, 12H, Ar-SO_3H), 8.20–6.65 (m, 48H, aromatic H), 4.35 (s, 16H, Ar-CH_2N), 4.30 (s, 16H, Ar-CH_2S), 4.10 (s, 16H, Ar-NH_4^+).

Tetracopper(II) Complex of [Tetrakis(macrocycle)phthalocyaninato]nickel(II) (**4c**): To a stirred solution of **4b** (0.05 g, 0.013 mmol) in water (10 ml) which was neutralized by the addition of aqueous 2 M NaOH a solution of $CuCl_2 \cdot 2\ H_2O$ (0.025 g, 0.15

mmol) in water (5 ml) was added. The mixture was refluxed for 2 h. After cooling to room temp., the solvent was removed by distillation until the total volume was 5 ml. A dark blue compound was precipitated by addition of ethanol (20 ml), filtered off, and washed with ethanol. This product was dissolved in DMF (5 ml) and reprecipitated with ethanol, filtered off and washed with ethanol and diethyl ether. The compound is soluble in water, DMSO and DMF. Yield of **4c** 0.015 g (30%). – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1}, 3020, 2920–2860, 1620, 1470, 1230, 1220–1120, 660.

[Octakis(N-p-tosyl)tetrakis(macrocycle)phthalocyaninato]-cobalt(II) (**5**): A mixture of **2b** (0.20 g, 0.25 mmol), anhydrous CoCl$_2$ (0.009 g, 0.070 mmol), and anhydrous quinoline (0.7 ml) was heated at 200–205°C under nitrogen with stirring and held at this temperature for 4 h. After cooling, the reaction mixture was treated with ethanol (20 ml) and then the crude product was washed with water and ethanol to remove the unreacted organic materials. The blue greenish powder was dissolved in chloroform (10 ml) and the solution filtered. The filtrate was chromatographed (Silica gel, chloroform). This compound is soluble in chloroform, dichloromethane, THF, DMSO, DMF. Yield of **5** 0.04 g (20%). – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2920–2860, 1600, 1470, 1370–1150, 660, 570. – MS (FAB), *m/z*: 3311 [M$^+$].

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