Synthesis and Characterization of Phthalocyanines Containing Four 14-Membered Tetraaza Macrocycles

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Metal phthalocyanines (M = Cu, Ni, Co, $SnCl_2$) **3–6** containing four 14-membered tetraaza macrocycles have been prepared. Detosylation of the aza functions has provided donor sites for binding four Ni^{2+} ions giving a pentanuclear complex which is extremely soluble in polar solvents. The mass spectrum of the [hexadecakis(*N*-*p*-tosyl)-tetrakis-macrocycle-phthalocyaninato]copper(II) **3** is described

Introduction of functional groups into chemically stable phthalocyanine cores impart novel properties to the products suitable for various applications[1]. Among these we may cite supramolecular assemblies formed in liquid state or in solution as a result of the planar geometry encountered in these molecules[2], alkali or transition metal binding[3], and enhanced solubility in common organic solvents caused by bulky substituents[4]. When these features are combined with the well-known delocalized electronic system and the useful electrochemical, photochemical, and optical behavior of phthalocyanines, a diversity of applications can be easily assumed[5].

We have previously synthesized for the first time four crown ether-substituted phthalocyanines which are soluble in common organic solvents and capable of binding alkali metal ions[3,6,7]. Additionally, these compounds show mesogenic properties and form ion channels through the crown ether moieties capable of conducting alkali metal ions[8]. Incorporation of monoaza crown ether units leads to products which additionally offer the advantage of being soluble in water over a wide pH range by quaternization of the aza function[9].

Tetraaza macrocycles show a tendency to form complexes with transition metal ions comparable with the interactions of crown ethers with alkali ions. Therefore, phthalocyanines peripherally containing these donor macrocycles are expected to form homo- or heteromultinuclear compounds. Preliminary findings on phthalocyanines with 14-membered tetraaza macrocycles[10] and a detailed study of a 15-membered derivative have been reported recently by our group[11].

The present paper describes the synthesis of metal phthalocyanines containing four 14-membered tetraaza macrocyclic units and their multinuclear complexes. The mass spectral data of the parent phthalocyanine molecule are also discussed.

Results and Discussion

The first step in the synthetic procedure outlined in Scheme 1 is the formation of the tetraaza macrocycle **1**. Starting from *N*,*N*′,*N*″,*N*‴-tetrakis(*p*-tolylsulfonyl)triethylenetetramine and 1,2-dibromo-4,5-bis(bromomethyl)benzene, we have accomplished cyclization in DMF in the presence of K_2CO_3 as the base[12,13]. The relatively high yield of the reaction product confirms the suitability of the tosylamino derivatives for cyclization. Although the dibromo derivative **1** can be used to prepare Cu-Pc directly, its dicyano derivative has been required for the synthesis of the other metal phthalocyanines. Conversion of **1** into dicyano derivative **2** was accomplished by the Rosenmund von Braun reaction by treatment with CuCN in DMF.

Cyclotetramerization of **2** in high-boiling solvents such as ethylene glycol and tetramethylurea (TMU) in the presence of the metal salt affords the desired metallophthalocyanine. Although the synthesis of these compounds is rather simple, their isolation and purification laborious. Making use of their solubility in common solvents, we have usually applied successively dissolution and reprecipitation steps and finally chromatographic separation. Consequently, the yields of the reaction products are very low. The two electrons required to achieve phthalocyanine formation are received from the metal salt when the dichloro Sn^{4+} phthalocyanine derivative is obtained from the phthalodinitrile derivative in 1-chloronaphthalene, thus the divalent tin derivative $SnCl_2$ has been used[14].

An important point encountered in these tetraaza macrocycle-substituted starting materials is the instability of the

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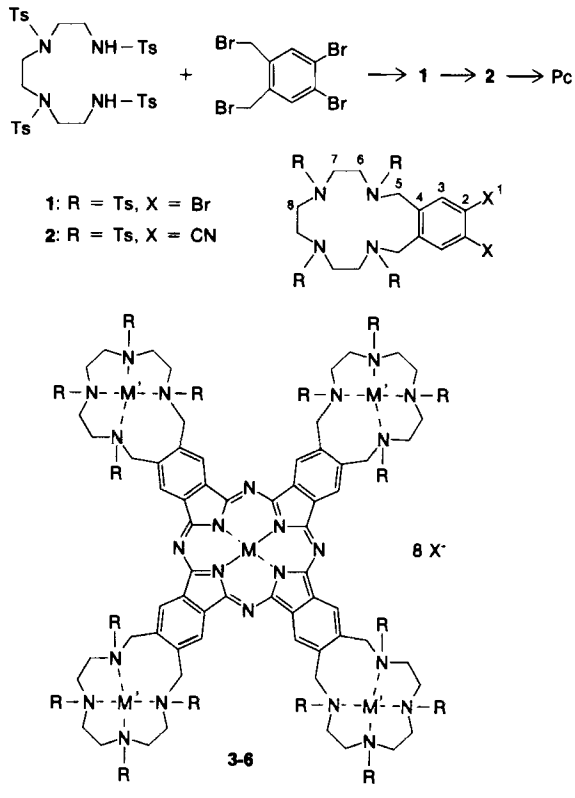
Scheme 1. Synthetic route to metal phthalocyanines



	R	M	M'	X
3	Ts	Cu	–	–
3a	H	Cu	–	–
3b	H	Cu	Ni	Cl
4	Ts	Ni	–	–
5	Ts	Co	–	–
6	Ts	$SnCl_2$	–	–

macrocycle under strongly basic and reductive conditions. Even the tosyl protecvtive group is not sufficient to convert the dicyano compound into the isoiminoindoline derivative or metal-free Pc. A great number of procedures used for the synthesis of metal-free Pc including direct interaction of the dicyano compound **2** with hydroquinone in a sealed tube[3,15], heating of **2** in DBU in the presence of alcohols at elevated temperatures[16], treatment of **2** with alkali metal pentanolates in 1-pentanol gave no indication of Pc formation[17]. The reason for this failure is probably that the detosylation of the macrocycle occurs before the cyclotetramerization reaction has begun.

As the Co^{2+}, Ni^{2+}, and Sn^{4+} analogs, the *N*-tosylated Cu-Pc derivative **3** is extremely soluble in organic solvents such as $CHCl_3$, CH_2Cl_2, DMSO, and DMF. Detosylation of **3** in conc. H_2SO_4 at 100°C and subsequent neutralization with 2 M NaOH lead to a product **3a** which is soluble in ethanol and methanol. Treatment of **3a** in ethanol with an excess amount of $NiCl_2$ results in the formation of a pentanuclear complex, which is extremely soluble in water.

Mass spectrometry is a powerful method for confirming the proposed structures of high molecular mass labile compounds such as phthalocyanines[3,18]. The two ionization techniques used for the characterization of the [hexadecakis-(*N*-*p*-tosyl)-tetrakis-macrocycle-phthalocyaninato]copper(II) **3** are fast atom bombardment and caesium ion gun mode. The samples are analyzed as solution in chloroform. Molecular ion species are observed in accord with the calculated isotopic distributions (Figure 1). The higher molecular mass fragment ions corresponding to cleavage of the 1–3 tosyl groups from **3** appear at m/z = 3568.3, 3413.2, and 3257.8.

NMR investigations of metal phthalocyanines **4** and **6** (M = Ni^{2+} or $Sn^{4+}Cl_2$) have provided the characteristic chemical shifts for the structures expected. An evident difference between the proton NMR spectra of **4** and **6** are the broad absorptions encountered in the case of **4**[9,19] which is the result of aggregation of planar phthalocyanine molecules at high concentrations generally used in NMR measurements. The deviation from planarity of the Sn phthalocyanine core and the presence of axial chloride ligands prevent the aggregation to a certain extent in **6**; consequently, the chemical shifts are sharp. The proton-decoupled ^{13}C-NMR spectrum of **6** closely resembles that of the dinitrile **2**, the only difference being the signal of the carbon atom of the cyano group in **2**.

The phthalocyanines **3**–**6** exhibit typical electronic spectra with intense Q and B bands[2,3] (Table 2). While the *N*-tosylated compounds are soluble in $CHCl_3$, their spectra in this solvent exhibit an intense Q band at the lowest energy side (≈ 670–690 nm) and a shoulder around 640 nm indicating the aggregation. Detosylated Cu phthalocyanine and its pentanuclear ($CuNi_4$) complex **3b** are soluble in ethanol/water mixtures, and their spectra are affected by the polar solvent as observed by the shift of the Q band to shorter wave lengths and at the same time by a decrease in their molar absorptivity.

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Experimental

IR (KBr): Perkin-Elmer 983 Spectrophotomer. – UV/Vis: Varian DMS 90. – Elemental analyses (Table 2): Instrumental Analytical Laboratory of TUBITAK Gebze Research Center. – ^1H NMR: Bruker (200 MHz). – MS: Jeol JMS-HX110A and JMS-SX102A spectrometers. The phthalocyanine samples were dissolved in chloroform (50 µl) and the ionization was accomplished with a caesium ion gun delivering about 2 µA (2.4 A flame current) of caesium ions with about 23 KeV energy. – The homogeneity of the products were tested in each step by TLC (SiO_2, methanol/chloroform).

1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazadecane was prepared according to a literature procedure[12].

14,15-Dibromo-2,5,8,11-tetrakis(p-tolylsulfonyl)-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrobenzo[l][1,4,7,10]tetrazacyclotetradecine (**1**): 1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazadecane (23.50 g, 30.80 mmol) was dissolved in anhydrous DMF (250 ml) containing finely ground anhydrous K_2CO_3 (10.20 g, 73.80 mmol). The obtained solution was stirred for 1 h at 30°C. Then a solution of

Table 1. Elemental analyses results

	Formula (Mol. mass)	Analysis Calcd. (Found) C	H	N	S	Cl	M
1	$C_{42}H_{46}Br_2N_4O_8S_4$ (1022.9)	49.32 (49.15)	4.53 (4.41)	5.48 (5.44)	12.53 (12.20)	–	–
2	$C_{44}H_{46}N_6O_8S_4$ (915.1)	57.75 (57.28)	5.07 (5.09)	9.18 (8.98)	14.01 (14.30)	–	–
3	$C_{176}H_{184}CuN_{24}O_{32}S_{16}$ (3724.1)	56.76 (56.83)	4.98 (4.97)	9.06 (8.87)	13.78 (14.10)	–	1.71 (1.80)
3a	$C_{64}H_{88}CuN_{24}$ (1257.1)	61.15 (60.90)	7.06 (7.01)	26.74 (25.98)	–	–	5.05 (4.90)
3b[a]	$C_{64}H_{88}Cl_8CuN_{24}Ni_4$ (1775.6)	43.30 (42.98)	5.00 (4.99)	18.93 (18.55)	–	15.97 (15.50)	3.58 (3.70)
4	$C_{176}H_{184}N_{24}NiO_{32}S_{16}$ (3719.3)	56.84 (56.83)	4.99 (4.87)	9.04 (9.01)	13.79 (13.60)	–	1.58 (1.70)
5	$C_{176}H_{184}CoN_{24}O_{32}S_{16}$ (3719.5)	56.83 (55.93)	4.99 (5.01)	9.04 (8.92)	13.79 (13.50)	–	1.58 (1.60)
6	$C_{176}H_{184}Cl_2N_{24}O_{32}S_{16}Sn$ (3850.2)	54.90 (54.20)	4.82 (4.82)	8.73 (8.68)	13.32 (13.50)	1.84 (1.90)	3.08 (3.20)

[a] M′ calcd. 13.22, found 13.10.

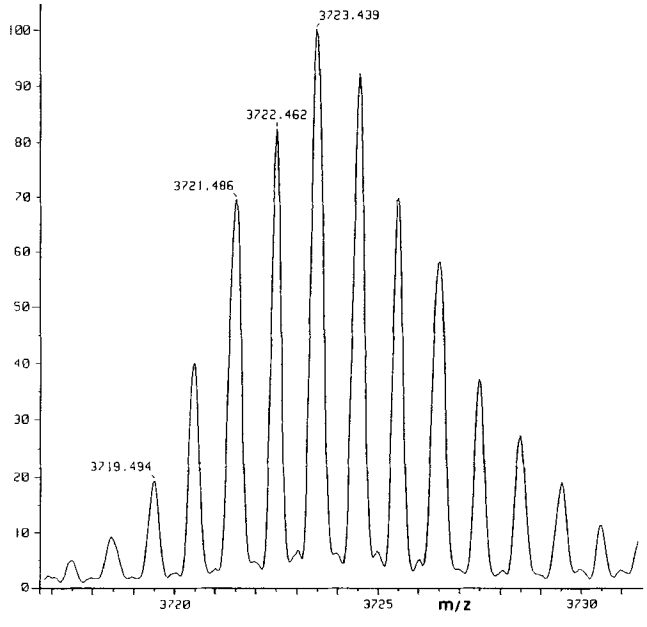

Figure 1. Molecular ions peaks for **3** and theoretical isotopic distributions. $C_{176}H_{184}CuN_{24}O_{32}S_{16}$, mass exact 3719.8336, ave. 3724.1406

Mass	Abund.	Mass	Abund.
3719.8336	21.9552	3725.8372	66.7328
3720.8365	48.5601	3726.8371	45.8508
3721.8365	80.2068	3727.8369	28.6423
3722.8371	98.0934	3728.8367	16.4335
3723.8372	100.0000	3729.8364	8.7350
3724.8373	87.0032	3730.8361	4.3305

1,2-dibromo-4,5-bis(bromomethyl)benzene (15.90 g, 37.80 mmol) in anhydrous DMF (200 ml) was added dropwise over a period of 8 h. After 24 h, the mixture was poured into ice/water (2000 ml). The resulting white solid was collected by filtration and washed with water to neutral pH. The wet solid was dissolved in CH_2Cl_2 (200 ml) and the solution dried with Na_2SO_4. The volume of the filtrate was reduced to 100 ml, and 30 ml of *n*-hexane was added. Finally, the crystalline white product was filtered, washed with diethyl ether, and dried in vacuo. This compound was soluble in chloroform, dichloromethane, ethanol, DMSO, and DMF. Yield of **1** 18 g (57%); m.p. 270°C. – IR (KBr): $\tilde{\nu}$ = 3080–2850 cm^{-1}, 1620, 1510, 1460, 1350, 1170, 1100, 940, 820, 750, 690, 660, 560. – ^1H NMR ($CDCl_3$): δ = 7.72–7.29 (m, 18H, aromatic H), 4.32 (s, 4H, Ar-CH_2N), 3.29 (t, 4H, NCH_2), 2.94 (t, 8H, NCH_2), 2.46 (s, 6H, Ar-CH_3), 2.44 (s, 6H, Ar-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 144.42 (Ts-Ar), 143.85 (Ts-Ar), 139.58 (C-4), 135.20 (Ts-Ar), 135.01 (Ts-Ar), 134.71 (C-3), 130.20 (Ts-Ar), 129.92 (Ts-Ar), 127.45 (Ts-Ar), 127.32 (Ts-Ar), 125.32 (C-2), 49.79, 49.37, 49.23 [C-5 to C-8], 21.61 (Ar-CH_3). – MS (70 eV), *m/z* (%): 1022 (11) [M^+].

2,5,8,11-Tetrakis(p-tolylsulfonyl)-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrobenzo[l][1,4,7,10]tetrazacyclotetradecine-14,15-dicarbonitrile (**2**): A round-bottom flask fitted with a condenser was evacuated, refilled three times with argon and flame-dried in vacuo. Under argon the flask was charged with CuCN (2.69 g, 30 mmol), **1** (10 g, 10 mmol), and anhydrous dimethylformamide (42 ml), and the mixture was heated to 170–175°C. It was then kept at this temp. for 14 h. During this time the resulting solution became dark brown. Then the volume of the solution was reduced to 10 ml. After cooling, it was mixed with aqueous NH_4OH (25%, 250 ml), and air was passed through the solution for 24 h. The solution became dark blue, and a green-brown precipitate formed. This precipitate was isolated by filtration and washed with water, until the filtrate was neutral and then dried in vacuo at 100°C. The green-brown precipitate was then chromatographed (silica gel, CH_2Cl_2) to furnish 3.5 g (38%) of **2**. The compound is soluble in chloroform, dichloromethane, DMF, and DMSO, m.p. 275°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3080–2850 cm^{-1}, 2220, 1620, 1510, 1460, 1350, 1170, 1100, 940, 820, 760, 690, 660, 555. – ^1H NMR ([D_6]DMSO): δ = 7.80–7.41 (m, 18H, aromatic H), 4.47 (s, 4H, Ar-CH_2N), 3.18 (t, 4H, NCH_2), 2.90 (t, 8H, NCH_2), 2.43 (s, 6H, Ar-CH_3), 2.41 (s, 6H, Ar-CH_3). – ^{13}C NMR ([D_6]DMSO): δ = 144.14 (Ts-Ar), 143.69 (Ts-Ar), 141.72 (C-4), 135.83 (Ts-Ar), 135.32 (Ts-Ar), 133.29 (C-3), 130.24 (Ts-Ar), 130.08 (Ts-Ar), 126.94 (Ts-Ar), 126.69 (Ts-Ar), 115.94 (C-1), 114.071 (C-2), 47.83, 47.00, 46.57 (C-5 to C-8), 20.97 (Ar-CH_3). – MS (70 eV), *m/z* (%): 914 (14) [M^+].

[Hexadecakis(N-p-tosyl)-tetrakis-macrocycle-phthalocyaninato]-copper(II) **3**: A mixture of **1** (5.20 g, 5 mmol), CuCN (1.20 g, 13.40 mmol), and dry tetramethylurea (TMU) (3.6 ml) was heated and stirred at 180–185°C in a sealed glass tube for 6 h under argon. After cooling to room temp. the dark blue mixture was diluted with ethanol (10 ml), and the crude product precipitated. This was filtered off and

Table 2. UV/Vis data for phthalocyanines **3**–**6**

	λ/nm (10^4 ε/dm^3 mol^{-1} cm^{-1})					
3[a]	682 (11.92)	650 (2.21)	614 (2.24)	345 (5.00)	241 (8.59)	
3a[b]	674 (5.85)	640 (3.84)		337 (4.85)	226 (7.27)	
3b[b]	676 (6.93)	639 (5.90)		340 (6.47)	225 (10.11)	
4[a]	675 (11.41)	640 (3.66)	609 (2.76)	338 (6.29)	298 (7.96)	241 (17.81)
5[a]	666 (14.52)	638 (4.15)	597 (3.14)	319 (7.45)	277 (5.91)	230 (14.82)
6[a]	690 (13.01)	622 (3.27)	357 (6.63)	336 (6.01)	229 (14.70)	

[a] In $CHCl_3$. – [b] In $EtOH/H_2O$ (8:1).

washed with hot ethanol to remove unreacted organic materials. The precipitate 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 then washed with H_2O, ethanol, and diethyl ether. This product was chromatographed (silica gel, $MeOH/CHCl_3$, 1:20) to afford 1.443 g (31%) of **3**. The compound is soluble in chloroform, dichloromethane, DMSO, DMF, and acetone. – IR (KBr): $\tilde{\nu}$ = 3050–2850 cm^{-1}, 1600, 1490, 1450, 1340, 1160, 1090, 1020, 940, 810, 750, 690, 660, 550.

(Tetrakis-macrocycle-phthalocyaninato)copper(II) **3a** *(Detosylation of* **3** *with* H_2SO_4*)*: Compound **3** (0.372 g, 0.1 mmol) was treated with conc. (98%) H_2SO_4 (10 ml) at 100°C for 3 h. After cooling the mixture was poured into cold ethanol (100 ml) and centrifuged. The greenish blue precipitate formed was mixed with EtOH to remove excess H_2SO_4. The precipitate was then dissolved in H_2O (30 ml) and the obtained solution filtered. The pH of this solution was raised to 12 by the addition of an aqueous solution of 2 M NaOH. The precipitate formed was centrifugated and washed several times with H_2O, then dried in vacuo at 100°C. Yield of **3a** 0.06 g (20%). This compound is soluble in methanol, ethanol, and DMSO. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1}, 2990–2850, 1620, 1490, 1450, 1325, 1150, 1100, 1020, 870, 800, 750, 690, 650, 550.

Tetranickel(II) Complex of (Tetrakis-macrocycle-phthalocyaninato)copper(II) **3b**: To a stirred solution of **3a** (0.050 g, 0.04 mmol) in anhydrous ethanol (20 ml) was added a solution of anhydrous $NiCl_2$ (0.042 g, 0.32 mmol) in anhydrous ethanol (3 ml). The mixture was refluxed for 4 h, and then the solvent was removed by distillation until the total volume was 5 ml. The resulting dark-blue precipitate was filtered off, washed with anhydrous ethanol, and then with diethyl ether. Yield: 0.055 g (77%). – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1}, 2980–2850, 1620, 1500, 1440, 1325, 1150, 1100, 1020, 870, 800, 750, 690, 650, 550.

*[Hexadecakis(N-p-tosyl)-tetrakis-macrocycle-phthalocyaninato]nickel(II)***4**: A mixture of **2** (0.366 g, 0.4 mmol), anhydrous $NiCl_2$ (0.013 g, 0.1 mmol), and dry DMF (0.5 ml) was heated and stirred at 155°C for 48 h under nitrogen. After cooling to room temp., the dark-blue mixture was diluted with methanol until the crude product precipitated. It was filtered off and washed with hot methanol. The precipitate was dissolved in chloroform (15 ml) and then reprecipitated from the solution with methanol. In order to remove unreacted organic material the crude product was dissolved in 1,1,2,2-tetrachloroethane (5 ml) and reprecipitated with toluene. These operations were repeated. Finally, the pure product was obtained by chromatography (Al_2O_3, $MeOH/CHCl_3$, 1:20). Yield of **4** 0.075 g (22%). The compound is soluble in chloroform, DMSO, and DMF. – IR (KBr): $\tilde{\nu}$ = 3050–2850 cm^{-1}, 1600, 1490, 1450, 1340, 1160, 1090, 1020, 940, 830, 750, 690, 660, 550. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.02–7.23 (m, 72H, aromatic H), 5.07 (s, 16H, Ar-CH_2N), 3.56–3.04 (m, 48H, NCH_2), 2.51 (s, 48H, Ar-CH_3).

[Hexadecakis(N-p-tosyl)-tetrakis-macrocycle-phthalocyaninato]cobalt(II) **5**: A mixture of **2** (0.366 g, 0.4 mmol), anhydrous $CoCl_2$ (0.019 g, 0.146 mmol), ammonium molybdate (0.002 g), and dry ethylene glycol (5 ml) was heated to 190–195°C under nitrogen with stirring and held at this temp. for 24 h. After cooling, an equal volume of water was added. The mixture was suction-filtered while still hot, and the precipitate was isolated from the filtrate, washed several times with hot water (ca. 90°C) and subsequently with ethanol. The blue greenish powder was dissolved in chloroform (ca. 20 ml) and the solution filtered. The filtrate was chromatographed (silica gel, $MeOH/CHCl_3$, 1:20). Yield of **5** 0.080 g (21%). The compound is soluble in chloroform, dichloromethane, DMF, and DMSO. – IR (KBr): $\tilde{\nu}$ = 3050–2850 cm^{-1}, 1600, 1510, 1450, 1340, 1160, 1090, 940, 820, 750, 685, 660, 550.

[Hexadecakis(N-p-tosyl)-tetrakis-macrocycle-phthalocyaninato]tin(IV) **6**: A mixture of **2** (1.258 g, 1.37 mmol), $SnCl_2$ (0.083 g, 0.44 mmol), and 1-chloronaphthalene (2.2 ml) was heated at 200–205°C under argon for 4 h. After cooling, the dark greenish blue mixture was diluted with ethanol (5 ml), and the crude product was precipitated. This was filtered off and washed with hot ethanol. The precipitate was then refluxed four times with ethanol and filtered off. The greenish blue powder was dissolved in 1,1,2,2-tetrachloroethane (10 ml) and the solution filtered. The product was precipitated from the hot filtrate by addition of hot toluene (ca. 40 ml). The precipitate was filtered off and then dried with diethyl ether. Yield of **6** 0.40 g (30%). The compound is soluble in chloroform, dichloromethane, DMSO, and DMF. – IR (KBr): $\tilde{\nu}$ = 3080–2850 cm^{-1}, 1600, 1500, 1455, 1340, 1180, 1100, 940, 820, 740, 690, 660, 555. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.06–7.29 (m, 72H, aromatic H), 5.17 (s, 16H, Ar-CH_2N), 3.34–3.10 (m, 48H, NCH_2), 2.24 (s, 48H, Ar-CH_3). – ^{13}C NMR ([D$_6$]DMSO): δ = 148.99 (C-1), 143.68 (Ts-Ar), 143.25 (Ts-Ar), 140.40 (C-4), 136.16 (Ts-Ar), 135.79 (Ts-Ar), 134.81 (C-2), 130.08 (Ts-Ar), 129.71 (Ts-Ar), 127.13 (Ts-Ar), 126.46 (Ts-Ar), 123.95 (C-3), 47.81, 47.23, 47.12 (C-5 to C-8), 20.61 (Ar-CH_3).

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