Synthesis and characterization of metal-free and metallophthalocyanines containing four 17-membered dioxa-triaza macrocycles†

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The synthesis and characterization of novel metal-free (**8**) and metal-containing (Cu, Ni or Co, **6**, **9**, **10**) derivatives of a symmetrically tetrasubstituted phthalocyanine derived from 17,18-dicyano-4,8,12-tri(toluene-*p*-sulfonyl)-1,2,3,4,5,6,7,8,9,10,11,12,13,14,15-pentadecahydrobenzo[1.15]dioxa[4.8.12]tetraazacycloheptadecine (**7**), which was synthesized in a multi-step reaction sequence, have been described. The *N*-tosylated derivatives are highly soluble in common organic solvents. The new compounds have been characterized by elemental analyses, ^{1}H and ^{13}C NMR, IR, UV/VIS and MS spectral data.

The chemistry of phthalocyanines and their metallo derivatives has been well-studied through several reviews and books.[1] The structures of the metal-free and metallated derivatives of phthalocyanines were investigated by Linstead and co-workers[2] in 1934. Metallophthalocyanines, besides their many other possible applications as, for example, dyes, pigments, catalysts, *etc*., have recently been investigated most intensively with respect to their electrical properties as photoconducting agents in photocopying machines[3] and as sensing elements in chemical sensors.[4] Phthalocyanines (Pc) have also been investigated mainly as a part of efforts to construct new types of materials for read-write disks and related information storage systems for computers, laser dyes and liquid crystal colour displays, as well as the biomimicry of natural systems.[5] After partial oxidation or reduction (doping) of phthalocyanines, good conducting or semiconducting properties have been observed.[6]

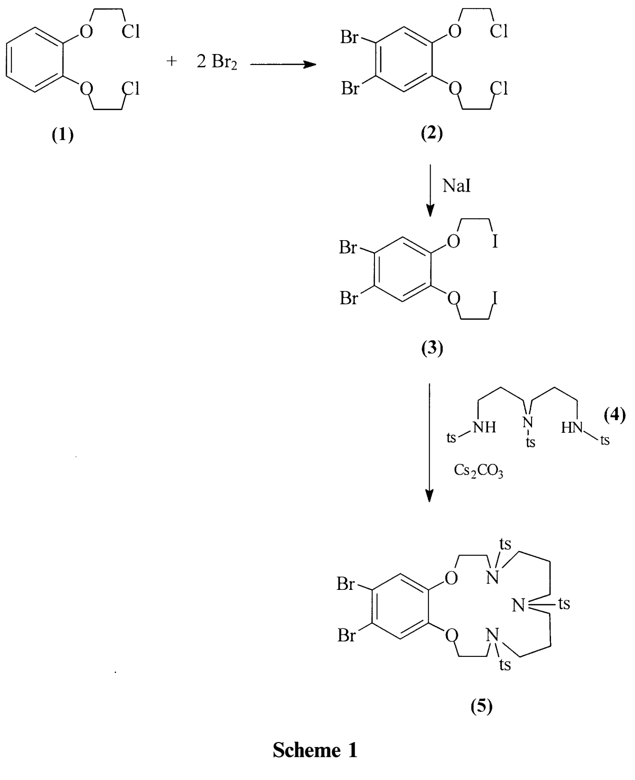
Many macrocyclic compounds such as polyethers, polyamines, polythioethers and other related compounds contain central hydrophilic cavities with either electronegative or electropositive binding atoms and exterior flexible frameworks exhibiting hydrophobic behaviour. These properties of their exteriors allow them to solubilize ionic substances in non-aqueous solvents and in membrane media.[1a] On the other hand, the solubility and physical and chemical properties of phthalocyanines can be tailored by making suitable substitutions on the aromatic rings.[7] The addition of macrocyclic moieties into the phthalocyanine molecule has provided considerable opportunity to investigate the properties of the metal-free or metallo derivatives by enhancing their solubility in various organic solvents.

We have previously synthesized series of phthalocyanines substituted with oxa-aza macrocycles. The effect of the aza-crown ether on the macrocyclic moiety is the same with the additional advantage of solubility in water over a wide pH range by quaternization of the aza functions.[8]

In this paper, we present the synthesis of a new phthalocyanine containing triaza-dioxa macrocylic moieties. While the combination of these different kinds of donor groups is expected to result in the coordination of both alkali and transition metal ions, the resulting compound is less stable than either cyclic polyether alkali metal complexes or polyaza macrocyclic transition metal complexes.[9] The present macrocycle (**5**) was tried as a substituent but no alkali or transition metal complexes could be isolated, owing to loosely coordinated metal ions on the macrocyclic moieties.

Results and Discussion

The preparations of the target metal-free (**8**) and metallophthalocyanines (**6**, **9**, **10**) are shown in Schemes 1 and 2. The structures of the compounds were demonstrated by a combination of elemental analysis, ^{1}H and ^{13}C NMR, IR, UV/VIS and mass spectral data. Metal-free phthalocyanine was prepared in a five-step reaction sequence from 1,2-bis(2-chloroethoxy)benzene.[10] The conversion of compound **1** to the dibromo derivative **2** was obtained in 74.5% yield when **1** was reacted with an equivalent amount of bromine. The presence of the singlet at $\delta = 7.16$ in the ^{1}H NMR spectra for the aromatic protons of **2** showed that the dibromination had occurred. Three signals at $\delta = 150.39$, 122.49 and 118.48 for the aromatic carbons were observed in the proton-decoupled



Scheme 1

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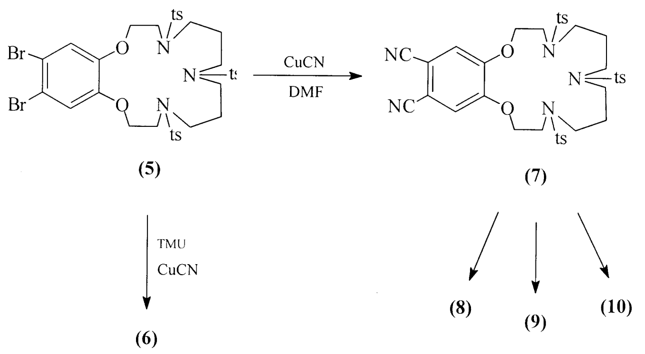
† Dedicated to Professor Ozer Bekaroğlu on the occasion of his 65th birthday.



Scheme 2

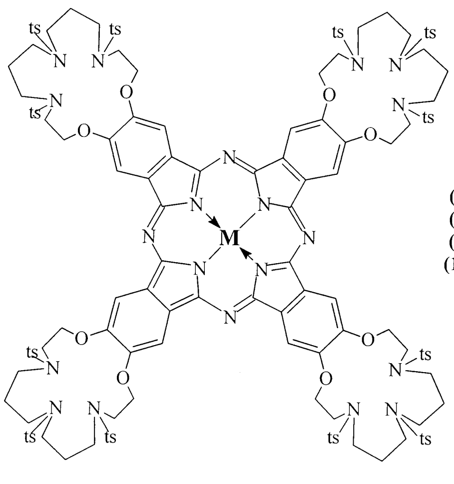
carbon-13 NMR spectrum of **2**, indicating that the substitution reaction has been completed. In the infrared spectrum of **2**, the sharp band of medium intensity occurring at 667 cm^{-1} is attributed to $\nu(Ar—Br)$,[5b] while a similar band at 1254–1213 cm^{-1} is assigned to $\nu(Ar—O—C)$. The fast atom bombardment (FAB) mass spectrum of this compound shows two dominant peaks at $m/z = 393$ and 394, which correspond to $[M]^+$ and $[M + 1]^+$, respectively.

2 was easily converted into the diiodo derivative **3** by reaction with NaI in dry acetone and the yield of the conversion reaction was rather high (67.3%).[11] The signals of the aromatic protons and aromatic carbons in the proton or carbon-13 NMR spectra of **3** are very similar to those of the precursor compound **2** except for the signals of carbons and protons connected to halogens ($—CH_2I$). The IR spectrum of this compound exhibits characteristic frequencies at 1255–1209 (Ar—O—C), 666 (Ar—Br) and 532 (C—I) cm^{-1}. The mass spectrum (FAB) and elemental analysis of this compound also support the replacement of chlorine by iodine, with the peaks at $m/z = 576$ and 577 indicating $[M]^+$ and $[M + 1]^+$ formation, respectively.

The cyclization reaction was performed under reasonably dilute conditions in dry polar solvent with Cs^+ as a template. The tritosilated dioxa-triaza macrocyclic compound **5** was obtained in 68% yield from dipropylenetriamine tritosilate (**4**) with 1,2-dibromo-4,5-bis(2-iodoethoxy)benzene[12] (**3**) in the presence of Cs_2CO_3 as a template agent and in DMF at room temperature in a Schlenk system under argon atmosphere. Analytical and spectroscopic data of **5** clearly confirm the success of the cyclization reaction. In the ^1H NMR spectrum of **5**, the chemical shifts belonging to NH protons in the precursor compound **4** disappear after the macrocyclization reaction. The singlet at $\delta = 7.35$ and the multiplets at $\delta = 7.70$ and 7.26 correspond to aromatic groups connected to $—OCH_2$ and SO_2. The chemical shifts belonging to methylene protons neighbouring nitrogen and oxygen show different values at $\delta = 4.27–4.06$ ($Ar—O—CH_2$) and $\delta = 3.81$ ($—CH_2N$), as expected. Proton-decoupled carbon-13 NMR spectral data are also in good agreement with the proposed structure (Scheme 1). The carbon resonances of the *p*-tolyl groups and the phenyl group connected macrocyclic moiety appear at $\delta = 145.62$, 138.33, 131.71, 129.08 and 150.08, 122.55, 118.84, respectively. The other carbon chemical shifts belonging to the methyl and methylene groups are observed respectively at $\delta = 23.49$ and 43.77, 31.13. In addition, comparison of the infrared data of **4** and **5** gives sufficient support for the proposed structure. The difference between the spectra of precursor compounds and the macrocyclic moiety is clear from the presence of characteristic vibrations belonging to the starting materials such as SO_2 (1157 and 1332 cm^{-1}),[13] Ar—H (3063 cm^{-1}), Ar—O—C (1249, 1200 cm^{-1}), *etc*., and the absence of N—H stretching vibrations. The mass spectrum (FAB positive, matrix *m*-nitrobenzyl alcohol) of **5**, which shows a molecular ion peak at $m/z = 914$ $[M + 1]^+$, confirms the proposed structure and rules out any polymeric or different macrocyclic forms.

The 17,18-dicyano-substituted dioxa-triaza macrocycle **7** was obtained from the dibromo derivative in 66% yield by refluxing in DMF with 3 equiv. of CuCN, according to the Rosenmund von Braun reaction.[14] The critical point in this route is to isolate the dicyano derivative, which was accomplished by keeping the concentration of the reactants sufficiently low and by making use of a moderately high boiling point solvent to avoid the formation of copper phthalocyanine.[15] In the IR spectrum of this compound, the intense absorption band at 2228 cm^{-1} corresponds to the $C\equiv N$ groups. The rest of the spectrum is closely similar to that of the precursor dibromo derivative, including the characteristic vibrations of the tosyl, ether, aromatic and aliphatic methylene groups. In the ^1H NMR spectrum of **7**, the aromatic protons of the cyano-substituted benzene appear as a singlet at $\delta = 7.53$ and the other chemical shifts are very similar to those of **5**. The ^{13}C NMR spectrum of **7** shows slightly different signals for the aromatic carbons due to the C—Br to $C—C\equiv N$ conversion, as expected. A close investigation of the mass spectrum of **7**, obtained by the FAB technique using *m*-nitrobenzyl alcohol matrix, in particular the region of the molecular ion ($m/z = 805$) and the other bigger fragment ions together with the corresponding leaving groups ($m/z = 650$ $[M - tosyl]^+$), confirm the proposed structure (Scheme 2).

Metallophthalocyanines have been synthesized either by the template reaction of dibromo derivatives of the macrocycle or by using isolated dicyano species of the above mentioned macrocycle as an intermediate step. The first route makes use of high boiling point solvents such as ethylene glycol or tetramethylurea (TMU) in the presence of CuCN to obtain the copper(II) phthalocyaninate complex **6**. The precipitated crude product was washed several times with ethanol to remove the unreacted organic material and was subsequently treated with a solution of NaCN in a mixture of water–ethanol (1 : 2) to separate the excess of CuCN.[16] It was then extracted with dichloromethane; the extract was dried over $MgSO_4$ and evaporated to dryness and the oily dark-green product was solidified by adding ethanol to obtain the pure product in 32% yield. As is the case with many phthalocyanines with bulky peripheral substituents, complex **6** was soluble in common organic solvents such as chloroform, dichloromethane, pyridine and dimethyl sulfoxide.[17] NMR measurements are precluded owing to the paramagnetic nature of the copper(II) phthalocyaninate core. However, comparison of the IR, UV/VIS and MS spectral and elemental analysis data gives sufficient support for the formation of the desired compound. Significant differences between the IR spectrum of the precursor dibromo compound **5** and the copper(II) phthalocyanine **6** do not appear clearly except in the C—Br vibrations. The value of the molecular ion observed shows good agreement with the calculated value for copper phthalocyanine ($m/z = 3301$ $[M + H_2O]^+$).



(6) M : Cu
(8) M : 2H
(9) M : Ni
(10) M : Co

The metal-free phthalocyanine **8** was obtained directly by the reaction of the dicyano derivative of the macrocycle **7** in hydroquinone as a uniphase fused melt in a Schlenk system; here, the two electrons required, in addition to the 16 π electrons of the 8 nitriles, to yield the 18 π-electron system of the phthalocyanine core were supplied by the oxidation of hydroquinone.[18] The yield of the product (32%) was fairly low as encountered for phthalocyanines with other bulky groups.[19] A diagnostic feature of the metal-free phthalocyanine formation from the precursor dicyano derivative **7** is the disappearance of the sharp C≡N vibration at 2228 cm^{-1} of the reactant. The stretching vibrations around 3467 cm^{-1} for **8** can be attributed to the N—H band of the inner core of the metal-free phthalocyanine. The rest of the infrared spectrum of **8** is closely similar to that of **7** and contains the characteristic stretching vibrations of tosyl and ether groups. Also, the NH protons of the metal-free phthalocyanine **8** could be identified easily in the ^1H NMR spectrum at $\delta = -5.85$, which shows the typical shielding of inner core protons as a broad band.[20] The high upfield shift of the cavity NH protons was also verified by deuterium exchange with D_2O. ^1H NMR investigations of the metal-free phthalocyanine **8** provided the characteristic chemical shifts for the expected structure. A common feature of the ^1H NMR spectrum of **8** is the broad absorption caused probably by the aggregation of Pc, which is frequently encountered at the concentrations used for NMR experiments.[19] The mass spectrum (FAB) of this compound supports the structure of the proposed formula; moreover, the peak at $m/z = 3068$ $[M - \text{tosyl} + 1]^+$ confirms the loss of the tosyl group.

The reaction of **7** in high boiling point dried solvents such as dimethylformamide or ethylene glycol with the appropriate metal salt gave the monomeric phthalocyanines **9** and **10** ($M = Ni^{II}$ or Co^{II}). One of the yields was fairly high (**9**, 52%) and the other one was rather low (**10**, 25%) and depended upon the metal ion, as expected. The most common characteristic feature of these complexes, **9** and **10**, is their high solubility in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, *N*,*N*-dimethylformamide and dimethyl sulfoxide. Cyclotetramerization of the dinitriles was confirmed by the disappearance of the sharp C≡N vibration at 2228 cm^{-1} of the precursor dicyano derivative **7**. The rest of the IR spectra of **9** and **10** are closely similar to those of **7**, including the characteristic vibrations of tosyl, aliphatic and aromatic groups. The ^1H NMR spectra of **8** and **9** are almost identical; the only difference that occurs is that the broad NH proton signals of **8** at *ca.* $\delta = -5.85$ disappear in **9**. Also, it should be mentioned that the peaks of the ^1H NMR spectrum are broad as encountered in some other soluble phthalocyanines. The aromatic protons, except on the tosyl groups, were shifted to lower field because of the π-electron ring current of the phthalocyanine core, even after complexation with Ni^{II}. ^1H NMR measurements are precluded owing to the paramagnetic nature of the cobalt(II) phthalocyanine **10**, similar to that of the copper(II) phthalocyanine. The formation of nickel(II) phthalocyanine is verified by the $[M - Ni - \text{tosyl}]^+$ peak at $m/z = 3065$, which has been measured by FAB mass spectroscopy. On the other hand, the mass spectrum of **10** did not exhibit a molecular ion; however, peaks at $m/z = 3083$, 2964, 2919 and 2403 were observed.

Phthalocyanines containing the 17-membered dioxa-triaza macrocycles **6**, **8**–**10**, show typical electronic spectra with two significant absorption regions: one of them in the visible region at 600–700 nm, which corresponds to the Q band attributed to the $\pi \rightarrow \pi^*$ transition from the HOMO to the LUMO of the Pc or Pc^{-2} rings, and the other in the UV region at 250–380 nm, which corresponds to the B band arising from the deeper Soret-like $\pi \rightarrow \pi^*$ transition.[21] The Q band in the metal-free species is no longer split and it appears to have three maxima of different intensities at 722, 682 and 654 nm. For the metallophthalocyanines **6**, **9**, **10**, the expected absorption appears around 681–672 nm in chloroform with the intense peak and shoulder on the higher energy side. Increasing the concentration leads to aggregation, which is easily monitored by the position of the Q band, which shifts to shorter wavelengths and the decrease in molar absorption coefficient. The intense absorptions at 681 nm (**6**) or 672 nm (**9**, **10**) are concentration dependent, decrease at higher values and give a shoulder around 645–622 nm, indicating the presence of aggregated species. The broadening of these absorptions was also explained as the result of the dimerization[1c] as well as a hypsochromic effect. On the other hand, while the monomeric species, in extremely dilute chloroform solution, with D_{2h} symmetry (metal-free derivative) shows two intense absorptions around 700 nm, the one having D_{4h} symmetry gives a single band in this region.[9]

Experimental

General methods

^1H and ^{13}C NMR spectra were recorded on Bruker ARX400 and Varian-Gemini 200 Fourier transform spectrometers. IR spectra were recorded on Perkin–Elmer 1600 and Mattson 1000 FTIR spectrophotometers as KBr pellets. Fast atom bombardment (FAB, matrix: *m*-nitrobenzyl alcohol) mass spectra of the phthalocyanines were measured on Kratos MS-50 triple analyzer and VG AutoSpec mass spectrometers. Optical spectra in the UV/VIS region were recorded with a Unicam UV2-100 spectrophotometer using 1 cm pathlength cuvettes at room temperature. Elemental analysis and metal contents of the compounds were performed on a Hewlett–Packard 185CHN analyzer and a Unicam 929 AA spectrometer, respectively. 1,2-Bis(2-chloroethoxy)benzene,[10] dipropylenetriaminetritosilate[11] and 1,2-dibromo-4,5-bis(bromomethyl)benzene[12] were prepared according to the reported procedures. Melting points were measured on an Electrothermal apparatus and are uncorrected.

Syntheses

1,2-Dibromo-4,5-bis(2-chloroethoxy)benzene, 2. A solution of bromine (42.4 g, 26.5 mmol) in glacial acetic acid (100 mL) was added dropwise to a solution of **1** (31.4 g, 31 mmol) in glacial acetic acid (150 mL) containing boron trifluoride ethyl ether complex (1 mL) for 4 h at 5 °C. Then the mixture was stirred 36 h at room temperature. During this time a copious amount of HBr evolved out of the solution and a precipitate appeared at the end of the reaction. Then the mixture was poured onto crushed ice (750 g) and stirred for 24 h. The resulting white solid was collected by filtration and washed with water, until the filtrate was neutral, and then dried *in vacuo*. The crude product was recrystallized from ethanol to yield white crystals. Yield: 39 g, 74.5%, mp 80 °C. Anal. calcd for $C_{10}H_{10}O_2Br_2Cl_2$: C, 30.53; H, 2.54. Found: C, 30.65; H, 2.43%. IR (KBr pellets, cm^{-1}): 3039 (Ar—H), 2990–2866 (C—H), 1254–1213 (Ar—O—C), 667 (C—Br), 657 (C—Cl). ^1H NMR ($CDCl_3$) δ: 7.16 (s, 2H, aromatic H), 4.30 (t, 4H, CH_2O), 3.86 (t, 4H, CH_2Cl); ^{13}C NMR ($CDCl_3$) δ: 150.39, 122.49, 118.48, 79.04, 43.75. MS (FAB positive, matrix: *m*-nitrobenzylalcohol) *m*/*z*: 394 $[M + 1]^+$, 393 $[M]^+$.

1,2-Dibromo-4,5-bis(2-iodoethoxy)benzene, 3. 2 (20 g, 50 mmol) was dissolved in dry acetone (500 mL) containing anhydrous NaI (30.3 g, 200 mmol) under an argon atmosphere and refluxed for 48 h. After a while, the solution turned cloudy and then the solid product precipitated. At the end of the refluxing period, the reaction mixture was cooled to room temperature and the precipitate was filtered off and washed with dry acetone. The mother liquor and the washing solvents were combined and evaporated to dryness. The oily residue was redissolved in chloroform (300 mL) and the organic phase was washed with water (2 × 150 mL) and dried over anhydrous $MgSO_4$. After filtration of the drying agent, the filtrate was evaporated to 15 mL, then the oily residue was placed in a refrigerator. The star-shaped crystals were separated by filtration and dried *in vacuo* at room temperature. Yield: 19.4 g, 67.3%, mp 73–75 °C. Anal. Calcd for $C_{10}H_{10}O_2Br_2I_2$: C, 20.79; H, 1.73. Found: C, 20.97; H, 1.60. IR (KBr pellets, cm^{-1}): 3028 (Ar—H), 2935–2866 (C—H), 1255–1209 (Ar—O—C), 666 (Ar—Br), 532 (C—I). ^1H NMR ($CDCl_3$) δ: 7.14 (s, 2H, aromatic H), 4.28 (t, 4H, CH_2O), 3.47 (t, 4H, CH_2I); ^{13}C NMR ($CDCl_3$) δ: 150.11, 122.42, 118.47, 72.72, 42.19. MS (FAB positive) *m/z*: 576 $[M]^+$, 575 $[M-1]^+$, 577 $[M+1]^+$.

17,18-Dibromo-4,8,12-tri(toluene-*p*-sulfonyl)-1,2,3,4,5,6,7,8,9,10,11,12,13,14,15-pentadecahydrobenzo[1.15]dioxa[4.8.12]triazacycloheptadecine, 5. A 1 L round-bottom flask containing anhydrous dimethylformamide (300 mL) fitted with a condenser was evacuated, refilled three times with argon and connected to a vacuum line. Under argon the flask was charged with dipropylenetriamine tritosilate (2.19 g, 5 mmol) and finely ground anhydrous Cs_2CO_3 (3.42 g, 10.5 mmol) and the mixture was stirred at room temperature. A solution of **3** (2.88 g, 5 mmol) in dry DMF (30 mL) was added dropwise to this mixture over 3 h and the reaction mixture was stirred at room temperature for 4 days. The reaction was monitored by thin layer chromatography [acetone–chloroform–petrolum ether (4 : 6 : 2)]. After evaporation of the reaction mixture to dryness, the oily residue was dissolved with dichloromethane (200 mL), then insoluble parts of the mixture were removed by filtration and washed with water (3 × 100 mL) and dried over anhydrous $MgSO_4$. The mixture was filtered off, washed with dry dichloromethane and evaporated to dryness to give an oily substance, which was dissolved in dichloromethane and purified by silica gel column chromatography. The elution was carried out successively with dichloromethane–hexane (70 : 30). The eluates were combined and concentrated to 20 mL and hexane was added until the beginning of a cloudy precipitate appeared, then the mixture was filtered off, washed with hexane and dried *in vacuo* to give a pale yellow crystalline powder. Yield: 3.11 g, 68%, mp 64–66 °C. Anal. calcd for $C_{37}H_{43}N_3O_8S_3Br_2$: C, 48.63; H, 4.70; N, 4.60. Found: C, 48.51; H, 4.55; N, 4.78. IR (KBr pellets, cm^{-1}): 3063 (Ar—H), 2992–2870 (C—H), 1332 (SO_2), 1249–1200 (Ar—O—C), 1157 (SO_2), 653 (C—Br). ^1H NMR ($CDCl_3$) δ: 7.70 (m, 6H, aromatic H), 7.35 (s, 2H, aromatic H), 7.26 (m, 6H, aromatic H), 4.27–4.06 (m, 4H, $-OCH_2$), 3.81 (t, 8H, NCH_2), 3.08–2.94 (m, 8H, CH_2), 2.40 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 150.08, 145.62, 138.33, 131.71, 129.08, 122.55, 119.84, 72.23–70.77, 50.30, 48.82, 43.77, 31.13, 23.49. MS (FAB positive) *m/z*: 950 $[M+2H_2O+1]^+$, 914 $[M+1]^+$, 758 $[M-\text{tosyl}]^+$.

17,18-Dicyano-4,8,12-tri(toluene-*p*-sulfonyl)-1,2,3,4,5,6,7,8,9,10,11,12,13,14,15-pentadecahydrobenzo[1.15]dioxa[4.8.12]triazacycloheptadecine, 7. A Schlenk tube was charged with the precursor dibromo compound (**5**) (2.29 g, 2.5 mmol), CuCN (0.67 g, 7.5 mmol) and dry DMF (25 mL) under argon atmosphere at room temperature. The reaction mixture was held and stirred at 175–180 °C for 12 h in an oil bath. During this time, the reaction mixture became dark brown-green. The heating was stopped and the reaction mixture was allowed to cool to room temperature, opened to air and diluted with aqueous NH_4OH (100 mL) and air was passed through the solution for 24 h. During this period, the solution became dark blue and a green precipitate was formed. The reaction mixture was filtered through a filter agent (Celite) and washed with dilute aqueous NH_4OH (10%) and with water until the filtrate was neutral and then dried. The obtained crude product was purified by column chromatography (silica gel; $CHCl_3$–petrolum ether, 5 : 1). Yield: 1.34 g, 66%, mp 178–180 °C. Anal. calcd for $C_{39}H_{43}N_5O_8S_3$: C, 58.13; H, 5.34; N, 8.69. Found: C, 58.28; H, 5.18; N, 8.84. IR (KBr pellets, cm^{-1}): 3062 (Ar—H), 2927–2873 (C—H), 2228 (C≡N), 1332 (SO_2), 1270–1215 (Ar—O—C), 1158 (SO_2). ^1H NMR ($CDCl_3$) δ: 7.65 (m, 6H, aromatic H), 7.53 (s, 2H, aromatic H), 7.37 (m, 6H, aromatic H), 4.17–4.07 (m, 4H, OCH_2), 3.73 (t, 8H, NCH_2), 3.02–2.90 (m, 8H, CH_2), 2.38 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 148.92, 144.87, 137.80, 131.39, 128.61, 121.47, 118.72, 116.67, 71.86–69.55, 48.01, 42.60, 42.18, 30.28, 22.72. MS (FAB positive) *m/z*: 806 $[M+1]^+$, 650 $[M-\text{tosyl}]^+$.

[Dodecakis(*N*-*p*-tosyl)-tetrakis-macrocycle-phthalocyaninato]copper(II), 6. Compound **5** (0.82 g, 0.9 mmol), CuCN (0.23 g, 2.6 mmol) and dry tetramethylurea (1 mL) were mixed in a well-stoppered Schlenk tube under an argon atmosphere. The mixture was heated and stirred at 180–185 °C for 6 h under inert conditions. After cooling to room temperature, the dark-green product was precipitated by pouring into ethanol (10 mL) and filtered off, then washed with ethanol. The crude product was then refluxed several times with a solution of NaCl in a mixture of water–ethanol (1 : 2) to remove the excess of CuCN, which subsequently was filtered off and the filtrate evaporated to dryness under vacuum. The crude product was dissolved in chloroform (10 mL) and washed with water, then dried over anhydrous $MgSO_4$. The drying agent was removed by filtration and the filtrate was evaporated to dryness. The oily dark-green residue was reprecipitated by adding ethanol and the precipitate was collected by filtration, then washed with ethanol and diethyl ether and dried *in vacuo*. Yield: 0.2035 g, 32%, mp 143–145 °C. Anal. calcd for $C_{156}H_{172}N_{20}O_{32}S_{12}Cu$: C, 57.01; H, 5.23; N, 8.52; Cu, 1.93. Found: C, 56.87; H, 5.11; N, 8.69; Cu, 2.12. IR (KBr pellets, cm^{-1}): 3065 (Ar—H), 2930–2880 (C—H), 1333 (SO_2), 1287–1221 (Ar—O—C), 1156 (SO_2). UV/VIS (in $CHCl_3$) λ_{max}/nm (10^{-5} ε/L mol^{-1} cm^{-1}): 722 (4.08), 681 (4.86), 644 (4.69), 624 (4.13), 417 (5.47), 384 (6.65), 342 (4.89), 294 (5.38), 243 (4.78). MS (FAB positive) *m/z*: 3301 $[M+H_2O]^+$.

Metal-free[dodecakis(*N*-*p*-tosyl)-tetrakis-macrocycle-phthalocyanine], 8. A mixture of the dicyano derivative of the macrocycle (**7**) (0.30 g. 0.37 mmol) and hydroquinone (0.041 g, 0.37 mmol; freshly purified by sublimation) was placed in a well-stopped Schlenk tube under argon atmosphere. The mixture was gently heated up to 200–210 °C and allowed to stand at this temperature for 6 h. During this time, the colour of the solution changed from purple to dark-green. At the end of the period, the reaction mixture was cooled to room temperature and dissolved in dichloromethane (15 mL) and then filtered. The extract was washed several times with water and preabsorbed onto silica gel (5 g), then the absorbed product was placed in the thimble of a Soxhlet extractor and extracted for 4 h with dichloromethane. The extract was evaporated to dryness and the oily dark-green product was precipitated by adding and stirring with ethanol (20 mL). It was filtered off and washed with water, ethanol and diethyl ether and then dried *in vacuo* to give a green powder. Yield: 0.096 g, 32%, mp 160–162 °C. Anal. Calcd for $C_{158}H_{174}N_{20}O_{32}S_{12}$: C, 58.10; H, 5.40; N, 8.69. Found: C, 58.28; H, 5.26; N, 8.51. IR (KBr pellets, cm^{-1}): 3467 (N—H), 3062 (Ar—H), 2924–2873 (C—H), 1334 (SO_2), 1289–1214 (Ar—O—C), 1157 (SO_2). ^1H NMR ($CDCl_3$) δ: 7.69 (m, 24H, aromatic H), 7.35 (m, 32H, aromatic H), 4.27–4.00 (m, 16H, OCH_2), 3.70 (m, 32H, NCH_2), 3.00 (m, 32H, CH_2), 2.49 (s, 36H, CH_3), -5.85 (br, 2H, NH). UV/VIS (in $CHCl_3$) λ_{max}/nm (10^{-5} ε/L mol^{-1} cm^{-1}): 728 (3.95), 682 (4.81), 654 (4.51), 592 (4.41), 404 (4.93), 340 (4.27), 294 (6.13), 243 (4.61). MS (FAB positive) *m*/*z*: 3068 $[M - \text{tosyl} + 1]^+$.

[Dodecakis(*N*-*p*-tosyl)-tetrakis-macrocycle-phthalocyaninato]nickel(II), 9. A well-stopped Schlenk tube was charged with **7** (0.30 g, 0.37 mmol), anhydrous $NiCl_2$ (0.012 g, 0.093 mmol) and dry dimethylformamide (2.5 mL) under argon and held at 160 °C for 24 h. After cooling to room temperature, the dark-green reaction mixture was diluted and precipitated with a mixture of ethanol–water (1 : 1, 125 mL). The resulting dark-green precipitate was filtered off, washed with hot ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.16 g, 52%, mp 202–205 °C. Anal. calcd for $C_{156}H_{172}N_{20}O_{32}S_{12}Ni$: C, 57.09; H, 5.24; N, 8.53; Ni, 1.79. Found: C, 56.93; H, 5.38; N, 8.74; Ni, 1.61. IR (KBr pellets, cm^{-1}): 3068 (Ar—H), 2927–2880 (C—H), 1334 (SO_2), 1289–1213 (Ar—O—C), 1157 (SO_2). ^1H NMR (DMSO-d_6) δ: 7.64 (m, 24H, aromatic H), 7.38 (m, 32H, aromatic H), 4.17–4.03 (m, 16H, OCH_2), 3.64 (m, 32H, NCH_2), 2.97 (m, 32H, CH_2), 2.35 (s, 36H, CH_3); ^{13}C NMR (DMSO-d_6) δ: 155.69, 144.98, 144.36, 137.76. 131.55. 128.64, 120.96, 118.03, 71.51–69.58, 47.70, 42.43, 39.16, 30.25, 22.72. UV/VIS (in $CHCl_3$) λ_{max}/nm (10^{-5} ε/L mol^{-1} cm^{-1}): 711 (4.06), 672 (4.85) 642 (4.59), 612 (4.53), 498 (4.19), 338 (5.42), 294 (4.91), 243 (6.24). MS (FAB positive) *m*/*z*: 3065 $[M - Ni - \text{tosyl}]^+$.

[Dodecakis(*N*-*p*-tosyl)-tetrakis-macrocycle-phthalocyaninato]cobalt(II), 10. A mixture of **7** (0.20 g, 0.25 mmol), anhydrous $CoCl_2$ (0.009 g, 0.068 mmol), ammonium molybdate (0.0013 g) and ethylene glycol (2 mL) was placed in a well-stopped Schlenk tube under argon atmosphere, then the mixture was heated at 190–200 °C for 6 h. The mixture was cooled to room temperature and precipitated by adding ethanol (20 mL). The precipitate that formed was filtered off and washed with water and ethanol. The crude product was dissolved in hot THF (20 mL) and the solution added dropwise into cold ethanol (35 mL), with stirring, to precipitate the product. It was filtered off, washed with ethanol and then with diethyl ether and dried *in vacuo*. Yield: 0.051 g, 25%, mp 196–198 °C. Anal. calcd for $C_{156}H_{172}N_{20}O_{32}S_{12}Co$: C, 57.09; H, 5.24; N, 8.53; Co, 1.79. Found: C, 57.28; H, 5.11; N, 8.72; Co, 1.58. IR (KBr pellets, cm^{-1}): 3063 (Ar—H), 2924–2870 (C—H), 1339 (SO_2), 1283–1210 (Ar—O—C), 1158 (SO_2). UV/VIS (in $CHCl_3$) λ_{max}/nm (10^{-5} ε/L mol^{-1} cm^{-1}): 714 (3.91), 672 (4.98), 645 (4.56), 608 (4.51), 498 (4.34), 387 (5.08), 342 (5.73), 291 (6.26), 243 (5.48). MS (FAB positive) *m*/*z*: 3083 $[M - Co - \text{tosyl} + H_2O]^+$, 2964, 2919, 2403.

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