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Synthesis and Characterization of New Metal-free and Metallophthalocyanines Containing Macrobicyclic Moieties

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The metal-free 5,10 and metallophthalocyanines 11–13 (M = Ni, Zn, Cu) fused in peripheral positions with diazadithiatetraoxa or diazahexaoxamacrobicycles have been prepared by bicyclotetramerization of the newly synthesized isoindolinediimine derivatives of cryptands 4,9 or dicyano substituted macrobicycles 3,8 in the presence of the corresponding metal salts or a strong organic base. The new compounds have been characterized by elemental analysis, ^{1}H and ^{13}C-NMR, IR, UV-visible and mass spectral data.

Keywords: Macrobicycle; Metal-free phthalocyanine; Metallophthalocyanine; Synthesis; Isoimino-indoline

INTRODUCTION

Phthalocyanines and their metal complexes have attracted considerable attention as a result of their diverse optical, electronic and coordination properties which have led to wide- ranging research for over 60 years [1–3]. In the last 20 years phthalocyanine chemistry is undergoing a renaissance because these compounds and their derivatives exhibit singular and unconventional properties interesting for applications in the areas of non-linear optics, liquid crystals, electrochromic processes involving thin films, gas or chemical sensors photosensitizers, catalysts and for mercaptan oxidations and as therapeutic agents in pharmacology [4–9]. A disadvantage of phthalocyanines is their limited solubility in common organic solvents. For most of these applications, phthalocyanines with long chains or macrocyclic moieties [10,11] had to be synthesized in order to facilitate the above mentioned purposes and to enhance solubility.

Cryptands in general is a polymacrocyclic ligand system of three-dimensional structure being able to encapsulate a metal ion. The remarkable group of these compounds was introduced by Lehn and his co-workers in 1969 [12–14]. Owing to their architectural and functional plasticity, macrobicyclic compounds are especially attractive for designing both bio-mimetic and abiotic receptor molecules for inorganic and organic substrates [15–17]. These compounds show extraordinary solubility and selectivity towards specific alkali and alkaline earth metal ions leading to complexation in aqueous and organic solutions, indeed more so than crown ethers [18,19].

The present paper reports the synthesis of metal-free phthalocyanines containing four mixed donor macrobicyclic moieties in the molecule; preliminary account of this work has been reported [20]. In the present paper, we describe the synthesis and characterization of the new class of metal-free and metallophthalocyanines, the diazadithiatetraoxa or diazahexaoxamacrobicyclic moieties and the phthalocyanines which may allow novel functionalized materials to be of importance in the preparation of analytical chemistry as new kinds of alkali or alkaline earth metal extraction agents.

RESULTS AND DISCUSSION

The synthesis of metal-free phthalocyanines **5,10** have been described in a preliminary communications [20] and summarized in Scheme 1.

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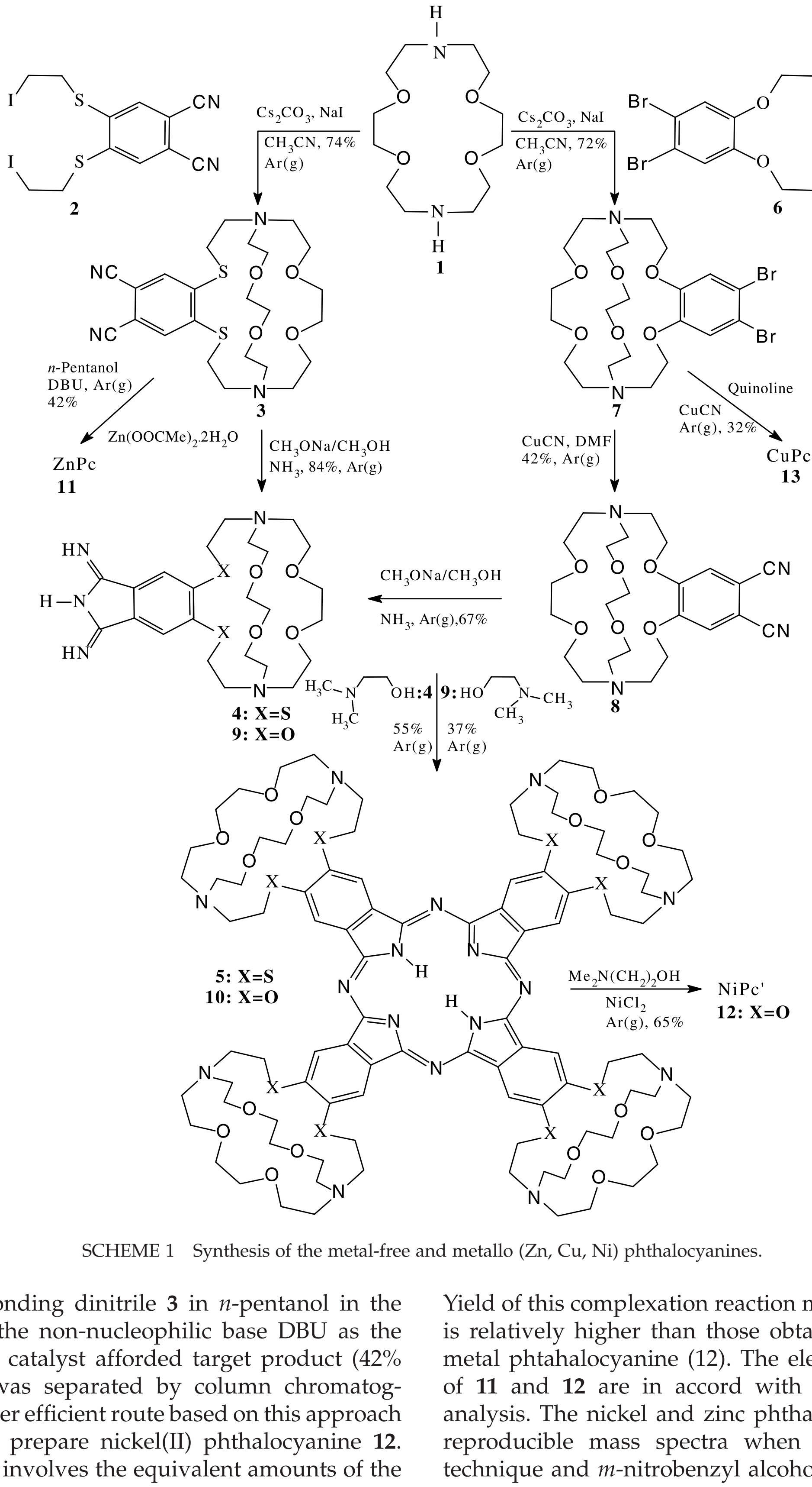
1,7,10,13-Tetraoxa-4,16-diazacyclooctadecane **1** [21–23] was reacted with a 25% excess of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene **2** [24,25] or 1,2-dibromo-4,5-bis(2-iodoethoxy)benzene **6** [26] in dry acetonitrile containing 0.25 equivalent of NaI and finely ground anhydrous Cs_2CO_3 as a template. Final purification by recrystallization or chromatography afforded products **3** and **7** in 74% and 72% yields, respectively. Analytical and spectroscopic data of **3** and **7** clearly confirm the success of the cyclization reaction. ^{1}H-NMR spectra of these compounds, the chemical shifts of NH protons in starting compound **1** disappear after the macrobicyclization reaction. The other resonances in the ^{1}H-NMR spectra, concerning methylene and aromatic protons are very similar to those of the precursor compounds. The proton-decoupled ^{13}C-NMR spectrum of **3** clearly indicates the presence of nitrile carbon atom at $\delta = 114.89$ ppm as ex-pected and for **5** is also in good agreement with the proposed structure. The IR spectrum of **3** was easily verified with the disappearance of N–H and presence of C≡N stretching vibrations at $2228\,cm^{-1}$. The difference between the IR spectrum of **1** and **7** is clear from the absence of characteristic vibrations such as N-H and C-I at $532\,cm^{-1}$ [27,28]. The compounds **3** and **7** displayed the expected molecular ion peaks at $m/z = 506$ $[M]^+$ and 582.1 $[M]^+$, respectively, in their mass spectra using the FAB technique and *m*-nitrobenzyl alcohol as matrix.

The conversion of the dibromo derivative of the diazahexaoxamacrobicycle **7** into the dicyano analogue **8** was performed in 42% yield after chromatographic separation from undesired byproducts by refluxing in a moderately high-boiling solvent such as dry DMF to avoid the formation of copper phthalocyanine derivatives [29,30], with an excess of CuCN, according to the Rosenmund von Braun reaction [31–33]. In the IR spectrum of this compound, the intense absorption at $2230\,cm^{-1}$ corresponds to the C≡N formation. The ^{1}H-NMR spectrum of **8** is in a good accord with the proposed structure. The aromatic protons of the cyanosubstituted benzene appear as a singlet at $\delta = 7.24$ ppm and the other chemical shifts are very similar to those of **7**. The ^{13}C-NMR spectrum of **8** shows slightly different signals at $\delta = 115.67$ ppm for the aromatic carbons due to the C–Br to C–C≡N conversion as expected. The signal at around 113.30 ppm related to C≡N groups are also consistent with the proposed structure. The mass spectrum of **8** contained an intense peak at $m/z = 474$ $[M]^+$ for the parent ion, which can be attributed to the formation of dicyano derivative. 1,3-Diiminoiso-indoline derivatives **4,9** were prepared following the standard Linstead procedure, bubbling ammonia gas through the solution of corresponding dicyano derivative **3,8** in dry methanol in the presence of catalytic amounts of sodium methoxide for over 8 h [34–38]. The isolation of these compounds **4,9** required column chromatographic separation on silica gel using methanol: chloroform (8:2) or methanol:dichloromethane (25:1) as eluents and gave 84% or 67% yields, respectively. The disappearance of the C≡N stretching vibrations belonging to the precursor dicyano compounds **3,8** and the appearance of new resonances concerning with imino groups at 3434 and $3348\,cm^{-1}$ confirm the formation of diiminoindoline derivatives. In the ^{1}H-NMR spectra of the compounds **4** and **9**, the chemical shifts which are characteristic of deuterium-exchangeable NH protons, appeared as the broad signal at $\delta = 8.46$ and 8.87 ppm, respectively. ^{13}C-NMR spectra of **4** and **9**, the disappearance of the C=N signals, along with the appearance of novel chemical shifts at $\delta = 169.18$ and 168.76 ppm concerning C=NH groups, are in good agreement with the desired structure. This is also supported by the presence of the characteristic molecular ion peaks at $m/z = 523$ $[M]^+$ and 491 $[M]^+$, respectively, in the mass spectra obtained using the FAB technique.

Condensation of four molecules of the diisoiminoindoline derivatives **4,9** into the metal-free phthalocyanines were carried out in 2-(dimethylamino)ethanol at reflux for 48 or 52 h under argon atmosphere and afforded the target compounds **5,10** in 55% or 37% yield, respectively, as the green amorphous solids after purification by using column chromatography on silica gel. The ^{1}H-NMR spectrum of the tetrameric metal-free phthalocyanine **5** showed the typical shielding of inner core protons as a broad resonance at $\delta = -3.85$ ppm which was attributed to the NH protons and identified easily with deuterium exchange. The inner core protons could not be observed in the proton NMR spectrum of **10** [39]. In the ^{13}C-NMR spectra of metal-free phthalocyanines, all signals are identical for the precursor isoiminoindoline derivatives of **4** and **9** except for the imino carbon atoms. The appearance of C=N signals which appear at $\delta = 152.66$ ppm for **5** and 152.17 ppm for **10** concerning the inner core instead of C=NH signals in **4** and **9** are supported the formation of phthalocyanines **5,10**. Bicyclotetramerization of the diiminoisoindoline derivatives were also confirmed by the disappearance of the sharp N–H vibrations at 3394 and $3415\,cm^{-1}$ in the IR spectra of **5** and **10**. The mass spectra of **5** and **10** showed the molecular ion peaks at m/z = 2027.2 $[M]^+$ and 1899 $[M + 1]^+$, respectively, and the fragmentation pattern closely following that of **4** and **9** indicating the high stability of the phthalocyanine moieties.

To prepare the metallophthalocyanines (M = Ni, Zn), different routes have been employed in Scheme 1. The conversion into zinc(II) phthalocyanine **11** was carried out by treatment with equivalent amounts of zinc(II) acetate dihydrate



SCHEME 1 Synthesis of the metal-free and metallo (Zn, Cu, Ni) phthalocyanines.

and corresponding dinitrile **3** in *n*-pentanol in the presence of the non-nucleophilic base DBU as the ring-forming catalyst afforded target product (42% yield) that was separated by column chromatography. Another efficient route based on this approach was used to prepare nickel(II) phthalocyanine **12**. This method involves the equivalent amounts of the anhydrous nickel(II) chloride and corresponding metal-free phthalocyanine **10** in 2-(dimethylamino) ethanol under argon atmosphere. Finally, nickel(II) phthalocyanine **12** was prepared in a 65% yield. Yield of this complexation reaction mentioned above is relatively higher than those obtained for similar metal phtahalocyanine (12). The elemental analysis of **11** and **12** are in accord with their calculated analysis. The nickel and zinc phthalocyanines gave reproducible mass spectra when using tha FAB technique and *m*-nitrobenzyl alcohol as matrix, and here we observed the M + 1 peaks, instead of molecular ions in **11** and **12** at m/z = 2091.4 and 1955.3 respectively. The ^{1}H-NMR spectra of Ni(II) and Zn(II) phthalocyanines were almost identical with those of the corresponding metal-free phthalocyanines, a significant difference being the disappearance of the broad inner core NH protons of **5** and **10**. The other differences in proton NMR data between metal-free phthalocyanines and metallophthalocyanines were the broad absorptions encountered in the case of compounds **11** and **12** [40–42] which were the result of aggregation of planar phthalocyanine molecules at the high concentration generally used in NMR measurements. The other characteristic NMR signals of **11** and **12** were quite similar to those of the precursor dicyano compounds **3** and metal-free phthalocyanine **10**. The significant difference between the IR spectra of dinitrile and metal-free phthalocyanine H_2Pc and metallophthalocyanines MPcs (M=Ni, Zn) was the disappearance of N-H stretching vibrations of the phthalocyanine core.

The bicyclotetramerization reaction of **7** was performed in dry quinoline in an excess amount of CuCN to obtain the copper(II) phthalocyanine **13** (Scheme 1). Heating and stirring the dibromo compound **7** at 210°C for 24 h in a standard Schlenk system under an argon atmosphere yielded a dark green reaction mixture which was diluted with ethanol: water (1:1) and refluxed to give the deep green crude product. Purification of this compound to analytical purity required column chromatographic separation on neutral alumina using chloroform-methanol (100:1) as eluent and gave an 32% yield. The IR spectra of **7** and **13** were dominated by macrobicycle vibrations. These spectra are very similar to those of the precursor compound and metal-free phthalocyanine **10**. The comparison of the infra-red data for this compounds gave sufficient support for the proposed structure. A diagnostic feature of the copper(II) phthalocyanine formation from the dibromo derivative of macrobicycle **7** was the disappearance of the C-Br absorption at 651 cm^{-1} of the starting material and the appearance of new vibrations at 1620 cm^{-1} concerning the C=N bands. A close investigation of the mass spectrum of the copper(II) phthalocyanine at $m/z = 1960.2$ $[M + 1]^+$ also confirmed the formation of the target complexation.

The UV-visible spectra of the metal-free phthalocyanines **5** in chloroform and **10** in chloroform in pyridine at room temperature are displayed in Figures 1–2. These spectra show the two characteristic intense the Q and B bands of metal-free phthalocyanines. The split Q bands for compound **5** and **10** in chloroform solution, which are the characteristics of this class of compounds, are observed at $\lambda = 736$, 706, 671 and 696, 676, 625 nm suggesting monomeric species, respectively. These two absorptions around 700 nm [43,44] are due to the $\pi \rightarrow \pi^*$ transition of the fully conjugated 18 π electron system [45,46]. The compound **5** and **10** have D_{2h} symmetry according to their UV-Vis spectra taken in chloroform whereas the

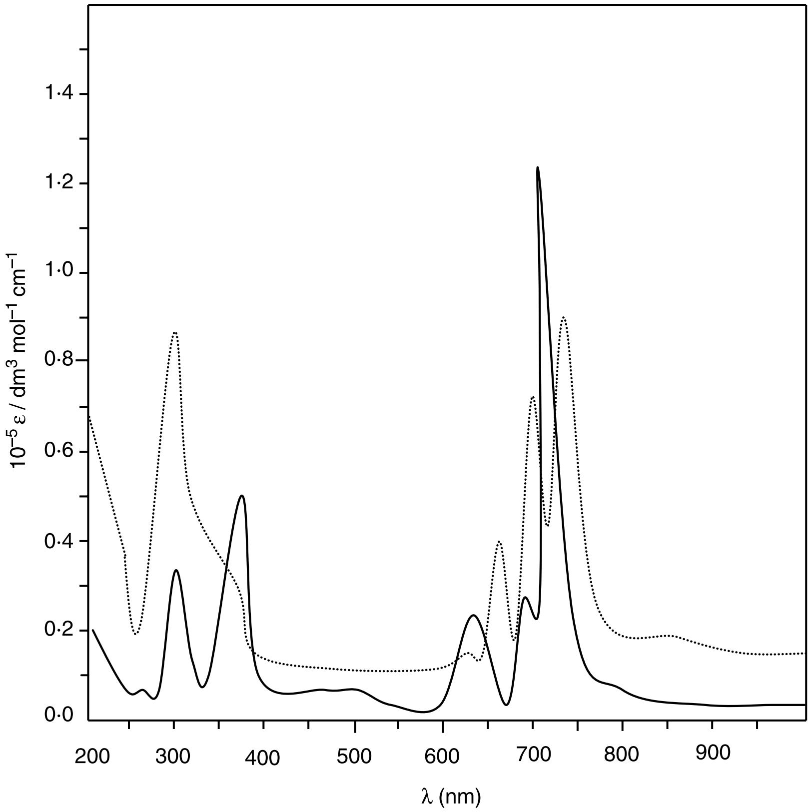


FIGURE 1 UV-VIS spectra of **5** (dotted line) in chloroform (1×10^{-5} M) and **11** (solid line) in pyridine (1×10^{-5} M).

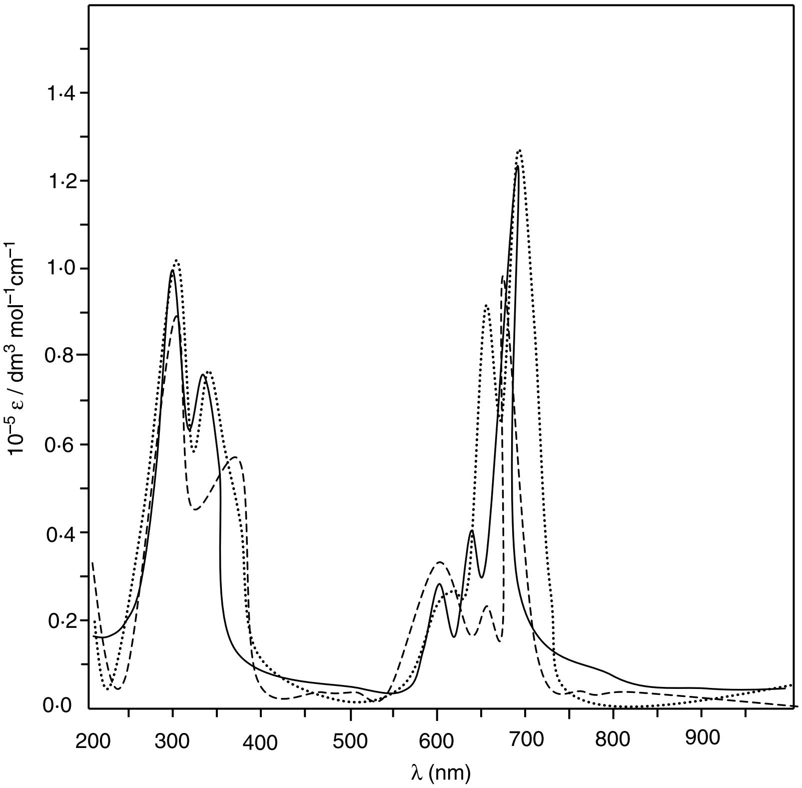


FIGURE 2 UV-VIS spectra of **10** (—) in pyridine (1×10^{-5} M), **10** (···) in chloroform (1×10^{-5} M) and **12** (---) n pyridine (1×10^{-5} M).

compound **10** has D_{4h} symmetry according to its UV-Vis spectrum in pyridine. Under normal conditions it is expected that these two products should have the same symmetry in chloroform or pyridine. However the compound **10** most likely was deprotonated in pyridine. That's the reason why their UV-Vis spectrum are different from each other.

The UV-visible spectra of solutions of metallophthalocyanines in pyridine at room temperature are shown in Figures 1–3. The Zn(II) (**11**), Ni(II) (**12**) and Cu(II) (**13**) phthalocyaninates showed the expected absorptions at main peaks of the Q and B bands appearing at 716, 687, 680, 678 and 329, 330, 315 nm, respectively. These results are typical of those of metal complexes of phthalocyanines with D_{4h} symmetry [47,48]. The longer wavelength encountered for the intense band of phthalocyaninatozinc(II) (**11**) is especially noteworthy. The shift of this band to the near-IR region is a result of S-substitution [49]. However, the presence of the shoulder at 687, 644, 652 and 614 nm corresponds to the monomeric and aggregated species in pyridine. Upon dilution (ca. 1×10^{-6} M), the absorption spectra of these compounds showed significant changes in band positions and molar absorptivities [50]. Increasing the concentration (1×10^{-4} M to 1×10^{-5} M) led to aggregation, which is easily monitored by the position of the Q-band, which shifted to shorter wavelengths and showed a decrease in molar absorption coefficient. On the other hand, since four bulky macrobicyclic groups are bound to the periphery of the metallophthalocyanines, the aggregations are not efficient as expected.

EXPERIMENTAL

^{1}H,^{13}C NMR and IR spectra of the compounds were recorded on a Varian XL-200 and on a Perkin-Elmer Spectrum one spectrometer. Fast atom bombardment mass spectra were recorded on a Varian MAT 711 and on a VG ZapSpec spectrometer using *m-nitrobenzyl* alcohol as matrix. The elemental analysis of the compounds were determined on a Hewlett-Packard 185 CHN analyser. The metal contents of the metallophthalocyanines were determined with a Unicam 929 AA spectrophotometer. Electronic spectra were recorded on a Unicam UV2-100 spectrophotometer. 1,7,10,13-Tetraoxa-l,16-diazacyclooctadecane (**1**) [21–23], 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene (**2**) [24,25] and 1,2-dibromo-4,5-bis(2-iodo-ethoxy) benzene (**3**) [26] were prepared as described previously. All solvents were reagent grade and purified according to the standard procedure [51].

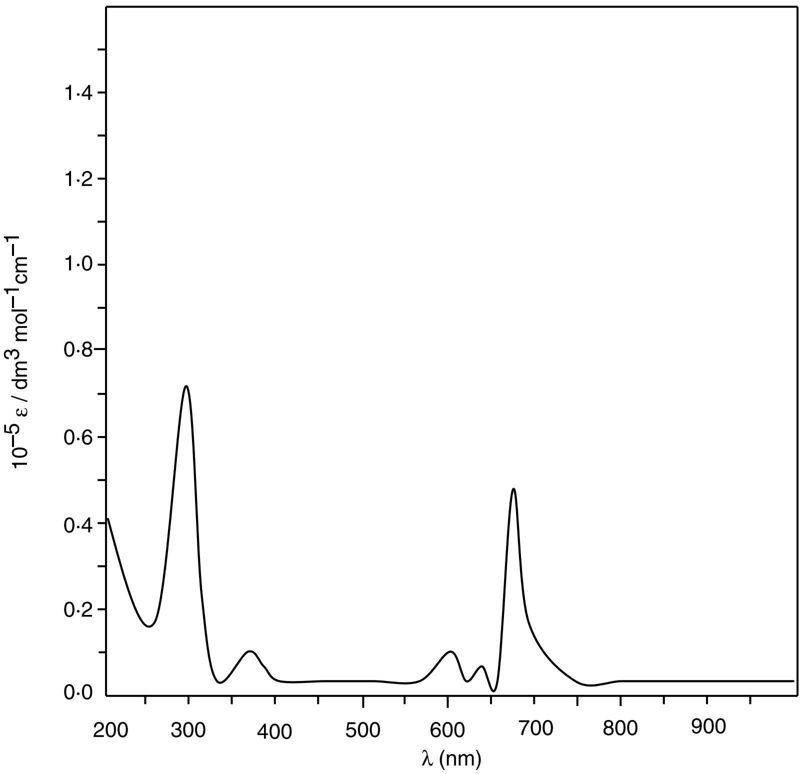


FIGURE 3 UV-VIS spectra of **13** in pyridine(1×10^{-5} M).

13,16,21,24-TETRAOXA-4,7-DITHIA-5,6-(4′,5′-DICYANOBENZO)-1,10-DIAZABICYCLO [8.8.8]HEXACOSANE (3)

A round-bottom flask containing dry acetonitrile (150 cm^3) and fitted with a condenser was evacuated, refilled three times with argon and connected to a vacuum line. Under argon, the flask was charged with **1** (1.05 g, 4 mmol), a three-fold excess of finely ground anhydrous Cs_2CO_3 (3.15 g, 12 mmol) and anhydrous NaI (0.3 g, 2 mmol) and the mixture was stirred at 45°C for 30 min. A solution of **2** (2.5 g, 5 mmol) in dry acetonitrile (25 cm^3) was added to this mixture and the reaction mixture was refluxed under argon for 5 days. The reaction was monitored by a thin layer chromatography [chloroform:petroleum ether:methanol (7:2:1)]. At the end of this period, the mixture was cooled to room temperature and filtered off, washed with dry acetonitrile and dichloromethane. The major liquior and the washing solvents were combined and evaporated to dryness under reduced pressure. The oily residue was chromatographed on silica gel [chloroform:petroleum ether: methanol (7:2: 1)] to give a pale brown solid. Yield: 1.5 g (74%), mp 204°C. Found (Calc. for $C_{24}H_{34}N_4O_4S_2$): C, 56.73 (56.92); H, 6.55 (6.72); N, 11.28 (11.06). IR (KBr pellets, cm^{-1}): 3078, 2942–2830, 2228, 1596, 1564, 1262, 1223, 1120. ^{1}H-NMR ($CDCl_3$): δ 7.51 (s,2H, ArH), 3.76 (m, 16H, CH_2O), 3.42 (m, 12H, CH_2N), 2.89 (s, 4H, CH_2S). ^{13}C-NMR ($CDCl_3$): δ 138.34 (ArCS), 132.37 (ArCH), 114.89 (C≡N), 112.73 (ArC), 68.67–66.76 (CH_2O), 54.13 (CH_2N), 28.02 (CH_2S). MS (FAB positive): m/z 506 [M]$^+$.

3,16,21,24-TETRAOXA-4,7-DITHIA-5,6-(4′,5′-ISOIMINOINDOLINE)-1,10-DIAZABICYCLO [8.8.8] HEXACOSANE (4)

A dry sodium methoxide (0.27 g, 5 mmol) in 20 cm^3 of dry methanol was added to a solution of **3** (1.265 g, 2.5 mmol) in methanol/*n*-buthanol mixture [200 cm^3 (3:1, v/v)] under argon atmosphere. Anhydrous ammonia was bubbled through the reaction mixture for 8 h at reflux temperature. The reaction was monitored by TLC using methanol:chloroform (8:2). At the end of this period, the ammonia inlet was stopped and the reaction mixture was evaporated to dryness under reduced pressure. The crude product was purified on silica gel using methanol:chloroform (8:2) as eluent. The eluent was evaporated to dryness and washed with petroleum ether and then dried *in vacuo.* The greenish yellow solid was crystallized from methanol. Yield: 1.1 g (84%), mp 215°C (dec.). Found (Calc. for $C_{24}H_{37}N_5O_4S_2$): C, 55:29 (55.06); H, 7.22 (7.07); N, 13.19 (13.38). IR (KBr pellets, cm^{-1}): 3434, 3248, 3072, 2942–2845, 1624, 1587, 1543, 1278, 1143. ^{1}H-NMR ($CDCl_3$): δ 8.46 (br, 3H, NH), 7.63 (s, 2H, Ar-H), 3.83 (m, 16H, CH_2O), 3.64 (m, 12 H, CH_2N), 2.75 (s, 4H, CH_2S). ^{13}C-NMR ($CDCl_3$): δ 169.18 (C=NH), 141.24 (ArCS), 133.34 (ArC), 131.43

(ArCH), 98.95–67.06 (CH_2O), 55.03 (CH_2N), 28.47 (CH_2S). MS (FAB positive): m/z 523 $[M]^+$.

METAL-FREE PHTHALOCYANINE (5)

Compound **4** (0.99 g, 1.9 mmol) and 1.5 cm^3 of dry 2-(dimethylamino)ethanol was placed in a Schlenk tube connected vacuum line under argon atmosphere. The mixture was heated and stirred to 100°C for 1 h. Then it was refluxed under argon for 48 h. After cooling to room temperature, the mixture was filtered off and washed with hot dry ethyl acetate (50 cm^3). The green crude product was purified on silica gel using chloroform: petroleum ether (6:4) as eluent. The solution was evaporated to dryness under reduced pressure and then the green solid was dried *in vacuo.* Yield: 0.53 g (55%), mp >300°C. Found (Calc. for $C_{96}H_{138}N_{16}O_{16}\,S_8$): C, 56.71 (56.86); H, 6.92 (6.81); N, 11.31 (11.05). IR (KBr pellets, cm^{-1}): 3394, 3066, 2917–2849, 1627, 1595, 1569, 1268, 1123. ^{1}H-NMR ($CDCl_3$) 8: −3.85 (br, 2H, NH), 7.89 (m, 8H, ArH), 3.85 (m, 64H, CH_2O), 3.60 (m, 48H, CH_2N), 2.81 (m, 16H, CH_2S). ^{13}C-NMR ($CDCl_3/d_5$-py): δ 152.66 (C═N), 139.46 (ArCS), 133.93 (ArCH), 120.12 (ArC), 69.32–67.58 (CH_2O), 55.41 (CH_2N), 28.64 (CH_2S). UV-Vis ($CHCl_3$): λ (nm)[10^{-5} ε (mol^{-1} cm^{-1})]) 736 (4.82), 706 (4.70), 363 (4.37), 330 (4.76). MS (FAB positive): m/z 2027.2 $[M]^+$.

4,7,13,16,21,24-HEXAOXA-5,6-(4′,5′-DIBROMOBENZO)-1,10-DIAZABICYCLO [8.8.8]HEXACOSANE (7)

Compound **1** (2.62 g, 10 mmol) was dissolved in dry acetonitrile (350 cm^3) containing anhydrous Cs_2CO_3 (9.78 g, 30 mmol) and dry NaI (0.45 g, 3 mmol) and purged under argon in a three necked round-bottom flask. This mixture was stirred at 50°C for 1 h and a solution of **6** (7.2 g, 12.5 mmol) in dry acetonitrile (100 cm^3) was added dropwise over a period of 3 h at the same temperature and the reaction mixture was refluxed and stirred under argon for 6 days. The reaction was monitored by TLC using chloroform:methanol (7:3). At the end of this period the solvent was removed under reduced pressure, mixed with water (20 cm^3) and then extracted with dichloromethane (3 × 50 cm^3). The combined extract was dried over $MgSO_4$ and then filtered and evaporated to dryness. The oily residue was purified by column chromatography [silica gel, chloroform:methanol (7:3)] to give the pale yellow product.Yield: 4.2 g (72%). Found (Calc. for $C_{22}H_{34}N_2O_6Br_2$: C, 45.51 (45.36); H, 5.69 (5.64); N, 5.04 (4.81). IR (KBr pellets, cm^{-1}): 3053, 2875, 1590, 1583, 1497, 1243, 1200, 651. ^{1}H-NMR ($CDCl_3$): δ 7.33 (s, 2H, ArH), 4.27 (s, 4H, $ArOCH_2$), 3.88 (m, 16H, CH_2O), 3.29 (m, 12H, CH_2N). ^{13}C-NMR ($CDCl_3$): 8 148.12 (Ar CO), 118.49 (ArCH), 116.25 (ArC–Br), 72.19 ($ArOCH_2$), 79.37–66.74 (CH_2O), 55.86 (CH_2N). MS (FAB positive): m/z 582.1 $[M]^+$.

4,7,13,16,21,24-HEXAOXA-5,6-(4′5′-DICYANOBENZO)-1, 10-DIAZABICYCLO[8.8.8]HEXACOSANE (8)

Compound **7** (4.07 g, 7 mmol), CuCN (1.88 g, 21 mmol), dry DMF (20 cm^3) and three drops of pyridine was placed in a Schlenk tube under argon and gently heated, then subsequently heated to 140°C. The reaction was monitored by TLC using chloroform: petroleum ether (7:3). The reaction mixture was kept at this temperature for 20 h, after which the solution was cooled to room temperature. After adding aqueous NH_4OH (200 cm^3) to the reaction mixture, air was passed through the solution for 48 h. Then it was washed with water until the filtrate was neutral and dried *in vacuo.* The crude product was placed in a Soxhlet extractor and extracted with chlorofonn for 3 days. The extract was evaporated to dryness under reduced pressure and dissolved in dry methanol (25 cm^3) and then placed in refrigerator at −18°C for overnight to give pale yellow crystallized product. Yield: 1.4 g (42%), mp 226°C. Found (Calc. for $C_{24}H_{34}N_4O_6$): C, 60.91 (60.75); H, 6.88 (7.17); N, 11.68 (11.81). IR (KBr pellets, cm^{-1}): 3049, 2920–2849, 2230, 1596, 1506, 1255, 1132. ^{1}H NMR ($CDCl_3$): δ 7.24 (s, 2H, ArH), 4.35 (s, 4H, $ArOCH_2$), 3.85 (m, 16H, CH_2O), 3.33 (m, 12H, CH_2N). ^{13}C-NMR ($CDCl_3$): δ 148.51 (ArCO), 120.23 (ArH), 115.67 (ArC), 113.30 (C≡N), 71.96 ($ArOCH_2$), 68.22–67.19 (CH_2O), 55.53 (CH_2N). MS (FAB positive): m/z 474 $[M]^+$.

4,7,13,16,21,24–HEXAOXA-5,6 - (4′,5′-ISOIMINOIN DOLINE)- 1, 10 - DIAZABICYCLO[8.8.8]HEXACOSANE (9)

Compound **8** (2.37 g, 5 mmol) was dissolved in dry methanol (250 cm^3) in a three necked round-bottom flask (500 cm^3) under argon atmosphere connected a vacuum line. A suspension of dry sodium methoxide (0.135 g, 2.5 mmol) in dry methanol (25 cm^3) was added to this solution and anhydrous ammonia bubbled through this solution at room temperature for 3 h. Then the reaction mixture was heated gently to 70°C and anhydrous ammonia was bubbled through rapidly for 6 h. At the end of this period, the ammonia inlet was stopped and the volume of the solution reduced to dryness under reduced pressure and then was chromatographed on silica gel [methanol:dichloromethane (25:1)]. The extract was evaporated to dryness and dried *in vacuo.*

The pale green solid was mixed dry ethanol (25 cm^3) and stirred several hours and then the formed product was filtered off, washed with petroleum ether several times and dried *in vacuo* over P_2O_5 to give pale green product. Yield: 1.65 g (67%), mp 248°C. Found (Calc. for $C_{24}H_{37}N_5O_6$): C, 58.47 (58.65); H, 7.37 (7.53); N, 14.43 (14.25). IR (KBr pellets, cm^{-1}): 3348, 3055, 2928–2853, 1632, 1599, 1457, 1289, 1125. ^{1}H-NMR ($CDCl_3$): δ8.87 (br, 3H, NH), 7.35 (s, 2H, ArH), 4.27 (s, 4H, ArO- CH_2), 3.82 (m, 16H, CH_2O), 3.25 (m,12H, CH_2N). ^{13}C-NMR ($CDCl_3$): δ168.76 (C=NH), 148.31 (ArCO), 111.80 (ArCH), 126.47 (ArC), 71.66 ($ArOCH_2$), 68.08–66.88 (CH_2O), 55.15 (CH_2N). MS (FAB positive): m/z 491 [M]$^+$.

METAL-FREE PHTHALOCYANINE (10)

Compound **9** (1.47 g, 3 mmol) and 2 cm^3 of dry 2-(dimethylamino)ethanol was placed in a Schlenk tube under argon atmosphere. The reaction mixture was heated gently to 100°C for 1 h then it was heated and stirred at 150°C for 52 h. After cooling to room temperature, the mixture was filtered, washed with hot ethyl acetate several times and dried *in vacuo.* The dark green crude product was chromatographed on neutral alumina using chloroform:methanol (9:1) as eluent. The extract was evaporated to dryness under reduced pressure and the dark green solid was washed with ethyl acetate, ethanol and diethyl ether and then dried *in vacuo.* Yield: 0.96 g (37%), mp >300°C. Found (Calc. for $C_{96}H_{138}N_{16}O_{24}$): C, 60.86 (60.69); H, 7.51 (7.27); N, 11.54 (11.80). IR (KBr pellets, cm^{-1}): 3415, 3041, 2915–2840, 1603, 1592, 1493, 1412, 1291, 1137, 1072. ^{1}H-NMR ($CDCl_3$): δ7.47 (m, 8H, ArH), 4.35 (m, 16H, ArO-CH_2), 3.85 (m, 64H, CH_2O), 3.35 (m, 48H, CH_2N). ^{13}C-NMR ($CDCl_3$/d_5-py): δ 152.17 (C=N), 148.16 (ArCO), 115.67 (ArCH), 127.20 (ArC), 71.60 ($ArOCH_2$), 68.24–66.94 (CH_2-O), 55.26 (CH_2N). UV-Vis (Chloroform): λ (nm) [(10^{-5} ε (mol^{-1} cm^{-1}]): 696 (5.21), 676 (4.96), 625 (4.54), 352 (4.89), 325 (5.04); UV-Vis (Pyridine): λ (nm) [(10^{-5} ε (mol^{-1}-cm^{-1}]): 685 (5.01), 662 (4.54), 618 (4.39), 349 (4.80), 325 (4.92). MS (FAB) positive): m/z 1899 [M + 1]$^+$.

ZINC (II) PHTHALOCYANINE (11)

A well-stopped Schlenk tube was charged with **3** (0.304 g, 0.6 mmol), $Zn(CH_3COO)_2$ $2H_2O$ (0.037 g, 0.2 mmol), dry *n*-pentanol (2 cm^3) and 4–5 drops of DBU under argon atmosphere. The reaction mixture was heated gently to 90°C for 1 h then held at 150°C for 24 h. The reaction was monitored by TLC using chloroform:methanol (100:1). After cooling to room temperature, the dark green reaction mixture was diluted and precipitated with a mixture of methanol: water [40 cm^3 (1:1)]. The resulting green precipitate was filtered off, washed with methanol, water and diethyl ether and then it was chromatographed on silica gel using chloroform:methanol (100:1) as eluent. The extract was evaporated to dryness and a mixture of methanol-diethyl ether [20 cm^3 (1:1)] was added to this solid and placed in refrigerator at −18°C for overnight. The green solid was filtered off, washed with methanol and diethyl ether and then dried *in vacuo*. Yield: 0.134 g (42%), mp >300°C. Found (Calc. for $C_{96}H_{136}N_{16}O_{16}S_8Zn$): C, 55.25 (55.14); H, 6.42 (6.51); N, 10.87 (10.72); Zn, 3.29 (3.13). IR (KBr pellets, cm^{-1}): 3069, 2923–2853, 1616, 1587, 1558, 1270, 1098. ^{1}H-NMR (d_6-DMSO): δ 7.80 (m, 8H, ArH), 3.78 (m, 64H, CH_2O), 3.55 (m, 48H, CH_2N), 2.78 (m, 16H, CH_2S). UV-Vis (py) λ (nm) [10^{-5} ε (mol^{-1} cm^{-1})]: 716 (5.11), 687 (4.43), 644 (4.38), 379 (4.72), 329 (4.54). MS (FAB positive): m/z 2091.4 [M + 1]$^+$.

NICKEL(II) PHTHALOCYANINE (12)

Compound **10** (0.38 g, 0.2 mmol), anhydrous $NiCl_2$ and 4 cm^3 of dry 2-(dimethylamino) ethanol was placed in a standard Schlenk tube under argon atmosphere and held at 160°C for 48 h. The reaction was monitored by TLC using pyridine:petroleum ether:methanol (8: 1.5:0.5). After cooling to room temperature, the reaction mixture was evaporated to dryness under reduced pressure and diluted with 25 cm^3 of a mixture of methanol:water (1:1). The stirred mixture was filtered off, washed with water and ethanol and then dried *in vacuo.* The dark green solid was chromotogtaphed on silica gel using pyridine:methanol (100:1) as eluent. The extract was evaporated to dryness and suspensed with a mixture of ethanol:diethyl ether (1:1) and filtered off, washed with the same mixture and then dried *in vacuo.* Yield: 0.25 g (65%), mp >300°C. Found (Calc. for C_{96} $H_{136}N_{16}O_{24}Ni$): C, 59.09 (58.93); H, 6.88 (6.96); N, 11.58 (11.46); Ni, 3.16 (3.00). IR (KBr pellets): 3045, 2922–2848, 1616, 1589, 1506, 1420, 1297, 1120. ^{1}H-NMR (d_6-DMSO): δ 7.56 (m, 8H, ArH), 4.42 (m, 16H, $ArOCH_2$), 3.92 (m, 64H, CH_2O), 3.41 (m, 48H, CH_2N). UV-Vis (py): λ (nm) [(10^{-5} ε (mol^{-1} cm^{-1})]: 680 (4.84), 652 (4.24), 614 (4.40), 359 (4.60), 330 (4.82). MS (FAB positive): m/z 1955.3 [M + l]$^+$.

COPPER(II) PHTHALOCYANINE (13)

Compound **7** (0.58 g, 1 mmol), CuCN (0.27 g, 3 mmol) and dry quinoline (1.5 cm^3) was placed in a standard Schlenk tube under argon atmosphere and held while stirring at 215°C for 24 h. At the end of this period, the mixture was cooled to room temperature and 30 cm^3 of ethanol was added to this mixture, and filtered and washed with ethanol and diethyl ether to remove any unreacted organic residue. The crude product was heated and stirred with a solution of NaCN (0.5 M) in a mixture of water: ethanol [75 cm^3 (1:3)] for 3 h and filtered off, washed with hot water, ethanol and diethyl ether. The dark green solid was chromatogtaphed on neutral alumina using chloroform: methanol (100:1) as eluent. The extract was evaporated to dryness and dried *in vacuo*. Yield: 0.16 g (32%), mp >300°C. Found (Calc. for $C_{96}H_{136}$-$N_{16}O_{34}Cu$): C, 58.92 (58.79); H, 6.81 (6.94); N, 11.64 (11.43); Cu, 3.42 (3.24). IR (KBr pellets, cm^{-1}): 3043, 2923–2850, 1620, 1590, 1502, 1425, 1293, 1122. UV-Vis (py): λ (nm) [$(10^{-5}\ \varepsilon\ (\mathrm{mol}^{-1}\ \mathrm{cm}^{-1})$]: 678 (4.52), 642 (3.24), 611 (3.40), 361 (3.60), 315 (4.70). MS (FAB positive): m/z 1960.2 $[M + 1]^+$.

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