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The synthesis and characterization of new metal-free and metalloporphyrazine containing macrobicyclic moieties

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Abstract

The synthesis and characterization of new metal-free (**8**) and metal derivatives of a symmetrically four substituted porphyrazines (**7**,**9**) derived from 15,18,23,26-tetraoxa-5,8-dithia-1,12-diazabicyclo[10.8.8]octacos-6-ene-6,7-dicarbonitrile (**6**), which were synthesized in a multi-step reaction sequence have been investigated. These compounds were prepared starting from dicyanoethylene containing macrobicycle which contains sulfur, oxygen as well as nitrogen heteroatoms. These pigments were characterized by ^{1}H, ^{13}C NMR, IR, UV–vis, mass spectrometry, microanalysis and AA spectrophotometry.

Keywords: Metal-free porphyrazine; Metalloporphyrazine; Mixed-donor macrobicycle; Template effect

1. Introduction

The synthesis, characterization and applications of tetrapyrrolic macrocycles such as phthalocyanines [1], porphyrins [2] and their aza-analogues have been investigated intensively in many directions, as biomedical agents, chemical sensors, liquid crystals, nonlinear optics, including their applications in materials science [3]. Tetraazaporphyrins, which are derived from tetraazaporphin skeleton and induced phthalocyanines, are the most widely investigated members of this family [4]. Although phthalocyanines and porphyrins have been well studied, porphyrazines have received considerably less attention.

However, due to the simple synthetic route for the synthesis of porphyrazines, via the template cyclotetramerisation of maleonitrile, these kinds of macrocyclic compounds are now subject of enhanced interest [5]. There is also a great interest in exploring novel structural modifications to the porphyrazine system, including the study of polynuclear derivatives and derivatives with specially designed peripheral substituents which coordinate with alkaline or transition metals [6].

Cryptands, in general is a polymacrocyclic ligand system of three-dimensional structure being capable of encapsulating a metal ion. The remarkable group of these compounds was introduced by Lehn and his co-workers in 1969 [7]. Owing to their architectural and functional plasticity, macrobicyclic compounds are especially attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic substrates. These compounds show extraordinary solubility and selectivity towards specific alkali or alkaline earth metal cations leading to complexation in aqueous and organic solutions, indeed more so than crown ether [8]. Especially, polynucleating systems containing several substrates or metal-binding sites which do not reside within the same macrocyclic framework are very active in the current research activity [9].

In the present paper, we describe for the first time the synthesis and characterization of a new class of metal-free and metalloporphyrazine containing diaza-tetraoxa-dithia macrobicyclic moieties. These new porphyrazines may allow new functionalized materials to be prepared, which are important for redox chemistry, the ligation of heavy metal ions; endocyclic,

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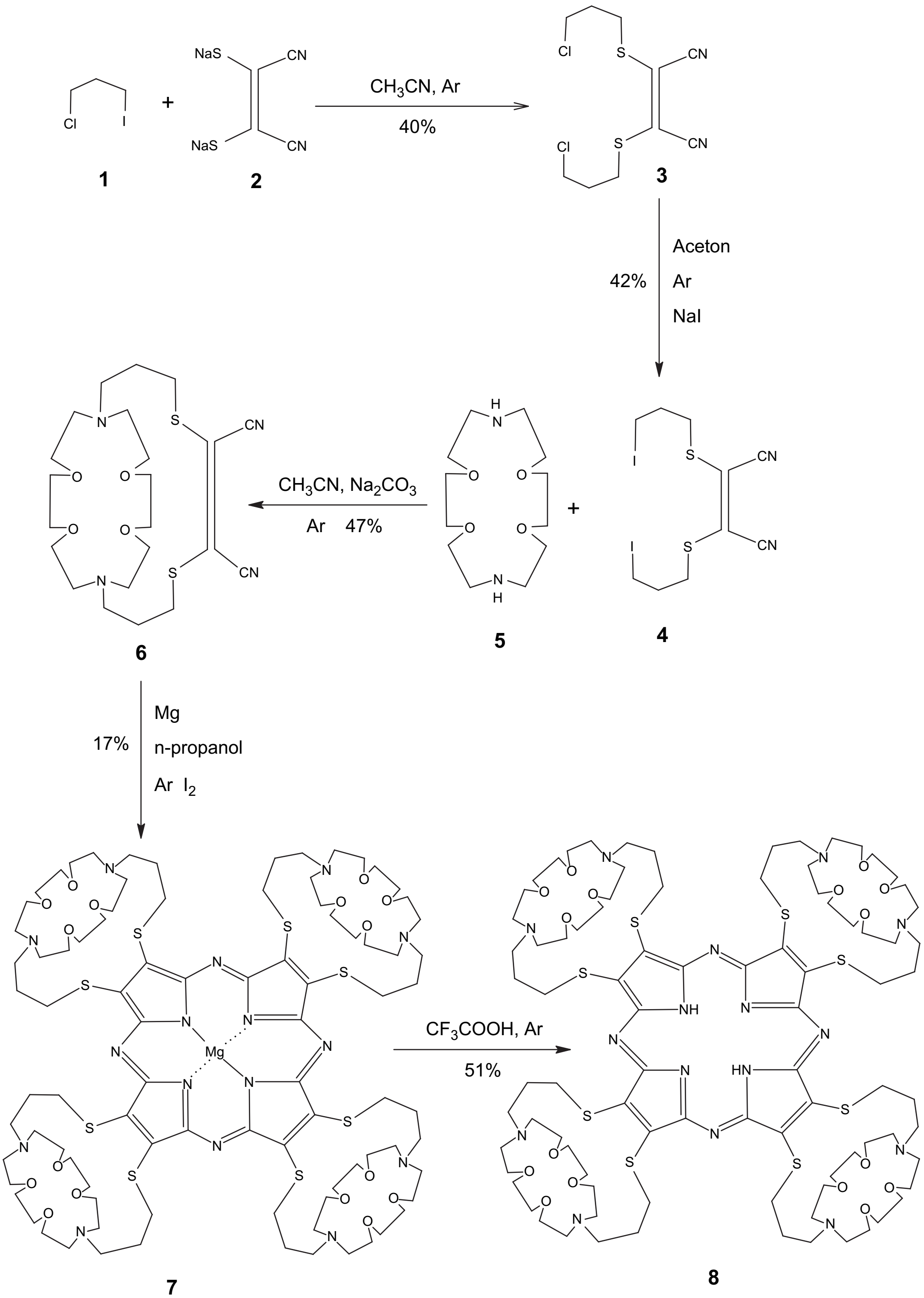
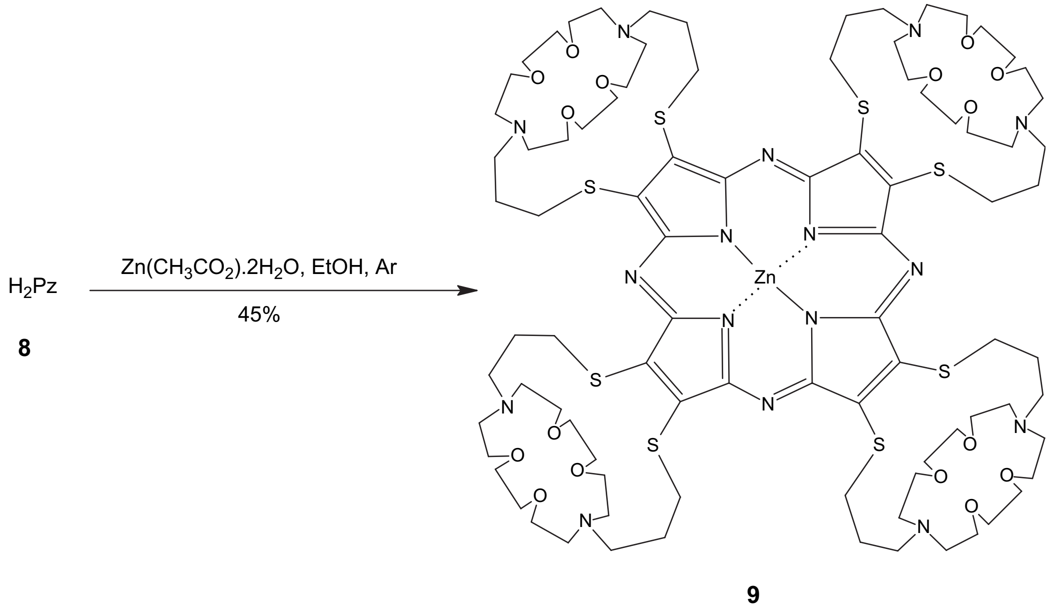
exocyclic complexes and as extraordinary complexing agents for Cs, Rb, organic molecules and ammonium cations [10].

2. Results and discussion

The synthesis of target compounds **7–9** is shown in Schemes 1 and 2. The key intermediate for metal-free or metalloporphyrazine compounds is dicarbonitrile containing macrobicyclic moiety **6** which was obtained in a three-step reaction sequence. Reaction of 3-iodo-1-chloropropane **1** and disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate **2** [11] in dry acetonitrile at room temperature under an argon atmosphere for 96 h afforded 1,10-dichloro-5,6-di-cyano-4,7-dithia-5-decene **3** in ca 40% yield after purification by chromatography.



Scheme 1. The synthesis of metal-free porohyrazine.



Scheme 2. The synthesis of zinc(II) porphyrazine.

Mass spectrum of this compound exhibited a molecular ion peak at $m/z = 296.6$ $[M + 1]^+$, which supports the structure. The ^1H NMR spectrum of **3** showed expected signals for $-CH_2$, $-SCH_2$ and $ClCH_2$ protons at $\delta = 2.13$, 3.25 and 3.62 ppm, respectively. The proton-decoupled ^{13}C NMR spectrum of **3** also clearly indicated the presence of nitrile carbons at $\delta = 111.64$ ppm. The disappearance of C—I and the presence of C≡N stretching vibrations at 2209 cm^{-1} seen in the IR spectrum of this compound also confirmed the formation of **3** (Scheme 1).

Using the known procedure [12] **3** was converted to the iodo derivative **4**, in dry acetone containing finely ground anhydrous NaI at reflux temperature, under an argon atmosphere, in 48% yield which was an interesting starting compound for the future synthesis of porphyrazine containing mono or polymacrocyclic moieties. The similarity of the IR spectra of **4** and **3** is very high except for the vibrations of CH_2—X groups. In the ^1H and ^{13}C NMR spectra of **4**, the characteristic signals of the protons and carbons are very similar to those of the precursor **3** except for the signals of carbons and protons connected to halogens ($-CH_2-I$). The IR spectrum of this compound exhibits characteristic frequencies at 534 cm^{-1} concerning CH_2—I groups. The mass spectrum and elemental analysis data of **4** also support the replacement of chlorine by iodine, with a peak at $m/z = 478.8$ indicating the formation of $[M]^+$.

The macrobicycle 15,18,23,26-tetraoxa-5,8-dithia-1,12-diazabicyclo[10.8.8]octacos-6-ene-6,7-dicarbonitrile **6** was obtained from **4** by the 1:1 reaction with 4,13-diaza-18-crown-6 **5** [13], in a threefold excess of Na_2CO_3, and 0.25 equiv. of NaI in dry acetonitrile. Purification by column chromatography gave **6** in 71.7% yield. Analytical and spectroscopic data of **6** clearly confirmed the success of the desired macrobicyclization reaction. In the ^1H NMR spectrum of **6**, the new resonances for CH_2O- and $-CH_2N-$ groups are at $\delta = 3.65$ and 3.15 ppm, respectively, and the disappearance of the NH signals belonging to **5** supports the formation of **6**. The ^{13}C NMR spectrum of the same compound **6** clearly indicated the characteristic signals due to the appearance of nitrile and azacrown carbons at $\delta = 112.71$, 68.43–66.40 and 52.50 ppm. The disappearance of N—H and the presence of C≡N stretching vibrations at 2209 cm^{-1} seen in the IR spectrum of this compound also confirmed the formation of **6**. Compound **6** displayed the expected molecular ion peak at $m/z = 485.1$ $[M + 1]^+$ its mass spectrum.

Conversion of **6** into porphyrazinatomagnesium **7** was achieved according to the standard Linstead and Whalley [14] co-macrocyclization of dinitriles **6** using magnesium as the template in *n*-propanol at reflux for 24 h under an argon atmosphere in 26% yield as a dark blue amorphous solid after purification by using column chromatography on silica gel. Since synthesis of porphyrazines from maleonitrile containing macrocyclic moieties has been reported [5,6], the steric hindrance encountered in the present case should be the consequence of appending bulky macrobicyclic groups on **6**. The decrease of the yield of the product **7** could be attributed to this effect [15]. In the ^1H and ^{13}C NMR spectra of **7**, the signals relating to $-CH_2O-$, $-CH_2-$, $-CH_2N-$ and $-CH_2S-$ groups in the macrobicyclic moieties and porphyrazine skeleton gave significant resonances characteristic of the proposed structure. This spectrum closely resembles that of the precursor compound (**6**). In the IR spectrum of **7**, after conversion of dinitrile derivative (**6**) to porphyrazinatomagnesium (Scheme 1) the disappearance of sharp C≡N and appearance of medium C=N stretching vibrations at 1645 cm^{-1} belonging to the synthesized compound support the formation of metalloporphyrazine. Porphyrazinatomagnesium (**7**) displays the expected molecular ion peak at $m/z = 1985.1$ $[M + Na + 2]^+$, which also supports the structure of the proposed formulation.

Porphyrazinatomagnesium **7** was demetallated by the treatment with trifluoroacetic acid at room temperature for 3 h to give the metal-free porphyrazine **8** [16] as purple powders, after purification by column chromatography on silica gel amounted to approximately 65.3%. ^{1}H NMR spectrum of metal-free porphyrazine **8** displayed broad signals and typical shielding of the inner core –NH protons, which are common features of the proton NMR spectra of metal-free porphyrazines [17]. These protons have been observed as a deuterium exchangeable signal at $\delta = -1.02$ ppm. The characteristic protons and carbon NMR chemical shifts belonging to the macrobicyclic moieties and metal-free porphyrazines skeleton showed significant absorbances for the proposed structure. ^{1}H and ^{13}C NMR spectra of this compound closely resemble that of the precursor compound as expected. The IR spectrum of this compound (**8**) also indicates the appearance of the medium N–H stretching vibration at 3285 cm^{-1} after the demetallation of **7** to metal-free porphyrazine **8**. The convenience of elemental analysis results and the mass spectrum of **8** contained a strong peak at $m/z = 1941.1$ $[M+3]^+$ for the parent ion, which can be attributed to the formation of metal-free porphyrazine containing four macrobicyclic moieties.

Zinc derivative ZnPz (**9**) was finally synthesized by the reaction of the metal-free porphyrazine (**8**) with $Zn(CH_3CO_2)_2 \cdot 2H_2O$ in a mixture of ethanol and chloroform. Attempts on purification by column chromatography on both silica gel and alumina were unsuccessful. The dark blue solid product purified by preparative thin layer chromatography amounted to approximately 45%. Elemental analysis and AA spectrophotometric results showed that a Zn(II) cation is coordinated to the per H_2Pz molecule. The zinc porphyrazine gave reproducible mass spectrum and here we observed the M + 2 peaks, instead of molecular ion in **9** $m/z = 2003.5$. The ^{1}H NMR spectrum of this compound was almost identical with that of the corresponding metal-free porphyrazine, a significant difference being the disappearance of the broad inner core NH protons of **8**. Also, it should be mentioned that the peaks of the proton NMR spectrum are broad as encountered in some other soluble porphyrazines. This effect may be related to the formation of aggregates which are frequently encountered at the concentrations used for NMR experiments [18]. Complexation of the metal-free porphyrazine was confirmed by the disappearance of the N–H stretching vibration at 3285 cm^{-1}. The rest of the IR spectrum of **9** is closely similar to that of **8**, including characteristic vibrations of macrobicycle and azomethine groups (Scheme 2).

The UV–vis absorption maxima and extinction coefficient of novel porphyrazinatomagnesium in chloroform solutions (10^{-5} M) at room temperature are shown in Fig. 1. UV–vis spectrum of **7** is dominated by two bands such as Q and B bands. The single sharp Q band at 673 nm is characteristic of a tetrapyrrolic macrocycle with D_{4h} symmetry. The magnesium porphyrazine derivatives containing small crown ether units peripherally show a red-shift of this band whereas **7**, which has the largest cryptand moieties showed a considerable red-shift as unexpected [5,6,19]. The Q band around 673 nm and an intense B (Soret) band in the near UV region of around 381 nm, both correlated to $\pi \rightarrow \pi^*$ transitions [17,20]. In addition, band around 495 nm could be attributed to $n \rightarrow \pi^*$ transitions that originate from the nonbonding electrons of the peripheral sulfur atoms and the macrocyclic π system [21]. Demetallation to produce the corresponding metal-free derivative results in the UV–vis spectrum with well resolved split Q band with absorbances at 716 and 668 nm as a consequence of the change in the symmetry of metal-free porphyrazine core from D_{4h} to D_{2h} as it has been suggested in similar compounds [22]. As mentioned above, the broad band around 500 nm which is observed for the metallated as well as for the metal-free porphyrazine has been ascribed to an $n \rightarrow \pi^*$ transition, which is similar to those reported for the other sulfur-appended porphyrazines [6,20,23]. The intense absorption band around 350 nm can be attributed to the so-called N-band, which is strengthened with respect to the Soret B band. It is obvious that the absorption spectra of **7–9** are broad compared to the spectra of phthalocyanines containing similar macrocyclic units and most other porphyrazines [5,6,24]. This result seems to be related to the presence of the sulfur substituents connected to the porphyrazine skeleton.

The UV–vis spectrum of zinc-coordinated derivative (**9**) in chloroform showed a single Q band at 678 nm as expected from D_{4h} symmetry, which was more intense than metal-free derivative of porphyrazine, since it is also observed for other peripherally macrocyclic substituted porphyrazines. While no significant change is observed for the Soret bands of this complex with respect to the MgPz (**7**). It is of interest to note the disappearance of the $n \rightarrow \pi^*$ absorption at around 500 nm in this complex (**9**). This phenomenon could be attributed by binding of Zn(II) ions to the n-orbitals of the connected sulfur atoms.

3. Experimental

^{1}H and ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer operating at 200.14 MHz using deuteriochloroform as the solvent and tetramethylsilane as an internal

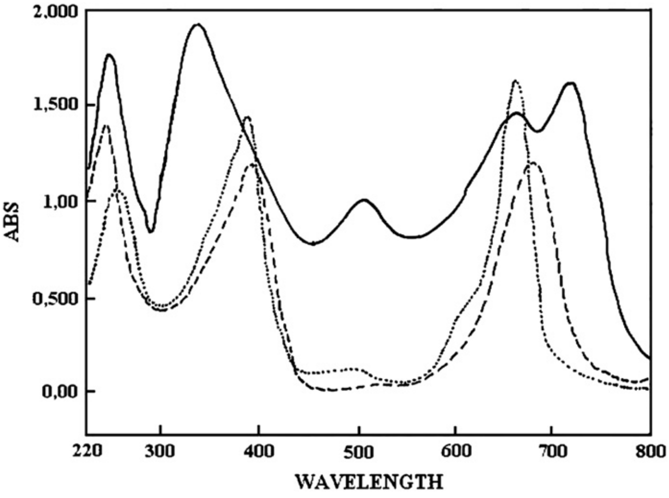


Fig. 1. UV–vis spectra of **7** (...), **8** (–) and **9** (- - -) in chloroform.

reference. IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer using KBr pellets. Mass spectra (EI) were measured on a Micromass Quatro LC/ULTIMA LC-MS MS spectrometer. Electronic spectra were recorded on a Unicam UV2-100 spectrophotometer which is double-beamed with thermostatically controlled cell blocks. All UV measurements were taken at 25 °C using quartz cells. Metal content of the metalloporphyrazine was determined with a Unicam 929 AA spectrophotometer. Melting points were determined on an electrothermal apparatus and are uncorrected.

Unless otherwise stated, all operations were carried out under an argon atmosphere in a vacuum line or using standard Schlenk techniques. *cis*-1,2-Dicyano-1,2-ethylenedithiolate was prepared according to the methods described in literature [11]. Other reagents were commercially available and were used without further purification unless otherwise noted. All solvents were dried and purified according to the standard procedure before use [25].

*3.1. 1,10-Dichloro-5,6-dicyano-4,7-dithia-6-decene (**3**)*

A round-bottom two necked flask containing **1** (8.17 g, 40 mmol) in dry acetonitrile (20 ml) was evacuated, refilled three times with argon and connected to a vacuum line. Under an argon atmosphere, the suspension of **2** (3.72 g, 20 mmol) in dry acetonitrile (30 ml) was added to the solution. The reaction mixture was stirred vigorously under an argon atmosphere at room temperature for 96 h. The reaction was monitored by a thin layer chromatography [chloroform:hexane (3:2)]. At the end of this period, the reaction mixture was filtered off, washed with dry acetonitrile and then evaporated to dryness under reduced pressure. The oily crude product was dissolved with chloroform (50 ml) and washed with water (2 × 30 ml). After drying over $MgSO_4$, the solvent was evaporated to dryness under reduced pressure and chromatographed on silica gel column [eluent (chloroform:hexane) (3:2)] to give a pale yellow oil. Yield: 4.73 g (40%). ^{1}H NMR ($CDCl_3$): δ 3.62 (t, 4H, CH_2Cl), 3.25 (t, 4H, SCH_2), 2.13 (q, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 120.95 (C=C), 111.64 (C≡N), 42.26 (CH_2Cl), 31.86 (SCH_2), 31.70 (CH_2). IR (NaCl disc): 2959–2857, 2209, 1500, 1437, 1350, 1311, 1271, 1174, 1044, 959, 825. MS: *m/z* 296.6 $[M+1]^+$. Anal. calcd for $C_{10}H_{12}N_2S_2Cl_2$: C, 40.67; H, 4.06; N, 9.49. Found: C, 40.96; H, 3.89; N, 9.31.

*3.2. 1,10-Diiodo-5,6-dicyano-4,7-dithia-6-decene (**4**)*

To dry solid NaI (5.31 g, 35.26 mmol) was added a solution of **3** (3.73 g, 12.64 mmol) in dry acetone (200 ml) in a round-bottom two necked flask under an argon atmosphere. The reaction mixture was refluxed and stirred under an argon atmosphere for 48 h. After cooling to room temperature, inorganic solid in the reaction mixture was removed by suction filtration and washed with dry acetone. The filtrate was evaporated under reduced pressure to dryness. The oily product was dissolved in diethyl ether and washed with concentrated aqueous solution of $Na_2S_2O_3$ (3 × 20 ml) and then dried over Na_2SO_4 overnight. The mixture was filtered through Celite and concentrated and then chromatographed on silica gel column [eluent (hexane:chloroform) (3:1)] affording compound **4** as pale yellow oil. Yield: 2.90 g (48%). ^{1}H NMR ($CDCl_3$): δ 3.25 (m, 8H, SCH_2, CH_2I), 2.15 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 121.06 (C=C), 111.82 (C≡N), 35.42 (CH_2I), 32.69 (S–CH_2), 30.12 (CH_2). IR (NaCl disc): 2956–2852, 2209, 1503, 1429, 1417, 1345, 1291, 1212, 1175, 1044, 943, 851. MS: *m/z* 478.8 $[M]^+$. Anal. calcd for $C_{10}H_{12}N_2S_2I_2$: C, 25.10; H, 2.51; N, 5.85. Found: C, 25.46; H, 2.89; N, 5.58.

*3.3. 15,18,23,26-Tetraoxa-5,8-dithia-1,12-diazabicyclo[10.8.8]octocos-6-ene-6,7-dicarbonitrile (**6**)*

A mixture of 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (**5**) (1g, 3.81 mmol) and anhydro Na_2CO_3 (1 g, 9.52 mmol) in dry acetonitrile (75 ml) was heated and refluxed for 1 h under an argon atmosphere. A solution of **4** (2.9 g, 4.19 mmol) in dry acetonitrile was added dropwise to the refluxing suspension during 1 h. The reaction mixture was refluxed for 5 days in the same condition. After the reaction was complete, the mixture was cooled to room temperature and filtered. The filtrate was rotary-evaporated to dryness, and the residue was dissolved in chloroform (50 ml) and washed with a large amount of water to remove NaI and other water-soluble materials, dried over $MgSO_4$ overnight. The organic phase was filtered through a pad of Celite and evaporated to dryness under reduced pressure. Dark purple oily product chromatographed on silica gel column [eluent (chloroform:methanol) (95:5)] gave macrobicycle **6** as a viscous pale purple oil. Yield: 1.32 g (71.7%). ^{1}H NMR ($CDCl_3$): δ 3.65 (m, 16H, OCH_2), 3.15 (m, 12H, NCH_2), 2.66 (t, 4H, SCH_2), 1.94 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 125.43(C=C), 112.71 (C≡N), 68.43–66.40 (OCH_2), 52.16 (NCH_2), 33.34 (SCH_2), 29.59 (CH_2). IR (NaCl disc): 2923–2979, 2209, 1567, 1417, 1353, 1298, 1176, 1103, 995, 830. MS: *m/z* 485.1 $[M+1]^+$. Anal. calcd for $C_{22}H_{36}N_4O_4S_2$: C, 54.54; H, 7.43; N,11.57. Found: C, 54.88; H, 7.67; N, 11.27.

*3.4. {Tetrakis(15,18,23,26-tetraoxa-5,8-dithia-1,12-diazabicyclo[10.8.8]octacosane)[6,7-b: 6′,7′-g: 6″,7″-l: 6‴,7‴-q]porphyrazinato}magnesium(II) (**7**)*

Magnesium turnings (0.09 g, 3.90 mmol) and small crystals of I_2 were added to dry *n*-propanol (20 ml) under an argon atmosphere. The mixture was refluxed until the magnesium had completely reacted to form a suspension of magnesium propoxide within 24 h. A solution of dicyano derivative of macrobicycle (**6**) (0.80 g, 1.64 mmol) in dry *n*-propanol (15 ml) was added dropwise to the refluxing suspension for over 1 h. After 24 h, the reaction mixture was filtered while hot. *n*-Propanol was removed by vacuum distillation. The deep blue crude product was purified by using preparative thin layer chromatography technique [neutral alumina (chloroform:methanol) (95:5)] to provide dark blue metalloporphyrazine. Yield: 0.55 g (26%), mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 3.57 (m, 64H, OCH_2), 3.12 (m, 48H, NCH_2), 2.62 (t, 16H, SCH_2), 1.82 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 157.57 (C=N), 130.08 (C=C), 69.58–67.11 (OCH_2), 54.45 (NCH_2), 31.76 (SCH_2), 29.54 (CH_2). IR (KBr pellets): 2923–2862, 1645, 1552, 1461, 1352, 1293, 1215, 1105, 1015, 935, 880. UV–vis [chloroform, λ_{max}/nm (log ε)]: 673 (4.28), 495 (3.27), 381 (4.21), 246 (3.94). MS: *m/z* 1985.1 $[M+Na+2]^+$. Anal. calcd for $C_{88}H_{144}N_{16}O_{16}S_8Mg$: C, 53.87; H, 7.34; N, 11.42. Found: C, 54.19, 7.04; N, 11.11.

*3.5. Tetrakis(15,18,23,26-tetraaza-5,8-dithia-1,12-diazabicyclo[10.8.8]octacosane)[6,7-b: 6′,7′-g: 6″,7″-l: 6‴,7‴-q]porphyrazine (**8**)*

Magnesium porphyrazine **7** (0.3 g, 0.15 mmol) was dissolved in a minimum amount of trifluoroacetic acid (2 ml) and stirred at room temperature for 3 h. The purple solution was poured over ice and neutralized with concentrated aqueous ammonia and extracted with chloroform (3 × 30 ml). The organic phase was washed with water until the latter was neutral and dried over $MgSO_4$ overnight and then evaporated to dryness under reduced pressure. The crude product purified by preparative thin layer chromatography [neutral alumina (chloroform:methanol) (97:3)] gave purple solid. Yield: 0.19 g (65.3%), mp > 300 °C. ^1H NMR ($CDCl_3$): δ 3.63 (m, 64H, OCH_2), 3.16 (m, 48H, HCH_2), 2.71 (m, 16H, SCH_2), 1.92 (m, 16H, CH_2), −1.02(s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ 167.81 (C=N), 130.93 (C=C), 70.70–68.15 (OCH_2), 55.34 (NCH_2), 38.68 (SCH_2), 29.72(CH_2). IR (KBr pellets): 3285, 2926–2856, 1655, 1602, 1577, 1461, 1377, 1347, 1271, 1121, 1071, 948, 858. UV–vis [chloroform, λ_{max}/nm (log ε)]: 716 (4.30), 668 (4.25), 510 (3.78), 350 (4.69), 248 (4.33). MS: *m/z* 1941.1 $[M+3]^+$. Anal. calcd for $C_{88}H_{146}N_{16}O_{16}S_8$: C, 54.48; H, 7.53; N, 11.55. Found: C, 54.88; H, 7.23; N, 11.77.

*3.6. {Tetrakis(15,18,23,26-tetraaza-5,8-dithia-1,12-diazabicyclo[10.8.8]octacosane)[6,7-b: 6′,7′-g: 6″,7″-l: 6‴,7‴-q]porphyrazinato}zinc(II) (**9**)*

A solution of $Zn(CH_3CO_2)\cdot 2H_2O$ (0.045 g, 0.25 mmol) in dry ethanol (15 ml) was added to a solution of metal-free porphyrazine (**8**) (0.050 g, 0.025 mmol) in dry chloroform (10 ml). The mixture was refluxed under an argon atmosphere and stirred for 18 h. At the end of this period, solvent was removed by vacuum distillation and the blue residue was dissolved with chloroform and washed with water (2 × 20 ml), dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The product purified by preparative thin layer chromatography [neutral alumina (chloroform:methanol)(95:5)] gave dark blue solid. Yield: 0.023 g (45%), mp > 300 °C. ^1H NMR ($CDCl_3$): δ 3.65 (m, 64H, OCH_2), 3.20 (m, 48H, NCH_2), 2.58 (m, 16H, SCH_2), 1.77 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 161.04 (C=N), 131.13 (C=C), 70.24–68.76 (OCH_2), 55.61 (NCH_2), 31.59 (SCH_2), 29.41 (CH_2). IR (KBr pellets): 2924–2853, 1662, 1593, 1568, 1482, 1359, 1336, 1291, 1112, 1090, 966, 871. UV–vis [chloroform, λ_{max}/nm (log ε)]: 678 (3.92), 384 (3.94), 254 (3.76). MS: *m/z* 2003.5 $[M+2]^+$. Anal. calcd for $C_{88}H_{144}N_{16}O_{16}S_8Zn$: C, 52.76; H, 7.19; N, 11.19; Zn, 3.26. Found: C, 53.11; H, 6.93; N, 11.01; Zn, 3.65.

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