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The synthesis and characterization of new metal-free and metallo porphyrazines bearing peripheral aza-18-crown-6 moieties

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Abstract

Metal-free and metalloporphyrazines bearing substituted aza-18-crown-6 moieties in peripheral positions were prepared and characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, UV–vis and MS spectral data.

Keywords: Metal-free porphyrazine; Magnesium porphyrazine; Zinc porphyrazine; Template effect; Mixed-donor macrocyclic

1. Introduction

Phthalocyanines and porphyrins have received considerable attention due to the number of applications in which these two families of compounds have been employed and also because of their interesting properties [1]. Porphyrins and their aza-analogues have been investigated intensively in many directions, such as biomedical agents, chemical sensors, liquid crystals, non-linear optics [2,3], magnetic [4] and catalytic [5] properties including their applications in materials science. Another family of similar conjugated macrocycles that have received considerably less attention than the phthalocyanines or porphyrins, are the porphyrazines, also called tetraazaporphyrazines [6,7]. Recently, a significant amount of studies have been realized about these topics. Hoffman and co-workers, for example, have reported the synthesis of polymetallic porphyrazines and a novel metal-linked porphyrazine dimer [8,9].

Porphyrins, phthalocyanines, and porphyrazines coordinate an extensive range of metal ions within their central cavities. In contrast to porphyrins, *meso*-substitution of nitrogen in tetraazaporphyrins modulates the electronic character and extended π-system of phthalocyanines and porphyrazines with peripheral metal coordination permits the preparation of a wide variety of multimetallic complexes with novel structural, spectroscopic, magnetic, and electronic properties. Especially, polynucleating systems containing several substrate or metal-binding sites which do not reside within the same macrocyclic framework is very active current research activity [10].

We have previously described the synthesis of new porphyrazines bearing in peripherally functionalized with symmetrical four diazatetraoxadithia macrobicycles [11]. In this study, the new monomeric metal-free (**5**) and metallo porphyrazines (**4**) bearing eight aza-18-crown-6 substituents in peripheral positions were synthesized and characterized.

2. Result and discussion

The first step in the synthetic procedure was to obtain dicarbonitrile derivative **3** bearing aza-18-crown-6 moieties. The general route for the synthesis of new porphyrazines is shown in Scheme 1. The reaction of 2 equiv of aza-18-crown-6 **1** and 1,10-diiodo-5,6-dicyano-4,7-dithia-5-decene **2** [11] in dry acetonitrile at reflux temperature under argon for 5 days afforded compound **3**. The new dicarbonitrile derivative **3** was obtained in ca. 64.9% yield after purification by column

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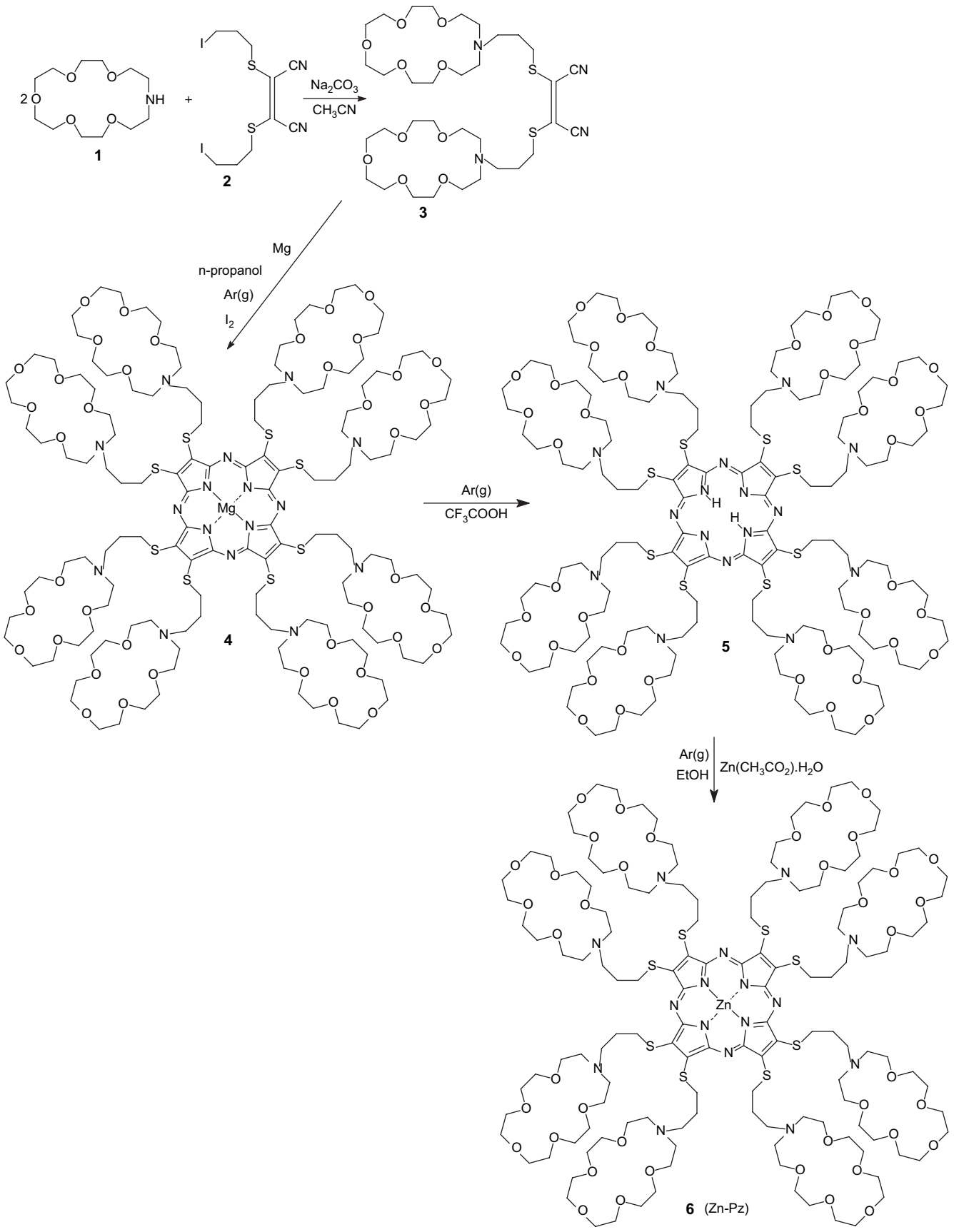

Scheme 1. The synthesis of the metal-free porphyrazine and metalloporphyrazines.

chromatography techniques. Mass spectrum of this compound exhibited a molecular ion peak at $m/z = 748$ $[M + 1]^+$, which supports the proposed formulation. ^{1}H NMR spectrum of **3** showed expected signals for $-OCH_2$, $-NCH_2$ and SCH_2 protons at $\delta = 3.71$, 3.27 and 2.63 ppm, respectively. The proton-decoupled ^{13}C NMR spectrum of **3** also clearly indicated the presence of nitrile carbons at $\delta = 111.69$ ppm. In the IR spectra of this compound, disappearance of N–H and C–I vibrations for compounds **1**,**2** and the presence of C≡N stretching vibrations at 2208 cm^{-1} confirm the formation of **3**. The elemental analysis data are consistent with the predicted formation of **3**.

Magnesium porphyrazinato **4** was obtained by the template reaction [6b] of compound **3** with magnesium propoxide in dry *n*-propanol under argon at reflux temperature in 36% yield as a dark blue amorphous solid after purification by using column chromatography. In the ^{1}H NMR spectrum of compound **4**, the signals related to $-CH_2O-$, $-CH_2N-$, $-CH_2S-$ and $-CH_2-$ groups were observed at $\delta = 3.65$, 3.26, 2.23 and 1.63 ppm, respectively. The proton-decoupled ^{13}C NMR spectrum of compound **4** also clearly indicated the disappearance of nitrile carbon signal for compound **3** at $\delta = 111.69$ and appearance of C=N carbon signal at 157.82 ppm., which supports the formation of compound **4**. These spectra closely resemble those of the precursor compound **3**. In the IR spectrum of compound **4**, after conversion of dinitrile derivative **3** to porphyrazinatomagnesium **4**, the disappearance of sharp C≡N stretching vibrations at 2208 cm^{-1} and appearance of C=N stretching vibrations at 1632 cm^{-1} belonging to the synthesized compound supports the formation of this compound. Porphyrazinatomagnesium (**4**) displays the expected molecular ion peak at $m/z = 3017$ $[M + 1]^+$, which also supports the structure of the proposed formulation.

The metal-free porphyrazine **5** was obtained [12] by the demetallation reaction of porphyrazinatomagnesium **4** with trifluoroacetic acid at room temperature for 3 h as a purple powders which after purification by column chromatography amounted to approximately 45%. ^{1}H NMR spectrum of metal-free porphyrazine **5** displayed broad signals and the typical shielding of inner core –NH protons, which is a common feature of the proton NMR spectra of metal-free porphyrazines [13] that has been observed as a deuterium exchangeable signal at $\delta = -1.80$ ppm. This is an evidence to explain that magnesium metal ion was binded to central cavity. The signals related to $-CH_2O-$, $-CH_2N-$, $-CH_2S-$ and $-CH_2-$ groups in the new compound **5** were observed at $\delta = 3.69$, 3.20, 2.40 and 1.78 ppm, respectively. The ^{13}C NMR spectrum of compound **5** clearly indicated the characteristic signals due to C=N, OCH_2 and NCH_2 carbons at $\delta = 167.81$, 70.70–68.15 and 38.70 ppm, respectively. The IR spectrum of compound **5** also indicates the appearance of the N–H stretching vibration at 3335 cm^{-1} after the formation of this compound. The mass spectrum of compound **5** showed a strong peak at $m/z = 2994$ $[M]^+$ for the parent ion, which can be attributed to the formation of metal-free porphyrazine **5**.

Zinc porphyrazine **6** was obtained by the reaction of metal-free porphyrazine **5** with $Zn(CH_3COO)_2 \cdot 2H_2O$ in dry ethanol under argon atmosphere at reflux temperature and afforded the desired compound **5** in 50% yield. The amorphous solid was purified using column chromatography. In the ^{1}H NMR spectrum of compound **6** the signals related to NH proton disappeared. It explained that the zinc metal ion interacted with central cavity and not the terminal unit. In the ^{1}H NMR spectrum of compound **6** the signals related to $-CH_2O$, CH_2N-, $-CH_2S-$ and $-CH_2$ groups were observed at $\delta = 3.52$, 3.15, 2.52 and 1.85 ppm, respectively. In the proton-decoupled ^{13}C NMR spectrum of compound **6** signals appear due to C=N, OCH_2 and NCH_2 carbons at $\delta = 155.00$, 68.00–66.41 and 37.32 ppm, respectively, which supports the formation of compound **6**. The IR spectrum of compound **6** closely resembles that of the precursor compound **5**, except NH stretching vibrations. Porphyrazinatozinc complex **5** displays the expected molecular ion peak at $m/z = 3057$ $[M]^+$, which also supports the structure of the target compound.

The UV–vis absorption spectrum of novel porphyrazinatomagnesium **4** in chloroform solutions (10^{-5} M) at room temperature is shown in Fig. 1. UV–vis spectrum of compound **4** exhibits two bands such as Q and B bands. The single sharp Q-band at 677 nm is characteristic of a tetrapyrolic macrocycle with D_{4h} symmetry. The Q-band at 677 nm is related to $\pi \rightarrow \pi^*$ transition [14]. This is due to the lowering of symmetry from four-fold (D_{4h}) to two-fold (D_{2h}) symmetry for metal-free derivative **5** and removal of the degeneracy of the eg LUMOs. Demetallation to produce the corresponding metal-free derivative results in the UV–vis spectrum with well resolved split Q-band with absorbance at 716 and 677 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 [15]. It is observed a slight red-shift of the soret band in metal-free compound **5**. This behavior observed in the soret and Q regions is typical for substituted porphyrazines. 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 **4**–**6** are broad compared to the spectra of phthalocyanines containing similar macrocyclic units and most other porphyrazines [16–18]. The broadening

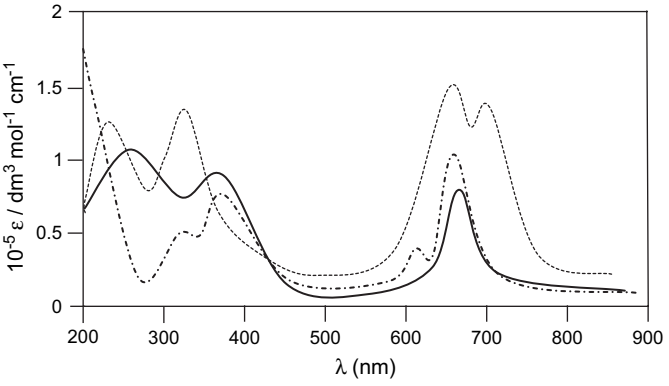

Fig. 1. UV–vis spectra of compounds **4** (–·–·–), **5** (···) and **6** (—) in chloroform.

of Q and B bands both of the metal-free and metalloporphyrazines is attributed to n → π* transition of the non-bonding electrons associated with peripheral S and N atoms [19]. This result also seems to be related to the presence of the sulfur substituents connected to the porphyrazine skeleton.

In the case of the Zn(II) derivative, the UV–vis spectrum of zinc-coordinated derivative **6** in chloroform showed a single band at 680 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.

3. Experimental

The IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer, using KBr pellets or NaCl disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$ and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer, respectively. Melting points were measured on an electrothermal apparatus and are uncorrected. 1-Aza-18-crown-6 **1** was purchased from Merck. 1,10-Diiodo-5,6-dicyano-4,7-dithia-5-decene was prepared according to the literature procedure [11]. Commercially available solvents were dried and purified by a conventional procedure [20].

3.1. (2*Z*)-2,3-Bis([3-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)propyl]thio)but-2-enedinitrile (*3*)

A mixture of 1-aza-18-crown-6 **1** (0.8 g, 3.04 mmol) and anhydrous Na_2CO_3 (0.81 g, 7.6 mmol) in dry acetonitrile (60 ml) was heated and refluxed for 1.5 h under argon atmosphere. A solution of 1,10-diiodo-5,6-dicyano-4,7-dithia-5-decene **2** (0.73 g, 1.52 mmol) in dry acetonitrile (15 ml) was added to the refluxing suspension. The reaction mixture was refluxed for 5 days in the same condition. After the reaction was completed, the reaction mixture was cooled to room temperature and filtered. The filtrate was rotary-evaporated to dryness, and the residue was dissolved in chloroform (20 ml) and washed with a large amount of water to remove NaI and other water-soluble materials, dried over $MgSO_4$ overnight and evaporated to dryness under reduced pressure. Dark purple oily product chromatographed on silica gel [eluent: chloroform] gave compound **3** as a viscous pale purple oil. Yield: 0.74 g (64.9%). ^{1}H NMR ($CDCl_3$): δ 3.71 (m, 40H, OCH_2), 3.27 (br, 12H, NCH_2), 2.63 (s, 4H, SCH_2), 1.94 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 127.96 (C═C), 111.69 (C≡N), 69.79–66.38 (OCH_2), 53.33 (NCH_2), 31.91 (SCH_2), 29.68 (CH_2). IR (NaCl disc): 2925–2958, 2208, 1619, 1458, 1353, 1295, 1249, 1171,1105, 949, 833. MS: *m/z* 748 $[M+1]^+$. Anal. calcd for $C_{34}H_{60}N_4O_{10}S_2$: C, 54.55; H, 8.02; N, 7.49. Found: C, 54.20; H, 7.92; N, 7.66.

3.2. Magnesium porphyrazine (*4*)

Magnesium powders (0.054 g, 2.24 mmol) and a small crystal iodine as initiator of I_2 were added to dry *n*-propanol (12 ml) under an argon atmosphere. The reaction mixture was refluxed until the magnesium had completely reacted to form a suspension of magnesium propoxide for 24 h. A solution of (2*Z*)-2,3-bis([3-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)propyl]thio)but-2-enedinitrile **3** (0.7 g, 0.94 mmol) in dry *n*-propanol (10 ml) was added dropwise to the refluxing suspension for over 1 h. The reaction mixture was stirred and refluxed under an argon atmosphere for 28 h. Then the reaction mixture was filtered hot and the precipitate was washed with CH_2Cl_2 until the washings were pale blue. The filtrate and washings were combined and evaporated to dryness by vacuum distillation to give a deep-blue crude product. The deep-blue crude product was purified by column chromatography on silica gel [eluent: chloroform–methanol (97:3)] gave compound **5** as a deep-blue solid. Yield: 0.25 g (36%), mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 3.65 (m, 160H, OCH_2), 3.26 (m, 16H, SCH_2), 2.23 (t, 48H, NCH_2), 1.63 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 157.82 (C═N), 130.90 (C═C), 68.43–66.40 (OCH_2), 53.70 (NCH_2), 32.95 (SCH_2), 29.59 (CH_2). IR (KBr pellets): 2918–2895, 1632, 1461, 1354, 1296, 1249, 1168, 1106, 949, 832. UV–vis [chloroform, λ_{max}/nm (log ε)]: 677 (4.92), 614 (4.38), 380 (4.83), 332 (4.63). MS: *m/z* = 3017 $[M+1]^+$. Anal. calcd for $C_{136}H_{240}N_{16}O_{40}S_8Mg$: C, 54.11; H, 7.96; N, 7.43. Found: C, 54.28; H, 7.83; N, 7.52.

3.3. Metal-free porphyrazine (*5*)

The magnesium porphyrazine **4** (0.2 g, 0.07 mmol) was dissolved in a minimum amount of trifluoroacetic acid (1 ml) and stirred at room temperature for 3 h. The purple solution was poured into ice water and neutralized with concentrated aqueous ammonia and extracted with chloroform (3 × 20 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 **5** purified by column chromatography on silica gel [eluent: chloroform] gave compound **5** as a purple solid. Yield: 0.09 g (45%), mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 3.69 (m, 160H, OCH_2), 3.20 (m, 16H, SCH_2), 2.40 (m, 48H, NCH_2), 1.78 (m, 16H, CH_2), −1.80 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ 167.81 (C═N), 132.42 (C═C), 70.70–68.15 (OCH_2), 38.70 (SCH_2), 29.71 (CH_2). IR (KBr pellets): 3335, 2922–2846, 1613, 1455, 1353, 1347, 1247, 1103, 949, 833, 755. UV–vis [chloroform, λ_{max}/nm (log ε)]: 716 (5.14), 677 (5.18), 346 (5.16), 245 (5.12). MS: *m/z* 2994 $[M^{\bullet}]^+$. Anal. calcd for $C_{136}H_{242}N_{16}O_{40}S_8$: C, 54.51; H, 8.08; N, 7.48. Found: C, 54.45; H, 7.95; N, 7.59.

3.4. Zn(II) porphyrazine (*6*)

A solution of $Zn(CH_3CO_2)\cdot 2H_2O$ (0.036 g, 0.20 mmol) in dry ethanol (6 ml) was added to a solution of metal-free

porphyrazine **5** (0.06 g, 0.020 mmol) in dry chloroform (6 ml). The mixture was refluxed under an argon atmosphere and stirred for 16 h. Then the solvent was removed by reduced vacuum and the blue residue was dissolved with chloroform and washed with water (2×15 ml), dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The product purified by column chromatography on silica gel [eluent: chloroform–methanol (97:3)] gave compound **6** as a dark blue solid. Yield: 0.03 g (50%), mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 3.52 (m, 160H, OCH_2), 3.15 (m, 16H, SCH_2), 2.52 (m, 48H, NCH_2), 1.85 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 155.00 (C=N), 130.19 (C=C), 68.00–68.14 (OCH_2), 37.32 (SCH_2), 29.62 (CH_2). IR (KBr pellets): 2924–2854, 1628, 1495, 1462, 1273, 1186. UV–vis [chloroform, λ_{max}/nm (log ε)]: 680 (4.80), 383 (4.90), 295 (5.04). MS: *m/z* 3057 $[M]^+$. Anal. calcd for $C_{136}H_{240}N_{16}S_8O_{40}Zn$: C, 53.39; H, 7.85; N, 7.32. Found: C, 53.48; H, 7.74; N, 7.40.

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