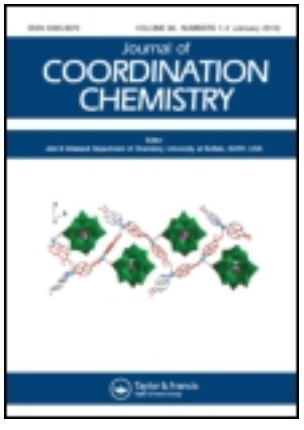

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New soluble porphyrazine derivatives containing electron-rich substituents

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New soluble porphyrazine derivatives containing electron-rich substituents

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Hydroxypropylsulfanyl groups of metal-free and metallo-porphyrazines (M=2H, Mg, Cu, Zn, or Co) have been prepared by the esterification with a carboxylate such as 1-naphthoic acid. The symmetrically functionalized porphyrazines with eight ester units were soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, tetrahydrofuran, acetone, and toluene and insoluble in water and *n*-hexane. The compounds have been characterized by FT-IR, UV–Vis, mass, ^1H, ^{13}C NMR, and elemental analysis.

Keywords: Porphyrazine; 1-Naphthoic acid; Esterification; Magnesium; Cobalt

1. Introduction

Porphyrins, phthalocyanines, tetrabenzoporphyrins, and porphyrazines, which can be denoted as tetrapyrrole derivatives, receive consideration because of both theoretical studies and applications in advanced materials science. Porphyrazines were first structurally characterized by Sir R.P. Linstead in 1937. They are part of a family of aromatic, tetrapyrrolic ring systems that can be divided into two distinct categories, namely porphyrins (P) and tetraazaporphyrins. The latter can be further divided into porphyrazines (Pz) and phthalocyanines (Pc), which contain benzenoid rings fused to the macrocyclic periphery. Due to their specific electronic and optical properties, potential applications of tetraazaporphyrins include biomedical agents, chemical sensors, liquid crystals, nonlinear optics, Langmuir–Blodgett films, and ladder polymers [1–9].

Porphyrazines that bear a range of carbon and heteroatom substituents fused directly to the macrocyclic periphery have gained increasing attention, due to the strong correlation between the nature of the substituent and the electronic and optical properties of the macrocyclic ring system, coupled with the relative ease of their synthetic preparation. Porphyrazines often display increased solubility in organic solvents compared with their phthalocyanine counterparts. Thus, porphyrazines maintain a unique position in the family of tetrapyrrolic macrocycles, and their straightforward synthesis, coupled with their tunable electronic and optical properties, renders them to be exciting candidates for a range of applications [10–19].

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Soluble tetrapyrrole derivatives were synthesized by our group during the last two decades. Substitution of several groups (e.g. 4-tert-buthylphenylthio [20], *o*-tolylthio and *p*-tolylthio [21], tosylaminoethylthio [22], 3-methylbutylthio [23], 1-naphthylmethylthio [24], 9-anthracenylmethylthio [25], 3,5-bis-trifluoromethyl-benzylthio [26], etc.) on the peripheral positions of porphyrazines has been accomplished by either starting with an unsaturated dinitrile precursor or a preformed porphyrazine with reactive functional groups that can be subsequently modified (e.g. crown ethers [27], ferrocenes [28], triphenylphosphine [29], acetoxy [30], 3-thiopropylpentafluorobenzoate [31], etc. have been incorporated by further condensation reactions).

Solubility is an important property for porphyrazines and most of their treatments are best determined in the soluble form. Because unsubstituted metal-free and metallo-porphyrazine structures are less soluble or insoluble in common organic solvents, synthesis of new porphyrazine systems should be designed such that the final porphyrazine derivatives are sufficiently soluble to carry out the desired activities. Compared to unsubstituted metal porphyrazines, ester-containing porphyrazines are highly soluble in chlorinated hydrocarbons such as dichloromethane and chloroform [27–33]. A further step for porphyrazine esters is the possibility to design supramolecular structures with donor groups on the ester moiety. The applications of ester-containing tetrapyrrole compounds are variable such as tumor growth suppressor [34], electro-photographic photoconductors [35], optical storage agent [36], and photosensitizer in photodynamic therapy [37, 38].

In this study, metal-free and metallo-porphyrazines (**4**–**8**) with eight 1-naphthyl units appending on the periphery through flexible propylthio-bridges have been synthesized through esterification of octakis (hydroxypropylthio) porphyrazinato magnesium with a 1-naphthoic acid in the presence of dicyclohexylcarbodiimide (DCCI) and toluene-*p*-sulfonic acid. Porphyrazines (**4**–**8**) with eight ester units were soluble in $CHCl_3$, CH_2Cl_2, tetrahydrofuran (THF), acetone, and toluene and insoluble in water and *n*-hexane. The compounds have been characterized by FT-IR, UV–Vis, mass, elemental analysis, ^{1}H NMR, and ^{13}C NMR.

2. Experimental

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were recorded on a Thermo Scientific 2000 instrument. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were taken in $CDCl_3$ solutions at 400.000, 100.577, and 376.308 MHz, respectively, recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer. Chemical shifts refer to TMS (^{1}H NMR and ^{13}C NMR) as the internal standards. By using the electrospray ionization (ESI) method, mass spectra were recorded on a Bruker Daltonics Micro-TOF and MALDI-TOF mass spectrometer. The instrument was operated in positive ion mode. All reactions were carried out under nitrogen atmosphere in dried solvents. All chemicals were used in a sufficient chemical purity. 1-Naphthoic acid, 3-chloro-1-propanol, N,N-dicyclohexylcarbodiimide (DCCI), toluene-*p*-sulfonic acid, N, N-dimethylformamide, chloroform, dichloromethane, pyridine, sodium sulfate, and sodium carbonate were purchased from Aldrich, Merck, or Alfa Aesar. Silica gel 60 (63–200 μm, Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed using Merck 60 F_{254} silica gel (pre-coated sheets, 0.2 mm thick).

The disodium salt of dithiomaleonitrile (**1**) was prepared according to previously reported procedures [39].

2.1. *2,3-Bis(3-hydroxypropylthio)maleonitrile (2)*

To a vigorously stirred suspension of the disodium salt of dithiomaleonitrile (5.59 g, 30.0 mM) in abs. EtOH (250 mL) under N_2, a solution of $ClCH_2CH_2CH_2OH$ (5.67 g, 60.0 mM) in abs. EtOH (10 mL) was added dropwise. After stirring for 72 h, the mixture was filtered and the filtrate was concentrated under vacuum. The reddish-brown oily residue was extracted several times with anhydrous *t*-BuOMe and after evaporation of the solvent in vacuum; a reddish-brown highly viscous product was obtained which was recrystallized from cold Et_2O as white crystals. Yield: 6.67 g (86%). FT-IR, $\nu_{max}/(cm^{-1})$: 3355 br (OH), 2988–2880 (CH, aliphatic), 2220 (C≡N), 1655 (C=C), 1058 (C–O). ^1H NMR (δ, ppm): 4.74 (2H, *t*, OH), 3.60 (4H, *t*, O–CH_2), 3.28 (4H, *t*, S–CH_2), 2.44 (*m*, 4H, –CH_2–). ^{13}C NMR (δ, ppm): 26.2, 29.9, 62.1, 116.0, 122.1. MS (ESI) *m/z*: 258.6 $[M]^+$.

2.2. *[2,3,7,8,12,13,17,18-octakis(3-hydroxypropylthio)porphyrazinato] Mg(II) (3)*

Mg turnings (6 mg, 0.25 mM) and a small I_2 crystal were refluxed in *n*-BuOH (20.0 mL) for about 8 h to obtain $Mg(BuO)_2$. 2,3-Bis(3-hydroxypropylthio)maleonitrile (**2**) (129 mg, 0.50 mM) was added to this solution and the mixture was refluxed for 12 h. The resulting blue-green suspension was filtered while hot, and the precipitate was washed with *n*-BuOH. The combined filtrates were evaporated, and the residue was washed with aqueous 10% Na_2CO_3 solution (100 mL). The suspension was centrifuged and washed with distilled H_2O. The blue-green highly viscous product was dissolved in MeOH, filtered, and finally, the solvent was evaporated in vacuum. Purification of the product was accomplished by column chromatography with silica gel using methanol/chloroform (1 : 20) as eluent. The colored product was soluble in methanol, ethanol, *n*-propanol, DMF, DMSO, and THF, but insoluble in *n*-hexane. Yield: 103 mg (78%). FT-IR, $\nu_{max}/(cm^{-1})$: 3333 (OH), 2958–2822 (CH, aliphatic), 1062 (C–O). ^1H NMR (δ, ppm): 4.58 (8H, *t*, OH), 4.40 (16H, *t*, O–CH_2), 3.68 (16H, *t*, S–CH_2), 2.46 (*m*, 16H, $-CH_2-$). ^{13}C NMR (δ, ppm): 26.0, 29.5, 61.7, 115.9, 121.7. MS (ESI) *m/z*: 1057.4 $[M]^+$.

2.3. *[2,3,7,8,12,13,17,18-octakis(3-thiopropyl 1-naphthoate)porphyrazinato] Mg(II) (4)*

Octakis(3-thiopropyl 1-naphthoate)porphyrazinato magnesium (**4**) was prepared through reaction of **3** (0.529 g, 0.5 mM), 1-naphthoic acid (2.066 g, 12 mM), DCCI (2.476 g, 12 mM), and toluene-*p*-sulfonic acid (0.095 g, 0.5 mM) in dry pyridine (30 mL) under N_2 at ambient temperature for 72 h. The suspension was filtered and the solvent was evaporated under vacuum. The residue was treated with $CHCl_3$ (100 mL) and the clear solution was extracted with 10% Na_2CO_3 solution (100 mL) and then with distilled water. The extraction was repeated several times with distilled water until pH was neutral. The chloroform phase was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The colored product was stirred in cold CH_2Cl_2, filtered and the solvent was evaporated under vacuum. The residue was treated with acetone. The purification of the product was accomplished by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1 : 50 v/v). The colored product was soluble in $CHCl_3$, CH_2Cl_2, THF, acetone, and toluene and insoluble in water and *n*-hexane. Yield: 722 mg (63%). FT-IR, $\nu_{max}/(cm^{-1})$: 3055 (CH, aromatic), 2945–2858 (CH, aliphatic), 1722 and 1258 (COO), 1652 (C=C, aromatic), 1460, 1326, 1215, 1159, 1023, 785, 625. ^1H NMR (δ, ppm): 8.10–7.76 (32H, *m*, Ar–H), 7.58–7.35

(24H, *m*, Ar–H), 4.68 (16H, *t*, O–CH_2), 4.12 (16H, *t*, S-CH_2), 2.54 (*m*, 16H, –CH_2–). ^{13}C NMR (δ, ppm): 26.1, 26.8, 63.5, 115.5, 121.7, 125.3, 126.3, 127.0, 127.9, 128.5, 129.2, 130.3, 132.1, 133.9, 134.5, 166.3. MS (ESI) *m/z*: 2291.8 $[M]^+$.

2.4. *[2,3,7,8,12,13,17,18-octakis(3-thiopropyl 1-naphthoate) H^{21}, H^{23} porphyrazine] (5)*

4 (229 mg, 0.1 mM) was dissolved in the minimum amount of trifluoroacetic acid (~3.00 mL) and stirred for 3 h at room temperature. When the reaction mixture was added to ice drop by drop and neutralized with 25% ammonia solution, precipitation occurred and the solution was filtered. The precipitate was extracted into chloroform, and the chloroform solution was twice extracted with distilled water. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a violet metal-free porphyrazine. **5** was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1 : 50 v/v). Yield: 172 mg (76%). FT-IR, $\nu_{max}/(cm^{-1})$: 3290 (N–H), 3046 (CH, aromatic), 2985–2850 (CH, aliphatic), 1727 and 1265 (COO), 1650 (C=C, aromatic), 1462, 1324, 1152, 1020, 745, 622. ^{1}H NMR (δ, ppm): 7.98–7.74 (32H, *m*, Ar–H), 7.54–7.32 (24H, *m*, Ar–H), 4.46 (16H, *t*, O–CH_2), 4.12 (16H, *t*, S–CH_2), 2.51 (*m*, 16H, –CH_2–), −1.20 (br s, 2H, NH). ^{13}C NMR (δ, ppm): 26.3, 26.7, 63.7, 115.8, 121.9, 125.0, 126.6, 126.6, 127.4, 128.3, 129.0, 130.0, 131.9, 133.6, 134.3, 166.1. MS (ESI) *m/z*: 2268.2 $[M]^+$.

2.5. *General procedure for metallo-porphyrazines (6–8)*

5 (113 mg, 0.05 mM) in $CHCl_3$ (10.0 mL) was stirred with the metal salt [$Co(OAc)_2$ (89 mg, 0.5 mM), $Cu(OAc)_2$ (91 mg, 0.5 mM), or $Zn(OAc)_2$ (92 mg, 0.5 mM)] in ethanol (15.0 mL) and refluxed under nitrogen for 6 h. Then, the precipitate composed of the crude product and excess metal salt was filtered. The precipitate was treated with $CHCl_3$, and the insoluble metal salts were removed by filtration. The filtrate was reduced to the minimum volume under reduced pressure and then added into *n*-hexane (150 mL) drop by drop to ensure precipitation. Finally, pure porphyrazine derivatives (**6**–**8**) were obtained by the column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:20 v/v).

2.5.1. [2,3,7,8,12,13,17,18-octakis(3-thiopropyl 1-naphthoate)porphyrazinato] Co(II) (6). Yield: 65 mg (56%). FT-IR, $\nu_{max}/(cm^{-1})$: 3040 (CH, aromatic), 2952–2855 (CH, aliphatic), 1720 and 1260 (COO), 1648 (C=C, aromatic), 1465, 1320, 1218, 1155, 1025, 775, 628. MS (ESI) *m/z*: 2325.1 $[M]^+$.

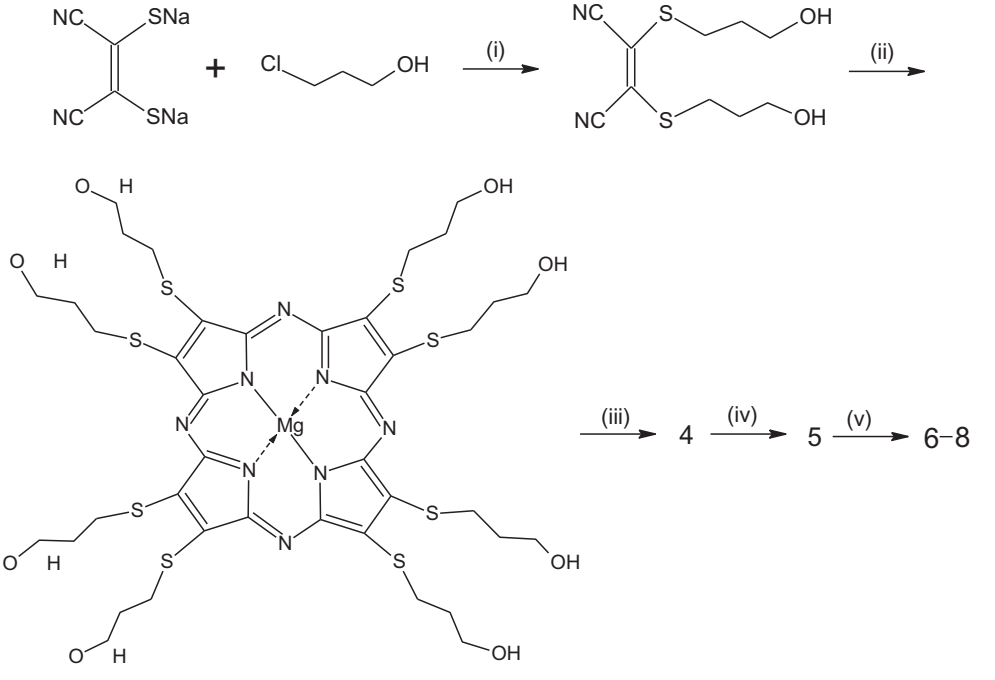
2.5.2. [2,3,7,8,12,13,17,18-octakis(3-thiopropyl 1-naphthoate)porphyrazinato] Cu(II) (7). Yield: 61 mg (52%). FT-IR, $\nu_{max}/(cm^{-1})$: 3050 (CH, aromatic), 2982–2850 (CH, aliphatic), 1725 and 1264 (COO), 1654 (C=C, aromatic), 1458, 1316, 1220, 1165, 1035, 746, 632. MS (ESI) *m/z*: 2330.8 $[M]^+$.

2.5.3. [2,3,7,8,12,13,17,18-octakis(3-thiopropyl 1-naphthoate)porphyrazinato] Zn(II) (8). Yield: 71 mg (61%). FT-IR, $\nu_{max}/(cm^{-1})$: 3046 (CH, aromatic), 2975–2856 (CH, aliphatic), 1727 and 1262 (COO), 1655 (C=C, aromatic), 1455, 1326, 1216, 1158, 1032,

754, 621. ^{1}H NMR (δ, ppm): 8.16–7.78 (32H, *m*, Ar–H), 7.56–7.30 (24H, *m*, Ar–H), 4.62 (16H, *t*, O–H_2), 4.15 (16H, *t*, S–CH_2), 2.55 (*m*, 16H, –CH_2–). MS (ESI) *m/z*: 2332.9 $[M]^+$.

3. Results and discussion

As proposed by Linstead, the unsaturated 1,2-dinitrile derivative should be prepared as the starting material [39, 40]. The disodium salt of dithiomaleonitrile (**1**) obtained from sodium cyanide and carbon disulfide in two steps was the starting point. Alkylation of the disodium salt of maleonitrile with 3-chloro-1-propanol in absolute ethanol gave 2,3-bis(3-hydroxypropylthio)maleonitrile (**2**), which was in the *cis*-form (Scheme 1). The reddish-brown product **2** was obtained in 86% yield. The presence of bulky electron-donating S-units is expected to increase the chemical stability and optical properties of porphyrazines [41]. By the template effect of magnesium, blue-green magnesium porphyrazinate (**3**) (Scheme 1) substituted with eight 3-hydroxypropylthio groups on the peripheral positions was synthesized by cyclotetramerization of 2,3-bis(3-hydroxypropylthio)maleonitrile (**2**) in the presence of magnesium butanolate [42–44]. It is soluble in methanol, ethanol, *n*-propanol, DMF, DMSO, and THF, but insoluble in apolar hydrocarbon solvents such as *n*-hexane. However, this method is not applicable if the substituents on the dinitrile are not sufficiently stable at temperatures above 120 °C in strongly basic media as in the case of 1-naphthyl groups. Consequently, the synthetic route preferred in the present work started with the preparation of octakis(3-hydroxypropylthio)porphyrazinato magnesium (**3**) as a reactive



Scheme 1. (i) Abs. EtOH; (ii) Mg turnings, I_2, *n*-BuOH; (iii) 1-naphthoic acid, DCCI, toluene-*p*-sulfonic acid, and dry pyridine; (iv) CF_3CO_2H; (v) EtOH, $CHCl_3$, and $Co(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$.

intermediate and the 1-naphthyl containing unit was condensed afterward. Octakis(3-thiopropyl 1-naphthoate)porphyrazinato magnesium (**4**) with eight 1-naphthyl units appending on the periphery through flexible alkylthio-bridges was synthesized through esterification of **3** with 1-naphthoic acid in the presence of DCCI and toluene-*p*-sulfonic acid.

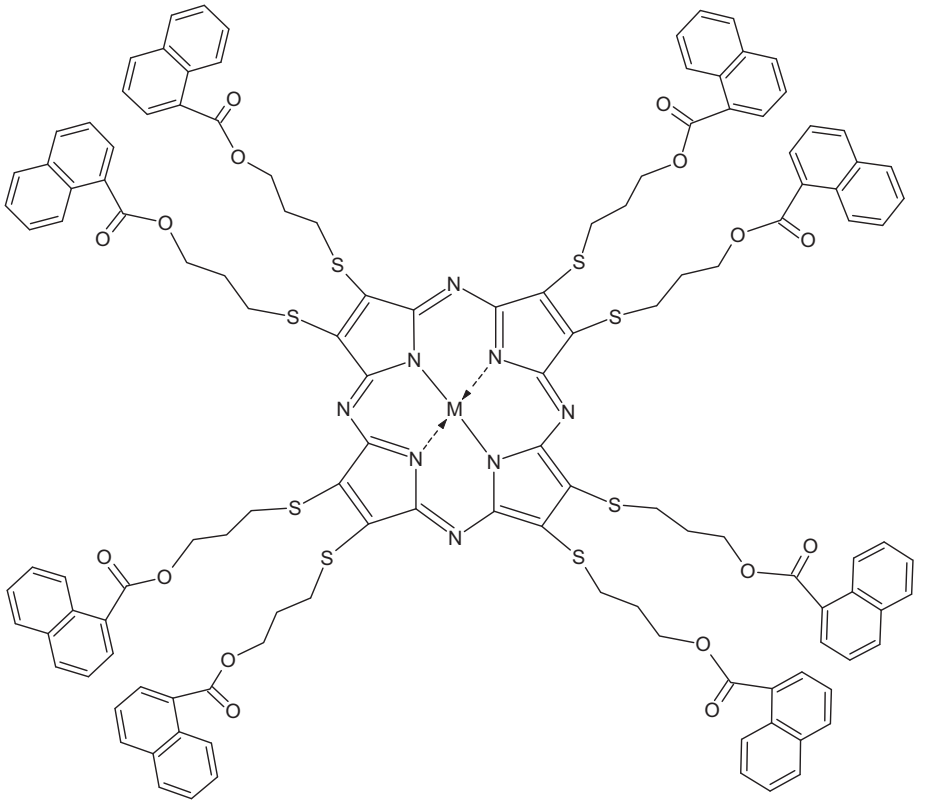
The aim of esterification is to enhance the solubility in common organic solvents. Although a number of different procedures could be tried for esterification, most of them resulted with partially esterified porphyrazines. The most efficient route for this esterification of the carboxylic acid and –OH on the porphyrazines was to carry out the reaction at room temperature in the presence of a strongly dehydrating agent such as DCCI. The byproduct dicyclohexylurea was eliminated by filtering the reaction mixture after treatment with cold dichloromethane. Ester groups provide good solubility, and they were selected because of the ease of their synthesis [27–33]. Mass spectrometric data indicate usage of the DCCI-mediated esterification system for octakis(hydroxypropylsulfanyl)porphyrazines ensured that all of the available –OH groups reacted. The choice of reaction time was based on routine TLC tests and changed with different conditions. Another purpose of this work was to see the effect of different esterification conditions on the reaction yield. Our results show that the best condition was to apply the DCCI:OH in 9 : 1 molar ratio. Other procedures involved using DCCI with toluene-*p*-sulfonic acid and –OH group in a molar ratio like 24 : 1 [27–31, 45, 41]. The yield of **4** was 63% (Scheme 1). The symmetrically functionalized porphyrazine with eight ester units was soluble in $CHCl_3$, CH_2Cl_2, THF, acetone, and toluene, and insoluble in water and *n*-hexane. The conversion of **4** into **5** was achieved by treatment with relatively strong acids (e.g. trifluoroacetic acid). Further reaction of **5** with cobalt(II)acetate, copper(II)acetate, and zinc(II)acetate led to the metal porphyrazinates (M=Co, Cu, Zn) (**6**–**8**) (figure 1).

The characterization of the products involved a combination of methods including FT-IR, UV–Vis, mass, ^{1}H, and ^{13}C NMR together with elemental analysis. Spectral investigations of all novel products were consistent with the assigned structures.

Elemental analyses correspond closely with the values calculated for **2**–**8** (table 1).

Comparison of the FT-IR spectra at each step gave some information on the structure of the compounds. FT-IR spectra of **3** show the C≡N vibration at 2220 cm^{-1} disappears with cyclotetramerization of **2**. This peak can be used to see the conversion and to detect any ligand impurities in the porphyrazine (**3**). In FT-IR spectra, the aromatic C–H peaks at 3055–3040 cm^{-1}, the aliphatic C–H peaks at 2985–2850 cm^{-1}, C=O peaks at 1727–1720 cm^{-1}, O–C=O peaks at 1265–1258 cm^{-1}, aromatic C=C peaks at 1655–1648 cm^{-1}, and a characteristic substituted naphthalene peak at 785–745 cm^{-1} for **4**–**8** [24, 47], the disappearance of the O–H peak around 3333 cm^{-1} for **3** and the N–H vibrations around 3290 cm^{-1} for **5**, together with the high solubility in chloroform and THF acquired after this reaction, are all evidence for formation of **4**–**8**.

^{1}H NMR spectra of **3** gave chemical shifts corresponding to O–H (triplet), O–CH_2 (triplet), S–CH_2 (triplet), and –CH_2– (multiplet) at 4.58, 4.40, 3.68, and 2.46 ppm, respectively. In the ^{1}H NMR spectrum of **4**, protons of naphthyl (multiplet), O–CH_2 (triplet), S–CH_2 (triplet), and –CH_2– (multiplet) are at 8.10–7.35, 4.68, 4.12, and 2.54 ppm, respectively. The N–H protons of **5** were also identified in the ^{1}H NMR spectrum with a broad peak at δ=−1.20 ppm, showing the typical shielding of inner core protons, a common feature of the ^{1}H NMR spectra of metal-free porphyrazines [27–33]. In the ^{13}C NMR spectra of diamagnetic porphyrazines **4**, **5**, and **8**, 16 different chemical shifts for the carbons were clearly seen.



M = Mg (**4**); 2H (**5**); Co (**6**); Cu (**7**); Zn (**8**)

Figure 1. 2,3,7,8,12,13,17,18-octakis(3-thiopropyl 1-naphthoate) substituted porphyrazines (**4**–**8**).

Mass spectrometric results of 1-naphthoate-substituted magnesium, metal-free, cobalt, copper, and zinc porphyrazines (**4**–**8**) confirmed the complete esterification of the –OH groups by the presence of molecular ion peaks, at *m/z*: 2291.8 $[M]^+$, 2268.2 $[M]^+$, 2325.1 $[M]^+$, 2330.8 $[M]^+$, and 2332.9 $[M]^+$, respectively. These data show that only one metal ion is coordinated to the porphyrazine core.

Electronic spectra were especially useful to establish the structure of the porphyrazines (**3**–**8**). UV–Vis spectra of the porphyrazine core are dominated by two intense bands, the Q band around 640 nm and the B band in the near UV region around 344 nm, both

Table 1. Elemental analyses of **2**–**8**.[a]

Compound	C	H	N	S
2	46.60 (46.49)	5.35 (5.46)	10.72 (10.84)	24.92 (24.82)
3	45.53 (45.42)	5.21 (5.34)	10.71 (10.59)	24.13 (24.25)
4	67.21 (67.10)	4.46 (4.58)	4.99 (4.89)	11.31 (11.20)
5	67.86 (67.76)	4.60 (4.71)	4.82 (4.94)	11.43 (11.31)
6	66.21 (66.10)	4.62 (4.51)	4.70 (4.82)	11.15 (11.03)
7	65.87 (65.97)	4.61 (4.50)	4.70 (4.81)	11.13 (11.01)
8	65.81 (65.92)	4.60 (4.49)	4.69 (4.80)	11.12 (11.00)

[a]Required values are given in parentheses.

correlated with $\pi \rightarrow \pi^*$ transitions [48, 49]. The presence of an electron-donating group on the periphery causes a bathochromic shift of the Q band. These two bands are present in all kinds of porphyrazines (**3**, **4**, **6**–**8**). UV–Vis spectra of metallo-porphyrazines (**4**, **6**–**8** in $CHCl_3$, 1×10^{-5} M) prepared in the present work exhibited intense single Q-band absorption at 632–644 nm and B bands at 342–348 nm (figure 2). For metal-free derivative (**5**), the Q band is split into two peaks at 620 and 676 nm as a consequence of the change in the symmetry of the porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h}. Here, in the case of porphyrazines with appending (3-thiopropyl 1-naphthoate) substituents in addition to absorptions of the porphyrazine core, an intense absorption due to the $\pi \rightarrow \pi^*$ transition of naphthalene appeared for all these porphyrazine derivatives (**4**–**8**) in the UV region at 288 nm [24, 47] (table 2). The four pyrrole moieties in the cavity of the porphyrazine macrocycle can accommodate only one metal unit with appropriate size [2, 10, 11]. The μ-nitrogens in the macrocycle which are accounted for in the fully conjugated 18 π-electron system cannot coordinate to extra metal ions [48, 49]; UV–Vis data of metallo-porphyrazines (**4**, **6**–**8**) show no shoulder in the Q band, which means no extra metal ions coordinate to the porphyrazine core. UV–Vis spectra of **7** (1×10^{-5} M) in solvents of different polarity (chloroform, dichloromethane, THF, and acetone) are given in Supplementary material. There is almost no difference with respect to changes in the nature of the solvent.

The aggregation behavior of porphyrazines in solution, which can be followed effectively by absorption measurements, is a good explanation for the interactions between the aromatic macrocycles of the porphyrazines. Aggregation, which is usually indicated as a coplanar association, depends on the concentration, nature of the solvent, nature of the substituents, complexed metal ions, and temperature [50–52]. The aggregation behavior of **6** was investigated for several concentrations in chloroform (Supplementary material). In chloroform, as the concentration was increased, the intensity of the Q-band absorption increased in parallel, and there were no new bands because of aggregated species [23]. The Beer–Lambert law was obeyed for **6** for concentrations ranging from 2×10^{-5} to 5×10^{-6} M dm^{-3} (Supplementary material).

In this work, we have described the synthesis, the spectral properties, and the preparation of new molecules in which planar porphyrazine cores have been peripherally

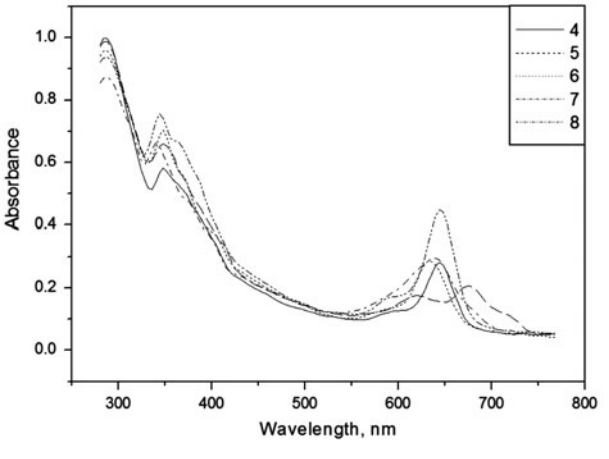


Figure 2. UV–Vis spectra of **4**–**8** in chloroform.

Table 2. UV–Vis data for the porphyrazines (**4**–**8**) in chloroform.

Compound	λ/nm (log ε/dm^3 M^{-1} cm^{-1})			
4	288 (5.00)	348 (4.77)	644 (4.45)	
5	284 (4.99)	348 (4.82)	620 (4.25)	676 (4.32)
6	288 (4.98)	346 (4.85)	632 (4.46)	
7	288 (4.94)	342 (4.82)	640 (4.47)	
8	288 (4.97)	344 (4.88)	644 (4.65)	

substituted with eight [3-thiopropyl 1-naphthoate] moieties through flexible bridges. A less soluble porphyrazine derivative containing reactive groups [53] can be used as a framework for subsequent reactions such as esterification. 1-Naphthoate-substituted porphyrazine derivatives show high solubility in solvents of different polarity from chloroform to acetone. Substitution of 1-naphthoate groups into the peripheral position of **3** imparts high solubility in chloroform, DCM, THF, and acetone. The increased solubility arises from higher solubility of the 1-naphthoate-substituted groups in polar organic solvents. The solubilities of **4** in chloroform, DCM, THF, and acetone were 45, 55, 61, and 64 mg/mL, respectively. When the polarity of the solvent increases, the solubility of **4** also increases as anticipated. The solubilities of **3** in THF, ethanol, and methanol were 36, 38, and 42 mg/mL, respectively. As a result of these solubility data for 1-naphthoate counterparts, it is clear that the main effect of solubility is due to the 1-naphthoate groups.

From stability of **4**–**8**, there have been many accounts of similar porphyrazines reported in the literature [27–33]. These are reported to be very stable ligands under the synthetic conditions mentioned in our manuscript since these methods are also standard literature methods for porphyrazine synthesis [27–33]. The ligands are aromatic structures and the macrocycle is expected to be very stable. The side chains contain ester and thioether functionalities which are quite stable under ordinary conditions. Therefore, ligand stability should not be an issue. Peripheral substituents with alkyl chain spacers at the porphyrazine core can affect the solubility of the molecule, whereas stability of the fully conjugated 18 π-electron system of the core can remain unaffected.

In conclusion, esterified porphyrazines surrounded with eight bulky (3-thiopropyl 1-naphthoate) units have been described; high electron density on the substituents results in a second absorption in the ultraviolet region of comparable intensity as the intense B band of porphyrazines. This study also shows that a poorly soluble porphyrazine derivative containing reactive units can be used as starting material for subsequent reactions such as esterification. We believe that some of the synthesized compounds might be utilized as catalysts, soluble dyes, and optical recording agents.

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