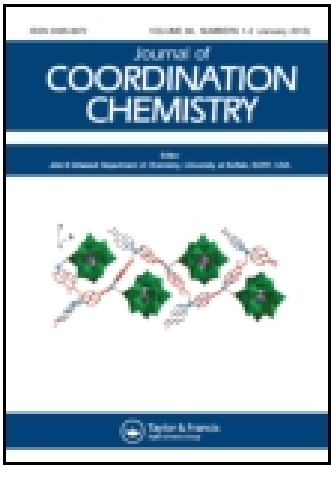

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Metal-free, metallo-porphyrazines, monomeric bisaxial complex $[FePz(py)_2]$ and the bridged complex $[FePz(pyz)]_n$ with eight (4-thiobutyl 4-biphenylcarboxylate) groups

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Metal-free, metallo-porphyrazines, monomeric bisaxial complex [FePz(py)$_2$] and the bridged complex [FePz(pyz)]$_n$ with eight (4-thiobutyl 4-biphenylcarboxylate) groups

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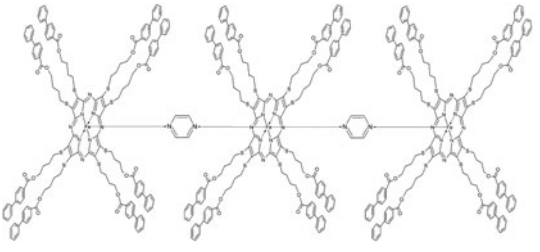

Metal-free and metallo-porphyrazines (M = Mg, Co, Cu, Zn, and ClFe) carrying eight hydroxybutylthio groups at peripheral positions were prepared from 2,3-bis(4-hydroxybutylthio) maleonitrile. The hydroxybutyl groups were incorporated by esterification of porphyrazine derivatives with 4-biphenylcarboxylic acid in the presence of dicyclohexylcarbodiimide and *p*-toluenesulfonic acid. Unlike the parent porphyrazine, the symmetrically functionalized porphyrazines with eight ester units were soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, acetone, and toluene and insoluble in water and *n*-hexane. Chloro-octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato iron(III) (FePzCl) was prepared by the reaction of metal-free porphyrazine with iron (II) acetate and further treatment with HCl solution. The monomeric bisaxial complex [FePz(py)$_2$] and the bridged complex [FePz(pyz)]$_n$ were formed as stable complexes by reacting FePzCl with pyridine and pyrazine, respectively. The newly synthesized compounds were characterized by elemental analysis, FT-IR, UV–vis, mass, ^{1}H and ^{13}C NMR spectroscopy.

Keywords: Porphyrazine; 4-Biphenylcarboxylic acid; Esterification; Shish kebab type oligomer; Iron

1. Introduction

Tetrapyrrole derivatives are of enormous technological importance for the manufacture of green and blue pigments, but other areas of current interest include application in catalysis, as thermally stable batteries, as chemical sensors, in electrochromism, liquid crystals, photodynamic therapy, and as modified supports for gas–solid chromatography [1]. The

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growing use of tetrapyrroles as advanced materials has encouraged the synthesis of new materials which differ in the central metal ion and peripheral substituents [2].

Peripherally functionalized porphyrazines should be considered as alternatives to phthalocyanines that have found extensive applications in many fields. These include material science, photodynamic therapy of tumors, pigments and dyes [3–6]. A range of different substituents provides porphyrazines with greatly enhanced organic solubility compared to their phthalocyanine counterparts, or additional donor sites to create multinuclear complexes [7–14]. Synthetic methods for a number of unsymmetrically substituted derivatives have been developed [15, 16].

We have been heavily engaged in the synthesis of porphyrazines carrying macrocyclic substituents. Substitution of several groups (e.g. 4-tert-buthylphenylthio [17], *o*-tolylthio and *p*-tolylthio [18], 1-naphthylmethylthio [19], 9-anthracenylmethylthio [20], 3,5-bis-trifluoromethyl-benzylthio [21], etc.) on the peripheral positions of porphyrazines has been accomplished by starting with an unsaturated dinitrile precursor or a preformed porphyrazine with reactive functional groups that can be subsequently modified (e.g. ferrocenes [22], triphenylphosphine [23], acetoxy [24], pentafluorobenzoate [25], 3,5-bis(trifluoromethyl)benzoate [26], 1-naphthoate [27], etc. have been incorporated by further condensation reactions). We have also synthesized and characterized shish kebab type oligomer with 2-fluoro-5-(trifluoromethyl) phenylacetate units [28] and soluble iron porphyrazine compounds with 2-fluoro-5-(trifluoromethyl)benzylthio substituents appending to the peripheral positions [29].

Solubility is an important property for porphyrazines; unsubstituted metal-free and metallo-porphyrazine structures are less or insoluble in common organic solvents. 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 soluble in chlorinated hydrocarbons such as dichloromethane and chloroform [22–28]. A further step for porphyrazine esters is the possibility to design supramolecular structures with donor groups on the ester.

In this article, we prepare a porphyrazine structure, on which eight 4-biphenylcarboxylate groups have been bound through flexible chains. Metal-free and metallo-porphyrazines (**4–8**) with eight (4-biphenylcarboxylate) units on the periphery through flexible thiobutyl-bridges have been synthesized through esterification of octakis(hydroxybutylthio) porphyrazinato magnesium with a 4-biphenylcarboxylic acid in the presence of dicyclohexylcarbodiimide (DCCI) and toluene-*p*-sulfonic acid. Porphyrazines (**4–8**) with eight ester units were soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, acetone, and toluene, but insoluble in water and *n*-hexane. Chloro-octakis (4-thiobutyl 4-biphenylcarboxylate) porphyrazinato iron(III) (FePzCl) (**9**) was prepared by reaction of metal-free porphyrazine with iron(II) acetate and further treatment with HCl solution. The monomeric bisaxial complex [FePz(py)$_2$] (**10**) as well as the bridged complex [FePz(pyz)]$_n$ (**11**) were formed as stable complexes by reacting FePzCl with pyridine and pyrazine, respectively. The compounds have been characterized by FT-IR, UV–vis, mass spectra, elemental analysis, ^{1}H NMR, and ^{13}C NMR.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer.

^{1}H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ solutions at 400.000 and 100.577 MHz, respectively, on a Bruker Ultra Shield Plus 400 MHz spectrometer. Chemical shifts refer to TMS (^{1}H NMR and ^{13}C NMR) as the internal standard. By using 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. Elemental analyses were recorded on a Thermo Scientific 2000 instrument. All reactions were carried out under nitrogen in dried solvents. All chemicals were used in a sufficient chemical purity. 4-Biphenylcarboxylic acid, 4-chloro-1-butanol, *N,N*-DCCI, toluene-*p*-sulfonic acid, *N,N*-dimethylformamide, chloroform, dichloromethane, toluene, acetone, diethyl ether, *t*-BuOMe, methanol, ethanol, *n*-butanol, *n*-hexane, pyridine, pyrazine, 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 (precoated sheets, 0.2 mm thick).

The disodium salt of dithiomaleonitrile (**1**) was prepared according to the previously reported procedure [30].

2.1. *2,3-Bis(4-hydroxybutylthio)maleonitrile (2)*

To a slowly stirred suspension of the disodium salt of dithiomaleonitrile (3.72 g, 20.0 mM) in absolute ethanol (200 mL) under nitrogen, a solution of 4-chloro-1-butanol (4.34 g, 40.0 mM) in absolute ethanol (10 mL) was added dropwise at ambient temperature. After 72 h of stirring, the mixture was filtered and the filtrate was concentrated under vacuum. The reddish-brown oily residue was extracted with anhydrous *t*-BuOMe (4 × 50 mL) and after evaporation of the solvent in vacuum, a reddish-brown highly viscous product was obtained which was recrystallized from cold diethyl ether as white crystals. Yield: 4.87 g (85%). FT-IR, ν_{max}/(cm^{-1}): 3335 br (OH), 2945–2870 (CH, aliphatic), 2210 (C≡N), 1655 (C=C), 1055 (C–O). ^{1}H NMR (δ, ppm): 4.65 (t, 2H, OH), 3.65 (t, 4H, O-CH_2), 3.30 (t, 4H, S–CH_2), 2.10 (m, 4H, –CH_2–), 1.75 (m, 4H, –CH_2–). ^{13}C NMR (δ, ppm): 26.4, 30.3, 31.5, 62.4, 115.3, 122.2. MS (ESI) *m/z*: 286.9 $[M]^+$.

2.2. *[2,3,7,8,12,13,17,18-Octakis(4-hydroxybutylthio)porphyrazinato] Mg(II) (3)*

Mg turnings (6 mg, 0.25 mM) with the addition of a small iodine crystal were refluxed overnight in dry *n*-butanol (20 mL). To this mixture, 2,3-bis(4-hydroxybutylthio)maleonitrile (**2**) (143 mg, 0.50 mM) was added and the suspension was refluxed with stirring for 6 h under nitrogen. The resulting blue–green suspension was filtered while hot and the precipitate was washed with *n*-butanol. 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 water. The blue–green highly viscous product was dissolved in methanol, filtered, and finally the solvent was evaporated in vacuum. The crude product was purified by chromatography on silica (methanol/chloroform 1/30 v/v). The product was soluble in methanol, ethanol, and tetrahydrofuran, but insoluble in *n*-hexane. Yield: 114 mg (78%). FT-IR, ν_{max}/(cm^{-1}): 3350 (OH), 2968–2830 (CH, aliphatic), 1068 (C–O). ^{1}H NMR (δ, ppm): 4.60 (t, 8H, OH), 3.62 (t, 16H, O–CH_2), 3.35 (t, 16H, S–CH_2), 2.15 (m, 16H, –CH_2–), 1.82 (m, 16H, –CH_2–). ^{13}C NMR (δ, ppm): 26.0, 30.5, 31.2, 62.6, 115.5, 122.0. MS (ESI) *m/z*: 1169.5, 1170.5, and 1172.5 $[M]^+$.

2.3. *[2,3,7,8,12,13,17,18-Octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] Mg(II) (4)*

Octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato magnesium (**4**) was prepared through reaction of **3** (0.581 g, 0.5 mM), 4-biphenylcarboxylic acid (2.38 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 nitrogen at ambient temperature for 72 h. The suspension was filtered and the solvent was evaporated in a vacuum. The residue was treated with chloroform (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 *in vacuo*. The colored product was stirred in cold dichloromethane, filtered, and the solvent was evaporated in a vacuum. The residue was treated with acetone. Purification of the product was accomplished by column chromatography (silica gel, methanol/chloroform, 1 : 50 v/v). The product was soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and toluene, but insoluble in water and *n*-hexane. Yield: 757 mg (58%). FT-IR, $\nu_{max}/(cm^{-1})$: 3066–3032 (CH, aromatic), 2954–2850 (CH, aliphatic), 1720 and 1265 (COO), 1665 (C=C, aromatic), 1610, 1425, 1412, 1305, 1218, 1148, 1004, 848, 768, 722, 692. ^{1}H NMR (δ, ppm): 7.95–7.75 (m, 32H, Ar–H), 7.67–7.29 (m, 40H, Ar–H), 4.62 (t, 16H, O–CH_2), 4.12 (t, 16H, S–CH_2), 2.26 (m, 16H, –CH_2–), 2.05 (m, 16H, –CH_2–). ^{13}C NMR (δ, ppm): 26.2, 28.2, 30.0, 64.3, 115.9, 122.1, 127.4, 127.9, 128.1, 128.3, 129.4, 141.0, 145.4, 146.5, 166.2. MS (ESI) *m/z*: 2610.9, 2611.9, and 2613.9 $[M]^+$.

2.4. *[2,3,7,8,12,13,17,18-Octakis(4-thiobutyl 4-biphenylcarboxylate) H^{21}, H^{23} porphyrazine] (5)*

Compound **4** (261 mg, 0.1 mM) was dissolved in trifluoroacetic acid (~3 mL). After stirring for 3 h at room temperature, the solution was added dropwise into ice to precipitate the product. Then, the mixture was filtered and the precipitate was washed with 10% ammonia solution. Subsequently, the product was washed with distilled water until free of traces of ammonia. Finally, the purple product was washed with ethanol and diethyl ether. Further purification was carried out on column chromatography (silica gel, methanol/chloroform 1/30 v/v). Yield: 166 mg (64%). FT-IR, $\nu_{max}/(cm^{-1})$: 3310 (N–H), 3070–3025 (CH, aromatic), 2945–2840 (CH, aliphatic), 1722 and 1262 (COO), 1658 (C=C, aromatic), 1614, 1428, 1415, 1308, 1222, 1145, 1008, 844, 772, 725, 695. ^{1}H NMR (δ, ppm): 7.90–7.70 (m, 32H, Ar–H), 7.62–7.32 (m, 40H, Ar–H), 4.65 (t, 16H, O–CH_2), 4.15 (t, 16H, S–CH_2), 2.29 (m, 16H, –CH_2–), 2.08 (m, 16H, –CH_2–), −1.25 (br s, 2H, NH). ^{13}C NMR (δ, ppm): 26.4, 28.4, 30.1, 64.2, 115.8, 122.3, 127.2, 127.7, 128.2, 128.5, 129.6, 141.1, 145.5, 146.3, 166.4. MS (ESI) *m/z*: 2589.8 $[M]^+$.

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

Compound **5** (129 mg, 0.05 mM) in $CHCl_3$ (10.0 mL) was stirred with [$Co(OAc)_2$ (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 chloroform 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 column chromatography (silica gel, methanol/chloroform 1 : 50 v/v).

2.5.1. [2,3,7,8,12,13,17,18-Octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] Co(II) (6). Yield: 100 mg (76%). FT-IR, $\nu_{max}/(cm^{-1})$: 3060–3028 (CH, aromatic), 2958–2845 (CH, aliphatic), 1718 and 1260 (COO), 1660 (C=C, aromatic), 1614, 1420, 1415, 1308, 1222, 1152, 1008, 844, 772, 725, 695. MS (ESI) *m/z*: 2646.7 $[M]^+$.

2.5.2. [2,3,7,8,12,13,17,18-Octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] Cu(II) (7). Yield: 95 mg (72%). FT-IR, $\nu_{max}/(cm^{-1})$: 3071–3026 (CH, aromatic), 2950–2855 (CH, aliphatic), 1722 and 1268 (COO), 1668 (C=C, aromatic), 1612, 1428, 1410, 1303, 1215, 1145, 1002, 846, 770, 720, 690. MS (ESI) *m/z*: 2651.4, 2652.4 $[M]^+$.

2.5.3. [2,3,7,8,12,13,17,18-Octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] Zn(II) (8). Yield: 106 mg (80%). FT-IR, $\nu_{max}/(cm^{-1})$: 3062–3034 (CH, aromatic), 2948–2858 (CH, aliphatic), 1716 and 1262 (COO), 1661 (C=C, aromatic), 1608, 1423, 1413, 1308, 1213, 1144, 1006, 846, 766, 724, 696. ^{1}H NMR (δ, ppm): 7.92–7.72 (m, 32H, Ar–H), 7.65–7.30 (m, 40H, Ar–H), 4.64 (t, 16H, O–CH_2), 4.10 (t, 16H, S–CH_2), 2.24 (m, 16H, –CH_2–), 2.06 (m, 16H, –CH_2–). ^{13}C NMR (δ, ppm): 26.0, 28.1, 30.0, 64.2, 115.8, 122.2, 127.5, 127.8, 128.0, 128.4, 129.5, 141.2, 145.2, 146.6, 166.4. MS (ESI) *m/z*: 2651.3, 2653.3, 2654.3, 2655.3, and 2657.3 $[M]^+$.

2.6. *Chloro-octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato iron(III) (FePzCl) (9)*

A mixture of **5** (129 mg, 0.05 mM) and $Fe(OAc)_2$ (435 mg, 2.50 mM) in acetic acid (20 mL) was heated at 120 °C for 24 h under nitrogen. The reaction was controlled continuously for the amount of any metal-free porphyrazine by UV–vis spectroscopy. After the reaction, the mixture was filtered and acetic acid (HOAc) was evaporated under reduced pressure. The residue was dissolved in chloroform (50 mL) and then extracted several times with 1 M, 100 mL HCl until no yellowish color of ferric salts was present in the aqueous phase. The chloroform solution was washed twice with water and dried over Na_2SO_4. When the solvent was evaporated, a green product was obtained. Further purification was carried out on column chromatography (silica gel, methanol/chloroform 1/50 v/v). Yield: 78 mg (58%). FT-IR, $\nu_{max}/(cm^{-1})$: 3070–3030 (CH, aromatic), 2955–2845 (CH, aliphatic), 1724 and 1266 (COO), 1663 (C=C, aromatic), 1614, 1424, 1411, 1308, 1216, 1145, 1095, 1001, 845, 769, 725, 691. MS (ESI) *m/z*: 2677.2, 2679.2, 2680.2, and 2681.2 $[M]^+$.

2.7. *Bis(pyridine)[octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] iron(II) [FePz(py)2] (10)*

Compound **9** (67 mg, 0.025 mM) was dissolved in benzene (10 mL) and pyridine (0.1 mL) was added. The mixture was refluxed for 5 h under N_2. After the solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and added dropwise to

DMF (10 mL). The precipitate formed was filtered and dried *in vacuo*. The pure porphyrazine was obtained by chromatography on silica gel using methanol/chloroform (1 : 20) mixture as eluent. Yield: 48 mg (68%). FT-IR, $\nu_{max}/(cm^{-1})$: 3065–3024 (CH, aromatic), 2956–2848 (CH, aliphatic), 1720 and 1263 (COO), 1655 (C=C, aromatic), 1602, 1585, 1424, 1415, 1308, 1220, 1146, 1004, 846, 764, 720, 695. ^{1}H NMR (δ, ppm): 7.97–7.73 (m, 32H, Ar–H), 7.69–7.32 (m, 40H, Ar–H), 6.92 (m, 4H, py-H_c), 4.80 (m, 2H, py-H_b), 4.60 (t, 16H, O–CH_2), 4.08 (t, 16H, S–CH_2), 2.32 (m, 4H, py-H_a), 2.22 (m, 16H, –CH_2–), 2.02 (m, 16H, –CH_2–). MS (ESI) *m/z*: 2799.8, 2801.8, 2802.8, and 2803.8 $[M]^+$.

2.8. *μ-Pyrazine[octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] iron(II) [FePz(pyz)]$_n$* (11)

Compound **9** (134 mg, 0.05 mM) was suspended in the melted pyrazine (400 mg, 5.0 mM) and heated for 24 h at 80 °C. After cooling, excess ligand was removed by high vacuum sublimation at 80 °C. Yield: 87 mg (64%). FT-IR, $\nu_{max}/(cm^{-1})$: 3060–3035 (CH, aromatic), 2960–2854 (CH, aliphatic), 1718 and 1263 (COO), 1662 (C=C, aromatic), 1612, 1581, 1426, 1410, 1309, 1214, 1145, 1009, 843, 765, 726, 695. ^{1}H NMR (δ, ppm): 7.95–7.70 (m, 32H, Ar–H), 7.72–7.30 (m, 40H, Ar–H), 4.60 (t, 16H, O–CH_2), 4.08 (t, 16H, S–CH_2), 2.29 (s, 4H, pyz-H), 2.20 (m, 16H, –CH_2–), 2.02 (m, 16H, –CH_2–).

3. Results and discussion

The alkylation product of the thiolate of disodium salt of dithiomaleonitrile with 4-chloro-1-butanol was chosen as the starting point for a soluble porphyrazine (scheme 1). The presence of bulky electron-donating S-group was expected to enhance the chemical stability and optical properties of porphyrazines [31]. The reddish-brown oily residue was obtained in high yield (85%). In the FT-IR spectrum of 2,3-bis(4-hydroxybutylthio)maleonitrile (**2**), stretching vibrations of OH, C–H (aliphatic), C≡N, and C=C groups were observed at 3335, 2945–2870, 2210, and 1655 cm^{-1}, comparable with those reported in the literature for similar compounds [9]. In the ^{1}H NMR spectrum of **2**, five different types of protons were clearly seen, triplets at 4.65, 3.65, 3.30 and multiplets at 2.10, 1.75 ppm correspond to OH, O–CH_2, S–CH_2, and two –CH_2– groups, respectively. The ratio of the integral values (1 : 2 : 2 : 2 : 2) also confirmed the proposed structure. Conversion of **2** into porphyrazine was achieved by the template effect of magnesium butanoate [7–14]. The reaction was feasible in *n*-propanol, but better yields were obtained in *n*-butanol (78%). Cyclotetramerization gave the blue–green octakis(4-hydroxybutylthio) porphyrazinato magnesium (**3**). It was soluble in methanol, ethanol, DMSO, and tetrahydrofuran, but insoluble in *n*-hexane. Elemental analyses corresponded closely with the values calculated for $C_{48}H_{72}N_8S_8O_8$ Mg. In the ^{1}H NMR spectrum of **3**, chemical shifts for OH, O–CH_2, S–CH_2, and two –CH_2– groups appear at 4.60, 3.62, 3.35, 2.15, and 1.82 ppm, respectively. In the FT-IR spectrum of **3**, as expected the C≡N stretching vibrations of the starting material disappear after porphyrazine formation. The fingerprint regions of divalent metallo-porphyrazines were almost identical. The synthetic route in the present work started with preparation of octakis(4-hydroxybutylthio)porphyrazinato magnesium (**3**) as a reactive intermediate and then 4-biphenylcarboxylate was condensed afterward. Octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato magnesium (**4**) with eight 4-biphenylcarboxylate groups on the periphery

through flexible alkylthio-bridges has been synthesized through esterification of **3** with a 4-biphenylcarboxylic acid in the presence of DCCI and toluene-*p*-sulfonic acid. Partially esterified porphyrazines were separated by column chromatography.

Octakis(4-thiobutyl 4-biphenylcarboxylate) substituted porphyrazinato magnesium (**4**) was demetallated by treatment with trifluoroacetic acid at room temperature to give the metal-free derivative (**5**), which was further metallated with anhydrous $Co(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$ to give the corresponding metallo-porphyrazines (**6–8**) (figure 1). A common property of all these 4-biphenylcarboxylate substituted porphyrazines was the solubility in chloroform, dichloromethane, tetrahydrofuran, acetone, and toluene.

The aim of esterification was to enhance the overall solubility in common organic solvents. Ester groups were known to provide good solubility, and they were selected because of the ease of their synthesis [22–28]. In esterification reactions mediated by DCCI, conversion of all alcohol functionalities to ester form has been accomplished; here, *p*-toluenesulfonic acid helped isolation from the urea formed. By referring to mass spectrometric data, the usage of DCCI-mediated esterification system for octakis (hydroxybutylthio) porphyrazines ensured that all of the available –OH groups reacted in the process. The choice of reaction time was based on routine TLC tests and changed with

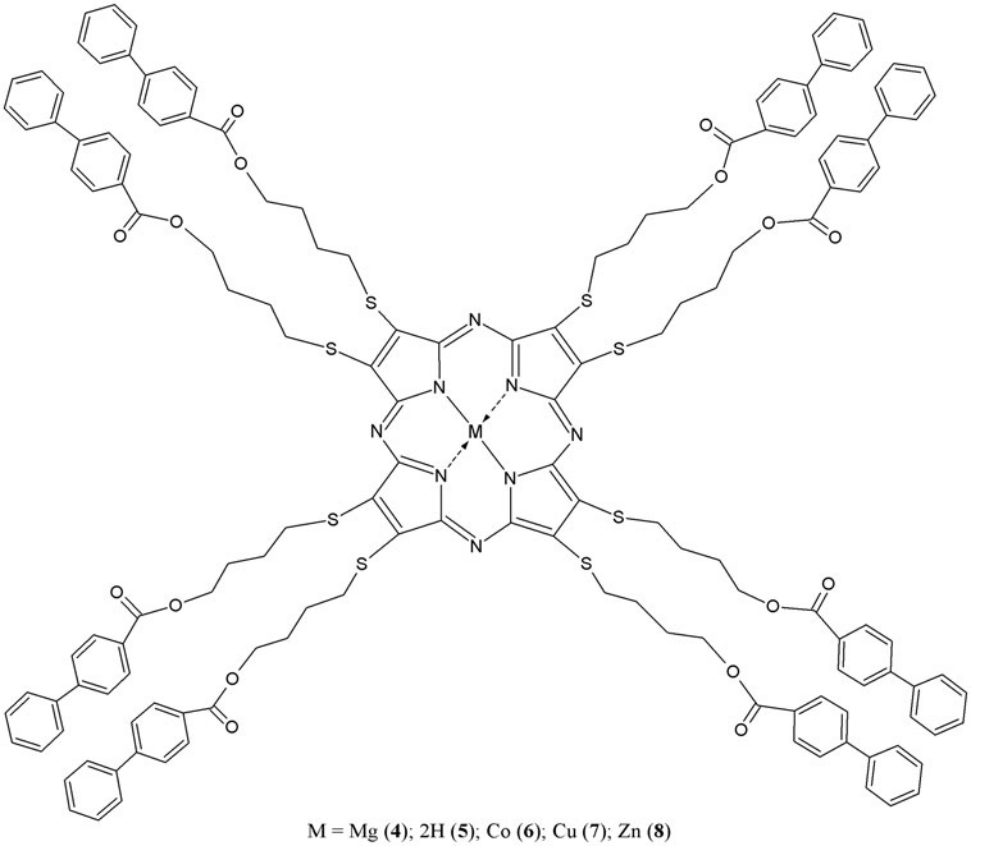


Figure 1. [2,3,7,8,12,13,17,18-Octakis(4-thiobutyl 4-biphenylcarboxylate)] substituted porphyrazines (**4–8**).

different conditions. Another aim of this study was to see the effect of different esterification conditions on reaction yield. Our results showed that the best condition was to utilize DCCI : OH group in 9 : 1 M ratio. Other procedures involved the usage of DCCI with toluene-*p*-sulfonic acid and –OH group in molar ratio like 24 : 1 : 1 [22–28].

Iron insertion into **5** was performed in acetic acid using anhydrous iron(II) acetate as the metal salt (scheme 2) [32, 33]. Although the reaction was performed under inert atmosphere, trace amounts of oxygen led to Fe(III) derivatives. Further exposure to air was almost inevitable during the work-up procedures, so the product was treated with dilute HCl solution to convert all of the trivalent iron products into FePzCl (**9**). The band at 1095 cm^{-1} in the FT-IR spectrum of **9** can be assigned to the contribution of axial ligands to CN-skeleton vibrations as encountered in octaphenyltetraazaporphyrins [34]. Another consequence of the presence of the axial chloride is the changes occurring in the Q-band absorption from an MPz derivative of D_{4h} symmetry (e.g. **4** where Q-band is at 675 nm as a single intense absorption) to C_{4v} symmetry [34, 35], resulting in an intense band at 588 nm together with two others at 544 and 680 nm of **10** [36].

Tetrapyrrole derivatives having transition metal ions, e.g. iron(II), in the center are of important interest while they form shish kebab type axially coordinated bridged complexes with bidentate coordinating ligands. Compound **9** can be easily reduced to axially coordinated **10** in the presence of ligands such as pyridine (figure 2). We have prepared bridged systems with pyrazine and an axially coordinated monomer with pyridine (scheme 2). While pyridine can react with **9** in benzene solutions, we perform the reaction with pyrazine only in melted excess ligand and the product is a bridged system (**11**) (not bisaxially coordinated monomer) (figure 3) [37].

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

Elemental analyses correspond closely with the values calculated for **3–11** (table 1).

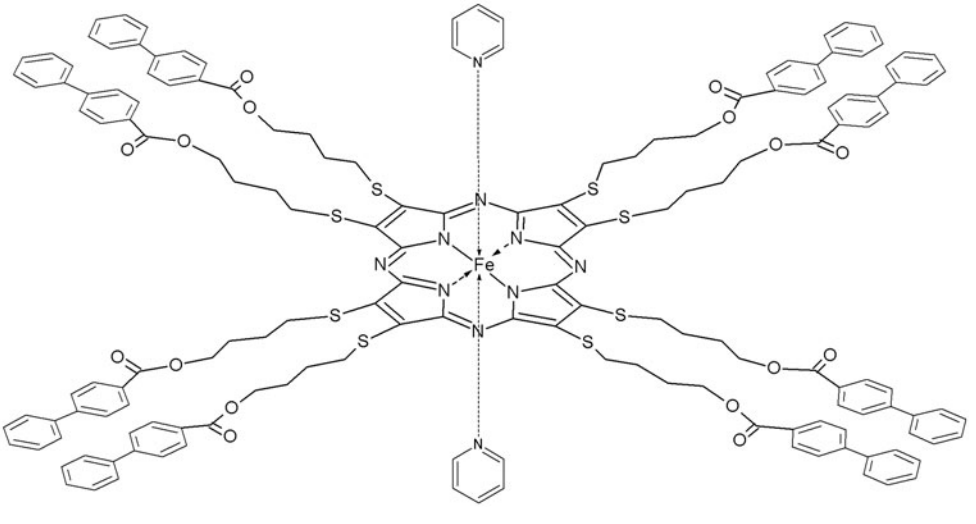


Figure 2. Bis(pyridine)[octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] iron(II) [FePz(py)$_2$] (**10**).

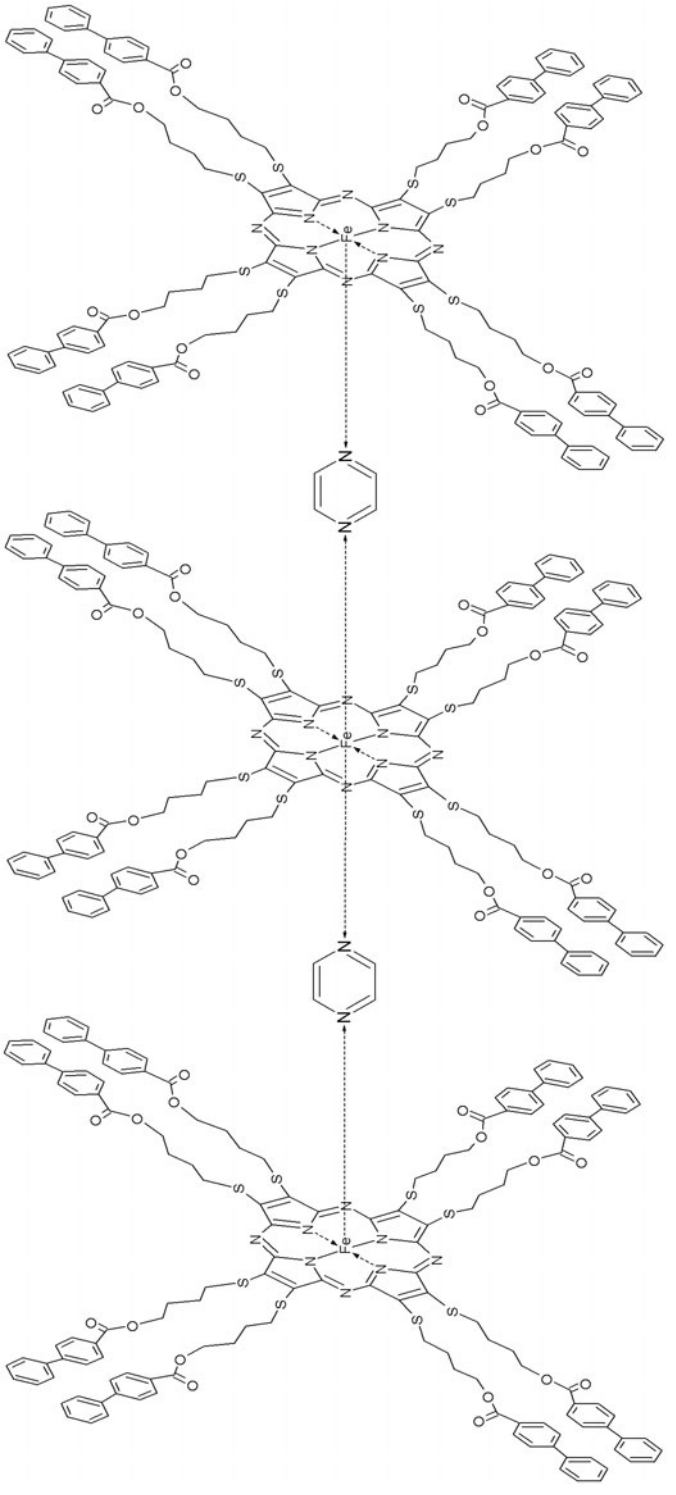


Figure 3. μ-Pyrazine[octakis(4-thiobutyl 4-biphenylcarboxylate) porphyrazinato] iron(II) [FePz(pyz)]$_n$ (**11**).

Table 1. Elemental analyses of **3–11**.*

Compound	C	H	N	S
3	49.42 (49.28)	6.20 (6.51)	9.42 (9.58)	22.06 (21.93)
4	69.80 (69.91)	5.37 (5.25)	4.18 (4.29)	9.94 (9.82)
5	70.63 (70.51)	5.49 (5.37)	4.20 (4.33)	9.80 (9.91)
6	69.10 (68.99)	5.06 (5.18)	4.35 (4.23)	9.80 (9.69)
7	68.75 (68.87)	5.29 (5.17)	4.10 (4.23)	9.80 (9.68)
8	68.94 (68.82)	5.05 (5.17)	4.34 (4.22)	9.79 (9.67)
9	68.29 (68.16)	5.25 (5.12)	4.06 (4.18)	9.70 (9.58)
10	69.58 (69.46)	5.37 (5.25)	5.12 (5.00)	9.29 (9.16)
11	68.68 (68.80)	5.30 (5.18)	5.02 (5.14)	9.55 (9.42)

*Required values are given in parentheses.

In the FT-IR spectra, the aromatic C–H peaks at 3071–3024 cm^{-1}, the aliphatic C–H peaks at 2960–2840 cm^{-1}, C=O peaks at 1724–1716 cm^{-1}, O–C=O peaks at 1268–1260 cm^{-1}, and the aromatic C=C peaks at 1668–1655 cm^{-1} for **4–11** [23–28], the disappearance of the O–H peak at 3350 cm^{-1} for **3** and the N–H vibrations at 3310 cm^{-1} for **5**, together with the high solubility in chloroform and tetrahydrofuran acquired after this reaction, are all evidence for formation of **4–8**. In the FT-IR spectrum of **10**, the newly appearing bands at 1585 cm^{-1} and 1220 cm^{-1} are likely to be due to the breathing mode of axial pyridine [37]. In the FT-IR spectrum of **11**, the stretching vibration at 1581 cm^{-1} is characteristic for the pyrazine [38].

^{1}H NMR spectrum of **3** represented chemical shifts corresponding to O–H (triplet), O–CH_2 (triplet), S–CH_2 (triplet), and two –CH_2– (multiplets) at 4.60, 3.62, 3.35, 2.15, and 1.82 ppm, respectively. In the ^{1}H NMR spectrum of **4**, two multiplets at 7.95–7.75 ppm and 7.67–7.29 ppm correspond to aromatic protons, a triplet at 4.62 ppm belongs to O–CH_2, a triplet at 4.12 ppm belongs to S–CH_2 and two multiplets at 2.26 ppm and 2.05 ppm belong to –CH_2–. Since the protons in the inner core of porphyrazine (**5**) were screened by aromatic π electrons of the macrocycle, they appeared at –1.25 ppm in the ^{1}H NMR [18–21, 23]. The ^{1}H NMR spectra of **10** and **11** (Supplemental data for this article can be accessed here http://dx.doi.org/10.1080/00958972.2013.867036) indicate an octahedrally coordinated Fe(II) complex. The chemical shift values of the axially coordinated ligands have been extensively affected by the 18–π electrons of the porphyrazine core, i.e. the peaks at 8.59, 7.75, and 7.38 ppm in free pyridine have been shifted to 6.92, 4.80, and 2.32 ppm, respectively, after binding axially to form [FePz(py)$_2$]. Similarly, there is only a single peak at 2.29 ppm for pyrazine protons in the bridged structure [FePz(pyz)]$_n$ [39–41]. In the ^{13}C

Table 2. UV–vis data for porphyrazines (**4–11**) in chloroform.

Compound	λ/nm (log ε/dm^3 mol^{-1} cm^{-1})			
4	379 (4.97)		675 (4.96)	
5	336 (4.95)	652 (4.75)		710 (4.78)
6	345 (4.83)		675 (4.88)	
7	353 (4.88)		679 (4.99)	
8	352 (4.93)		683 (4.99)	
9	348 (4.95)	544 (4.29)	588 (4.14)	680 (3.95)
10	350 (4.92)		594 (4.62)	
11	352 (4.85)		626 (4.43)	712 (4.35)

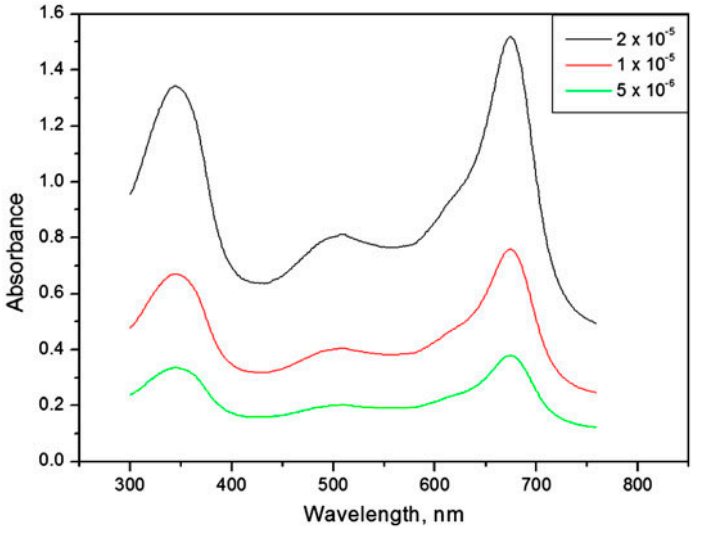
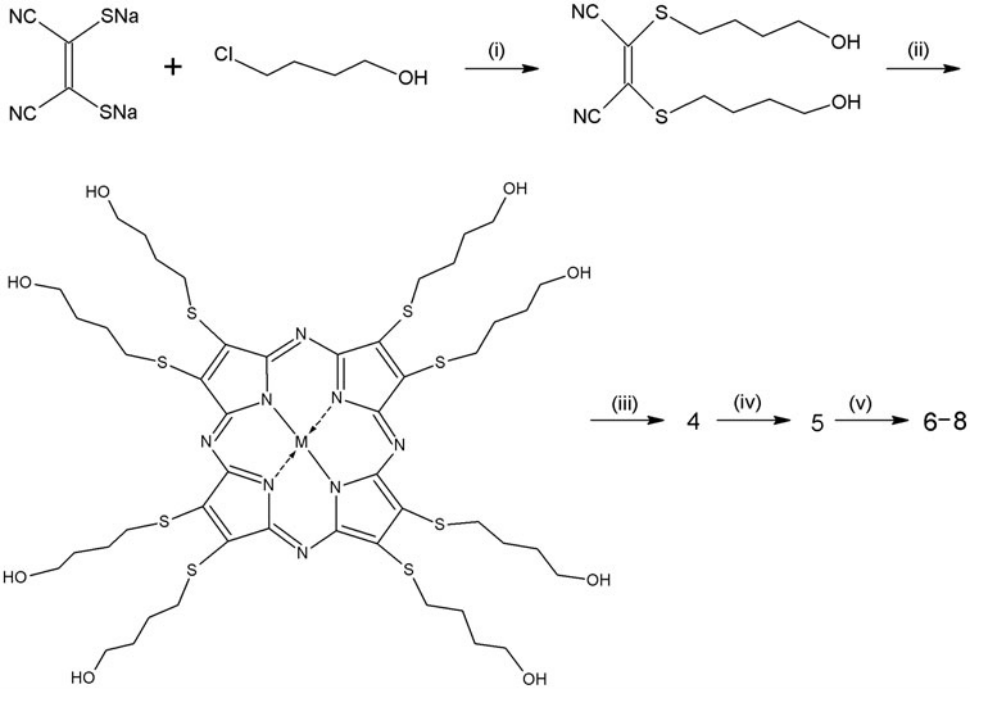
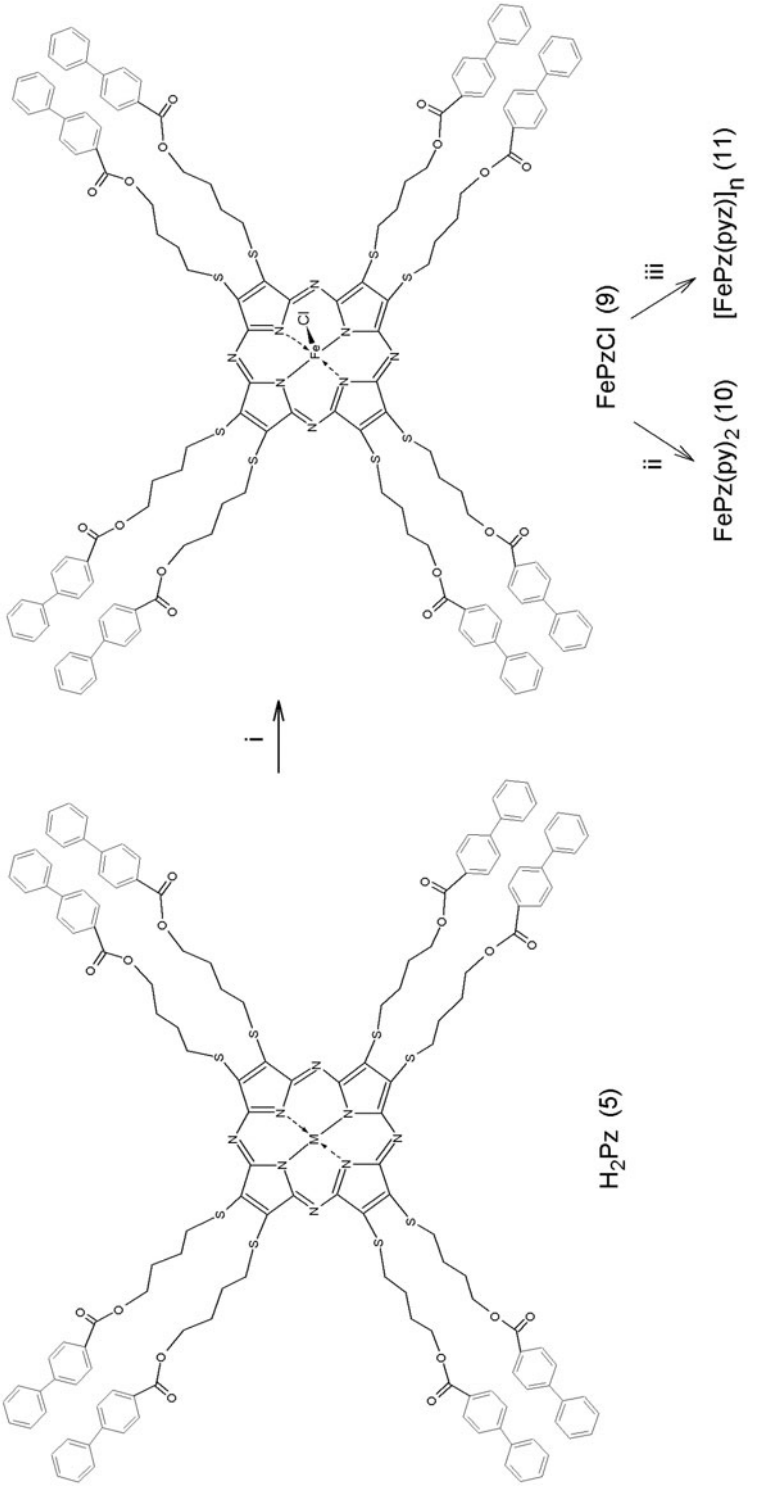


Figure 4. UV–vis spectra of **6** in chloroform at different concentrations.



Scheme 1. (i) Abs. EtOH; (ii) Mg turnings, I2, *n*-BuOH; (iii) 4-biphenylcarboxylic acid, DCCI, *p*-toluenesulfonic acid and pyridine; (iv) CF_3CO_2H; (v) EtOH, $CHCl_3$ and $Co(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$.



Scheme 2. (i) $Fe(OAc)_2$, acetic acid, HCl; (ii) pyridine; and (iii) pyrazine.

NMR spectra of diamagnetic porphyrazines (**4**, **5**, **8**), 15 different single chemical shifts for carbon atoms were clearly seen.

The mass spectrometry data of porphyrazines (**3–10**) gave the characteristic molecular ion peaks at *m/z*: 1170.5 $[M]^+$, 2611.9 $[M]^+$, 2589.8 $[M]^+$, 2646.7 $[M]^+$, 2651.4 $[M]^+$, 2653.3 $[M]^+$, 2679.2 $[M]^+$, and 2801.8 $[M]^+$, respectively, confirming the proposed structures. The theoretical molecular mass of each complex was calculated by using the average atomic weights of metals (given in Periodic table). There was only one main metal peak in Cu, Zn, Fe, and Mg complexes.

Electronic spectra can be used to differentiate metal-free and metallo-porphyrazines. As expected for **4** and **6–8** of D_{4h} symmetry, there is a single Q-band absorption in the low energy region and a single B-band. These absorptions correspond to $\pi \rightarrow \pi^*$ transition and are observed around 675–683 and 336–379 nm (Supplementary data). While Q-band absorptions are split into two peaks at around 600–700 nm in **5**, the same absorptions appear as a single peak in **4** and **6–8**. Thus, the single intense peak at 675 nm for **4** corresponds with two relatively weak peaks at 652 and 710 nm in the metal-free analog (**5**). The reason for the splitting is the change of symmetry from D_{4h} to D_{2h}. The presence of the axial chloride changes the Q-band absorption from an MPz derivative of D_{4h} symmetry (e.g. MgPz where Q-band is at 675 nm as a single intense absorption) to C_{4v} symmetry, resulting in an intense band at 588 nm together with two others at 544 and 680 nm (**9**) (Supplementary data). The Q-bands at 594 and 626 nm in the UV–vis spectra of $[FePz(py)_2]$ (**10**) (Supplementary data) and $[FePz(pyz)]_n$ (**11**) (Supplementary data) confirm coordination of the pyridine and pyrazine ligands to the metal ion (table 2).

The aggregation behavior of **6** was investigated at different molarities in chloroform (figure 4). As the concentration was increased, the intensity of the Q-band absorption increased in parallel and there were no new bands because of aggregation. The range of concentrations was from 5×10^{-6} to 2×10^{-5} M dm^{-3} (figure 4). UV–vis spectra of **7** in solvents of different polarity (acetone, chloroform, tetrahydrofuran, and dichloromethane) are given in Supplementary data. There is almost no difference with respect to the changes in the nature of the solvent.

Similar differences occur in the oxidation state of the metal ion when a bidentate ligand such as pyrazine is used instead of pyridine. Bidentate ligands formed a bridge between the metal centers in a shish kebab type oligomer [42, 43]. In the UV–vis spectrum of **11**, the Q-band absorption at 626 nm shifted to longer wavelength (*ca.* 32 nm) when compared with the monomeric structure (**10**) obtained with pyridine. There was also a shoulder around 712 nm in the electronic spectra after oligomer formation.

In the present article, synthesis and spectral properties of soluble esterified porphyrazines surrounded with eight bulky (4-thiobutyl 4-biphenylcarboxylate) groups have been described. The monomeric bisaxial complex $[FePz(py)_2]$ as well as the bridged complex, shish kebab type olygomer, $[FePz(pyz)]_n$ were formed as stable complexes by reacting FePzCl with pyridine and pyrazine, respectively. Solubilities of metallo-porphyrazines in common solvents were enhanced. This study showed that the Fe(II)Pz macrocycle reacts in excess liquid pyrazine to form exclusively a polymeric compound as was the case for most tetraaza annulenes. Also, a poorly soluble porphyrazine derivative containing reactive groups can be used as a framework for subsequent reactions such as esterification.

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