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Metal-free, metallo-, oligomeric, and monomeric porphyrazine complexes of (3-thiopropyl anthraquinone-2-carboxylate) units

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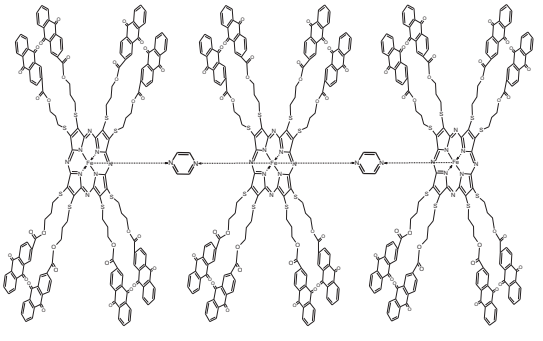

Metal-free and metallo-porphyrazines (M = Mg, 2H, Co, Cu, Zn, or ClFe) with eight (3-thiopropyl anthraquinone-2-carboxylate) units appending on the periphery through flexible alkylthio-bridges have been synthesized through esterification of octakis(hydroxypropylthio) porphyrazinato magnesium with anthraquinone-2-carboxylic acid in the presence of dicyclohexylcarbodiimide (DCCI) and toluene-*p*-sulfonic acid. The synthesized compounds were characterized by FT-IR, UV–vis, ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis.

Metal-free and several metallo-porphyrazines (M = Mg, 2H, Co, Cu, or Zn) carrying eight (3-thiopropyl anthraquinone-2-carboxylate) groups at the peripheral positions were synthesized from octakis(3-hydroxypropylthio)porphyrazinato] Mg(II). Symmetrically functionalized porphyrazines with eight ester units were soluble in common organic solvents. Chloro-octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato iron(III) (FePzCl) was prepared by the reaction of metal-free porphyrazine with iron(II) acetate and further treatment with hydrochloric acid solution. The oligomeric structure $[FePz(pyz)]_n$ and the monomeric compound $[FePz(py)_2]$ were formed as stable complexes by reacting FePzCl with pyrazine and pyridine, respectively. The porphyrazine compounds were characterized by different spectroscopic methods.

Keywords: Anthraquinone-2-carboxylic acid; Shish kebab type oligomer; Pyrazine; Esterification; Porphyrazine

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1. Introduction

Tetrapyrrole complexes are excellent functional materials and diverse chemical, and technological applications have been developed around these interesting and advanced materials [1–3]. Possible technological applications of tetrapyrroles, such as semi-conductivity, electrochromic displays, chemical sensors, and catalysts, have encouraged many researchers to synthesize various types of metal derivatives [4–12].

The exceptional chemical and physical properties of these compounds can be due to various substituents on the benzo rings. The range of solubility for porphyrazines becomes very important for these applications, since several porphyrazines are poorly soluble in organic solvents and water. The solubility of porphyrazines can be increased by adding different kinds of substituents such as bulky or long-chain alkyl, alkylthio, or alkoxy groups at the periphery and axial positions of the porphyrazine ring [13–21]. The most extensively investigated soluble-substituted tetrapyrroles are the tetra- and octa-substituted derivatives and tetra-substituted ones usually show higher solubility [22]. The formation of constitutional isomers and the higher dipole moment of the tetra-substituted tetrapyrroles resulting from the unsymmetrical arrangement of the substituents in the periphery give higher solubility of these systems [23].

The applications of ester-containing tetrapyrrole complexes are variable. For example, some esters [24] showed gas sensor response against NO_x gasses, whereas some showed characteristics of liquid crystals with glassy transitions [25, 26]. However, some patents and publications reported that ester-containing tetrapyrroles could be used as electrophotographic photoconductors [27], photosensitizers in photodynamic therapy [28, 29], optical storage agent [30], and tumor growth suppressor [31].

Solubility is a significant property of porphyrazines and most of their treatments are best investigated in soluble form. Because unsubstituted parent metal-free and most of the metallo-porphyrazines are less soluble in common organic solvents, the synthesis of new porphyrazine systems should be designed so that the final porphyrazine derivatives are soluble enough to perform the desired activities. A common means for preparing soluble porphyrazines is to attach functional groups like 4-tert-butylphenylthio [32], *o*-tolylthio, and *p*-tolylthio [33], pentafluorobenzylthio [34], 1-naphthylmethylthio [35], 9-anthracenylmethylthio [36], 3,5-bis(trifluoromethyl)benzylthio [37] at the peripheral and axial positions of the porphyrazine ring. Compared with unsubstituted parent metallo-porphyrazines, ester-containing porphyrazines and phthalocyanines (e.g. triphenylphosphine [38], acetoxy [39], 9-anthroyl [40], tetra(acetoxyethylthio) [41], pentafluorobenzoate [42], 3,5-bis(trifluoromethyl)benzoate [43], 1-naphthoate [44]) are highly soluble in chlorinated hydrocarbons. We have also synthesized and characterized shish kebab-type oligomer with 2-fluoro-5-(trifluoromethyl)phenylacetate units [45], 9-anthracenylmethylthio iron porphyrazine derivatives [46], and soluble iron porphyrazine compounds with 2-fluoro-5-(trifluoromethyl)benzylthio substituents appending to the peripheral positions [47].

The expected properties of metallo-porphyrazine derivatives are almost entirely based on a redox or electron transfer reaction. The electron transfer of metallo-porphyrazine is estimated by the electrode reaction, since they have many applications in thin-layer films. The electron transfer properties of metallo-porphyrazine derivatives can be utilized not only to make thin-layer films but also to fix soluble ones. It is requisite, therefore, to study the redox properties of metallo-porphyrazine derivatives in order to reclaim their use for further applications. Anthraquinone derivatives, as the biggest group of natural quinones and historically the most important ones, have been widely used in chemistry, biochemistry, and

industry [48]. The essential role of anthraquinones in biological electron transport [49] and industrial methods as redox catalysts [50] has led to extensive research of their electrochemical behavior [51]. Although porphyrin–anthraquinone dyads have been many times encountered [52], phthalocyanine–anthraquinone dyads are less studied [53].

In the present article, our aim is to synthesize a series of metallo- and metal-free porphyrazines functionalized with peripheral anthraquinone-2-carboxylate substituents through flexible oxypropylthio-bridges, enhancing their solubility in common solvents and at the same time prohibiting their aggregation. Anthraquinone has been chosen as a substituent in this study as it is known to have oxidation and reduction properties, and its CV shows a typical reversible two-step one-electron redox reaction. The redox of metallo-porphyrazine derivatives is due to the interaction between the porphyrazine ring and the central metal [54, 55]. We report herein the synthesis and characterization of new readily soluble metallo-porphyrazines with (3-thiopropyl anthraquinone-2-carboxylate) containing substituents on the periphery, and we also report on the effects of the substituents on the spectroscopic and aggregation properties of the porphyrazine derivatives in different solvents and at various concentrations in chloroform. Then, we prepared chloro-octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato iron(III) (FePzCl) (**8**) by the reaction of metal-free porphyrazine with iron(II) acetate and further treatment with hydrochloric acid solution. The oligomeric compound $[FePz(pyz)]_n$ (**9**) and the monomeric complex $[FePz(py)_2]$ (**10**) were obtained as stable structures by reacting FePzCl with pyrazine and pyridine, respectively. The newly synthesized complexes were characterized by FT-IR, UV–vis, ^1H, and ^{13}C NMR, mass spectrometry, and elemental analysis.

2. Experimental

Electronic spectra were recorded on a Unicam UV2 spectrophotometer and IR spectra on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. ^1H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ solutions at 400 and 100 MHz, respectively, and recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer. Chemical shifts refer to TMS (^1H and ^{13}C NMR) as the internal standards. Mass spectra were recorded on a Bruker Daltonics Micro-TOF and MALDI-TOF mass spectrometer using the electrospray ionization (ESI) method. The instrument was operated in positive ion mode. Elemental analyses were recorded on a Thermo Scientific 2000 instrument. All reactions were performed under N_2 in dried solvents. All chemicals were in sufficient chemical purity. Anthraquinone-2-carboxylic acid, 3-chloro-1-propanol, methyl *tert*-butyl ether, N,N-dicyclohexylcarbodiimide, toluene-*p*-sulfonic, acid, N,N-dimethylformamide, chloroform, dichloromethane, pyridine, pyrazine, toluene, acetone, ethanol, methanol, *n*-butanol, trifluoroacetic acid, tetrahydrofuran, sodium sulfate, and sodium carbonate were purchased from Aldrich, Merck, or Alfa Aesar.

The disodium salt of dithiomaleonitrile (**1**) [56] and [2,3,7,8,12,13,17,18-octakis(3-hydroxypropylthio)porphyrazinato] Mg(II) (**2**) [42] was prepared according to previously reported procedures.

2.1. *{2,3,7,8,12,13,17,18-Octakis[3-thiopropyl anthraquinone-2-carboxylate] porphyrazinato} Mg(II) (3)*

Octakis[3-thiopropyl anthraquinone-2-carboxylate] porphyrazinato-magnesium (**3**) was prepared through the reaction of **2** (0.529 g, 0.5 mM), anthraquinone-2-carboxylic acid

(3.026 g, 12 mM), dicyclohexylcarbodiimide (DCCI) (2.476 g, 12 mM), and toluene-*p*-sulfonic acid (0.086 g, 0.5 mM) in dry pyridine (40 mL) under N_2 at room temperature for 84 h. The suspension was filtered and the solvent was evaporated in vacuum. The residue was treated with $CHCl_3$ (120 mL) and the clear solution was extracted with 10% Na_2CO_3 solution (150 mL) and then with water. The extraction was repeated many times with water until pH was neutral. The chloroform phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuum. The product was stirred in cold dichloromethane, filtered, and the solvent was evaporated in *vacuo*. The residue was treated with acetone. The purification of the product was performed 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: 704 mg (48%). FT-IR, $\nu_{max}/(cm^{-1})$: 3068–3028 (CH, aromatic), 2975–2860 (CH, aliphatic), 1718 and 1260 (COO), 1665 (C=C, aromatic), 1590, 1562, 1485, 1330, 1286, 1122, 1048, 972, 935, 872, 702, 636. ^{1}H NMR (δ, ppm): 7.88–7.62 (m, 24H, Ar–H), 7.56–7.28 (m, 32H, Ar–H), 4.68 (t, 16H, O–CH_2), 4.12 (t, 16H, S–CH_2), 2.58 (m, 16H, –CH_2–). ^{13}C NMR (δ, ppm): 26.2, 26.6, 63.6, 115.3, 122.2, 129.5, 130.3, 132.5, 133.0, 133.5, 134.0, 138.3, 165.7, 182.6. MS (ESI) *m/z*: 2931.9 $[M]^+$.

2.2. *{2,3,7,8,12,13,17,18-Octakis[3-thiopropyl anthraquinone-2-carboxylate] H^{21}, H^{23} porphyrazine} (4)*

3 (293 mg, 0.1 mM) was dissolved in the minimum amount of trifluoroacetic acid (~4 mL) and stirred for 3 h at room temperature. When the reaction mixture was added to ice dropwise and neutralized with 25% ammonia solution, precipitation occurred and it was filtered. The precipitate was extracted into chloroform and the chloroform solution was extracted with water at least twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a violet-colored metal-free porphyrazine. **4** was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1 : 50 v/v). Yield: 157 mg (54%). FT-IR, $\nu_{max}/(cm^{-1})$: 3310 (N–H), 3072–3032 (CH, aromatic), 2988–2852 (CH, aliphatic), 1724 and 1266 (COO), 1652 (C=C, aromatic), 1595, 1558, 1481, 1338, 1282, 1126, 1054, 976, 932, 876, 708, 632. ^{1}H NMR (δ, ppm): 7.85–7.60 (m, 24H, Ar–H), 7.58–7.30 (m, 32H, Ar–H), 4.62 (t, 16H, O–CH_2), 4.16 (t, 16H, S–CH_2), 2.62 (m, 16H, –CH_2–), −1.05 (br s, 2H, NH). ^{13}C NMR (δ, ppm): 26.0, 26.8, 63.5, 115.4, 122.0, 129.7, 130.1, 132.7, 133.2, 133.7, 134.2, 138.5, 165.4, 182.3. MS (ESI) *m/z*: 2909.8 $[M]^+$.

2.3. *General procedure for metallo-porphyrazines (5–7)*

4 (145 mg, 0.05 mM) in $CHCl_3$ (10 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 mL) and refluxed under nitrogen for about 8 h. Then, the precipitate composed of the crude product and the excess metal salt was eliminated. The precipitate was treated with chloroform and the insoluble metal salts were removed by filtration. The filtrate was reduced to minimum volume under reduced pressure and then added to *n*-hexane (150 mL) dropwise to accomplish precipitation. Finally, the pure porphyrazine derivatives (**5–7**) were isolated by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1 : 20 v/v).

2.3.1. {2,3,7,8,12,13,17,18-Octakis[3-thiopropyl anthraquinone-2-carboxylate] porphyrazinato} Co(II) (5). *Yield* 107 mg (72%). FT-IR, $\nu_{max}/(cm^{-1})$: 3070–3025 (CH, aromatic), 2980–2855 (CH, aliphatic), 1715 and 1266 (COO), 1661 (C=C, aromatic), 1586, 1558, 1488, 1336, 1282, 1125, 1044, 975, 932, 875, 705, 633. MS (ESI) *m/z*: 2966.8 $[M]^+$.

2.3.2. {2,3,7,8,12,13,17,18-Octakis[3-thiopropyl anthraquinone-2-carboxylate] porphyrazinato} Cu(II) (6). *Yield* 98 mg (66%). FT-IR, $\nu_{max}/(cm^{-1})$: 3072–3030 (CH, aromatic), 2968–2850 (CH, aliphatic), 1725 and 1260 (COO), 1663 (C=C, aromatic), 1590, 1562, 1490, 1339, 1280, 1128, 1048, 971, 936, 879, 708, 630. MS (ESI) *m/z*: 2970.1 $[M]^+$.

2.3.3. {2,3,7,8,12,13,17,18-Octakis [3-thiopropyl anthraquinone-2-carboxylate] porphyrazinato} Zn(II) (7). *Yield* 113 mg (76%). FT-IR, $\nu_{max}/(cm^{-1})$: 3068–3028 (CH, aromatic), 2977–2862 (CH, aliphatic), 1712 and 1264 (COO), 1667 (C=C, aromatic), 1594, 1568, 1486, 1333, 1285, 1124, 1052, 974, 938, 872, 703, 634. ^{1}H NMR (δ, ppm): 7.90–7.64 (m, 24H, Ar–H), 7.58–7.32 (m, 32H, Ar–H), 4.72 (t, 16H, O–CH_2), 4.10 (t, 16H, S–CH_2), 2.56 (m, 16H, -CH_2–). ^{13}C NMR (δ, ppm): 26.5, 26.8, 63.8, 115.1, 122.4, 129.8, 130.5, 132.2, 133.2, 133.8, 134.2, 138.5, 165.9, 182.2. MS (ESI) *m/z*: 2973.1 $[M]^+$.

2.4. *Chloro-octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato iron(III) (FePzCl) (8)*

4 (145 mg, 0.05 mM) and $Fe(OAc)_2$ (435 mg, 2.50 mM) in CH_3COOH (20 mL) were reacted at 130 °C for 36 h under N_2 atmosphere. Using the UV–vis spectrophotometric method, the amount of metal-free porphyrazine was determined. After the completion of the reaction, the mixture was filtered and CH_3COOH was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$ (60 mL) and then extracted several times with 100 mL of 1 M hydrochloric acid until no yellowish color of iron salts remained in the aqueous solution. The chloroform solution was washed twice with distilled water and dried over Na_2SO_4. When the chloroform was removed, a blue-green compound was obtained. Further purification was performed with column chromatography (silica gel, methanol/chloroform 1/50 v/v). Yield: 96 mg (64%). FT-IR, $\nu_{max}/(cm^{-1})$: 3075–3035 (CH, aromatic), 2968–2849 (CH, aliphatic), 1728 and 1262 (COO), 1660 (C=C, aromatic), 1610, 1575, 1480, 1320, 1282, 1120, 1088, 979, 942, 875, 712, 638. MS (ESI) *m/z*: 2998.9 $[M]^+$.

2.5. *μ-Pyrazine[octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato] iron (II) [FePz(pyz)]$_n$ (9)*

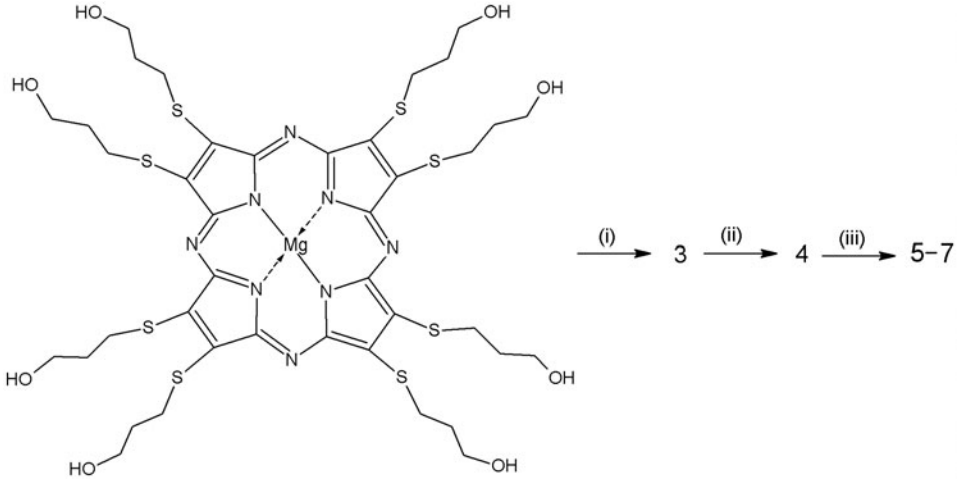
8 (150 mg, 0.05 mM) was reacted with the melted pyrazine compound (400 mg, 5.0 mM) and heated for 36 h at 85 °C. After the reaction was cooled, a large amount of ligand was eliminated by high vacuum sublimation at 85 °C. Yield: 103 mg (68%). FT-IR, $\nu_{max}/(cm^{-1})$: 3066–3038 (CH, aromatic), 2956–2850 (CH, aliphatic), 1721 and 1260 (COO), 1664 (C=C, aromatic), 1615, 1580, 1425, 1412, 1307, 1218, 1140, 1005, 846, 763, 723, 698. ^{1}H NMR (δ, ppm): 7.91–7.68 (m, 24H, Ar–H), 7.59–7.32 (m, 32H, Ar–H), 4.66 (t, 16H, O–CH_2), 4.02 (t, 16H, S–CH_2), 2.26 (s, 4H, pyz–H), 2.52 (m, 16H, –CH_2–).

2.6. *Bis(pyridine)[octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato] iron(II) [FePz(py)$_2$] (10)*

8 (75 mg, 0.025 mM) was dissolved in benzene (15 mL) and dry pyridine (0.1 mL) was added to it. The mixture was refluxed for 8 h under N_2. After the removal of benzene under reduced pressure, the residue was dissolved in diethyl ether and added dropwise to DMF (15 mL). The precipitate formed was filtered and dried *in vacuo*. The target porphyrazine complex was purified by chromatography on silica gel using methanol/chloroform (1 : 50) mixture as eluent. Yield: 56 mg (72%). FT-IR, ν_{max}/(cm^{-1}): 3060–3020 (CH, aromatic), 2964–2842 (CH, aliphatic), 1714 and 1268 (COO), 1659 (C=C, aromatic), 1610, 1588, 1420, 1405, 1302, 1228, 1141, 1011, 842, 769, 729, 691. ^{1}H NMR (δ, ppm): 7.94–7.70 (m, 24H, Ar–H), 7.60–7.30 (m, 32H, Ar–H), 6.88 (m, 4H, py-H$_c$), 4.82 (m, 2H, py-H$_b$), 4.63 (t, 16H, O–sCH$_2$), 4.06 (t, 16H, S–CH$_2$), 2.30 (m, 4H, py-H$_a$), 2.55 (m, 16H, –CH$_2$–). MS (ESI) *m/z*: 3121.1 [M]$^+$.

3. Results and discussion

The disodium salt of dithiomaleonitrile (**1**) is the starting point for a porphyrazine structure with eight 3-thiopropyl anthraquinone-2-carboxylate groups bound to the periphery through flexible chains. **1** was obtained in two steps from carbon disulfide and sodium cyanide [56]. The bulky electron-donating S-group is expected to enhance the chemical stability and optical properties of porphyrazines [57]. Treatment of **1** with 3-chloro-1-propanol gives the unsaturated 2,3-bis(3-hydroxypropylthio)maleonitrile suitable for cyclotetramerization to give octakis(3-hydroxypropylthio)porphyrazinato] Mg(II) (**2**) in the presence of magnesium *n*-BuOH as recently reported by Wöhrle *et al.* [58] with higher polymethylene chain lengths (scheme 1).



Scheme 1. (i) Anthraquinone-2-carboxylic acid, DCCI, toluene-p-sulfonic acid, and pyridine; (ii) CF_3CO_2H; (iii) EtOH, $CHCl_3$, and $Co(OAc)_2$, $Cu(OAc)_2$, or $Zn(OAc)_2$.

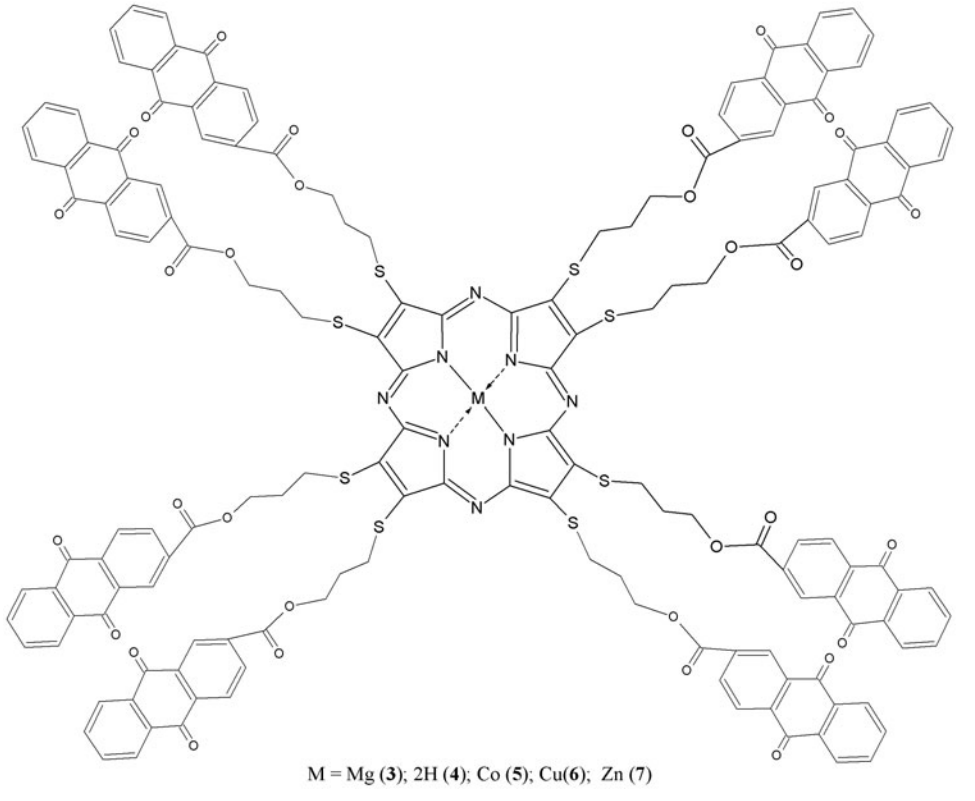
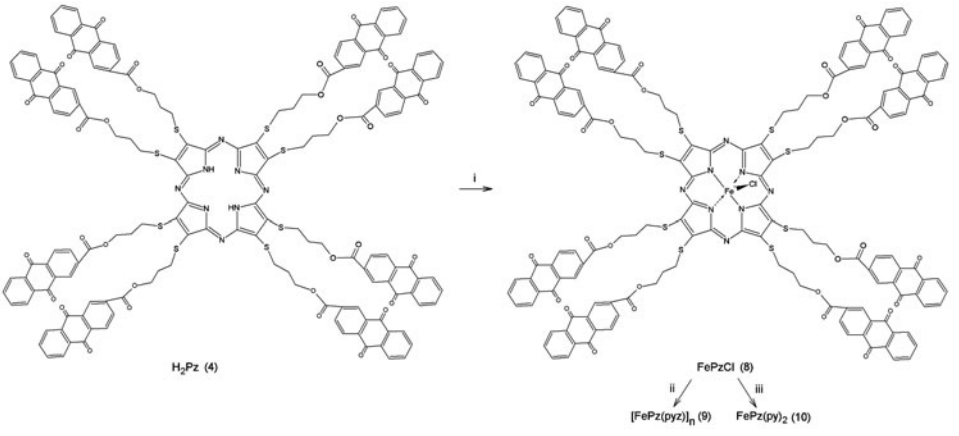


Figure 1. [2,3,7,8,12,13,17,18-Octakis(3-thiopropyl anthraquinone-2-carboxylate)] substituted porphyrazines (**3**–**7**).

Ester groups ensure high solubility, and they are selected in spite of the facility of their synthesis [38–45]. The most effective method for this condensation reaction of carboxylic acid and –OH groups on porphyrazines is to perform the reaction at ambient temperature in the presence of an extremely dehydrating reactant such as DCCI.

The by-product dicyclohexylurea was removed by filtering the reaction mixture after treatment with cold DCM. Using mass spectrometry data, DCCI-mediated esterification system for octakis(hydroxypropylsulfanyl)porphyrazines confirmed that all of the suitable –OH groups reacted in the method. TLC tests were carried out for the reaction time and changed with different circumstances. The other aim of this study was to realize the effect of different esterification circumstances on the reaction yield. Our data prove that the best condition was to use DCCI:OH group in 9 : 1 molar ratio. Other procedures include the use of DCCI with toluene-*p*-sulfonic acid and –OH group in a molar ratio of 24 : 1 [38–45, 58]. The yield of **3** was 48% (scheme 1). The symmetrically functionalized porphyrazine with eight ester units was soluble in common organic solvents such as chloroform, dichloromethane, THF, acetone, and toluene and insoluble in water and *n*-hexane. Octakis[3-thiopropyl anthraquinone-2-carboxylate]-substituted porphyrazinato-magnesium (**3**) was a suitable intermediate for preparing porphyrazines with different metal(II) ions in the center (figure 1). The known method of treatment with CF_3COOH led to the metal-free derivative (**4**) which was further



Scheme 2. (i) $Fe(OAc)_2$, acetic acid, HCl; (ii) Pyrazine; (iii) Pyridine.

reacted with cobalt(II), copper(II), or zinc(II) acetate to give structures having the respective metal ions in the porphyrazine core (M=Co, Cu, Zn) (**5–7**) (figure 1).

The addition of iron(II) to **4** was carried out in CH_3COOH using anhydrous Fe $(CH_3COO)_2$ as the metal salt (scheme 2) [59, 60]. Although the reaction was performed under inert atmosphere, a little amount of oxygen led to Fe(III) derivatives. Further exposure to air was almost unavoidable during the experiment, so the product was treated with dilute hydrochloric acid solution to convert all of the trivalent iron compounds into FePzCl (**8**). In the FT-IR spectrum of **8**, the band at 1088 cm^{-1} arises from the contribution of axial ligands to CN-skeleton vibrations as encountered in octaphenyltetraazaporphyrins. Another result of having axial chloride is the changes occurring in the Q-band absorption from a metallo-porphyrazine derivative of D_{4h} symmetry (e.g. **3** where Q-band is at 644 nm as a single intense absorption) to C_{4v} symmetry, resulting in an intense band at 584 nm together with two others at 540 and 648 nm of **8** [61].

Tetrapyrrole complexes having iron(II) in the center are of interest as they form shish kebab-type axially coordinated bridged complexes with bidentate coordinating ligands. We have synthesized a bridged compound with pyrazine and a monomeric complex with pyridine (scheme 2). We perform the reaction with pyrazine only in melted ligand and the product is a bridged system (**9**) (oligomeric compound) (figure 2) [62]. **8** can be easily reduced to axially coordinated **10** in the presence of ligands such as pyridine (figure 3).

The newly synthesized structures were characterized by elemental analysis, FT-IR, UV–vis, mass spectrometry, ^1H, and ^{13}C NMR. Spectral investigations into all products were consistent with the proposed complexes.

Elemental analyses correspond closely with the values calculated for **3–10** (table 1).

FT-IR spectra gave insights into the nature of the compounds. After conversion of the unsaturated 2,3-bis(3-hydroxypropylthio)maleonitrile into magnesium porphyrazinate (**2**), the C≡N stretching vibration disappeared. In the case of porphyrazines (**3–7**) with [3-thiopropyl anthraquinone-2-carboxylate] substituents, the aromatic C–H stretch was at 3075–3020 cm^{-1}, the aliphatic C–H stretch at 2988–2842 cm^{-1}, O–C=O peaks at 1260–1268 cm^{-1}, the aromatic C=C peaks at 1667–1652 cm^{-1} as strong absorptions and the C=O vibration of the ester group at 1712–1728 cm^{-1} for **3–10**. The disappearance of the O–H

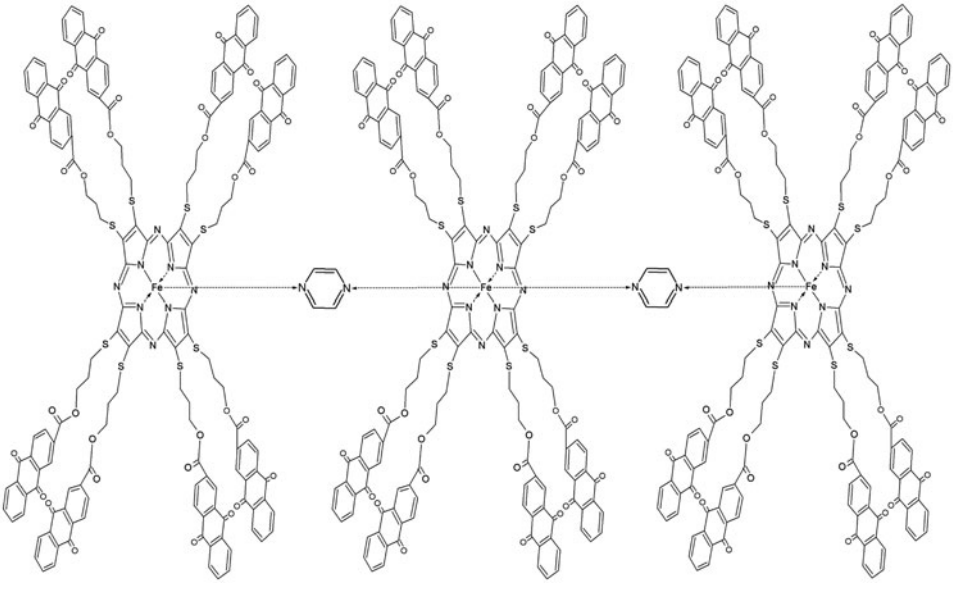


Figure 2. μ-Pyrazine[octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato] iron(II) [FePz(pyz)]$_n$ (**9**).

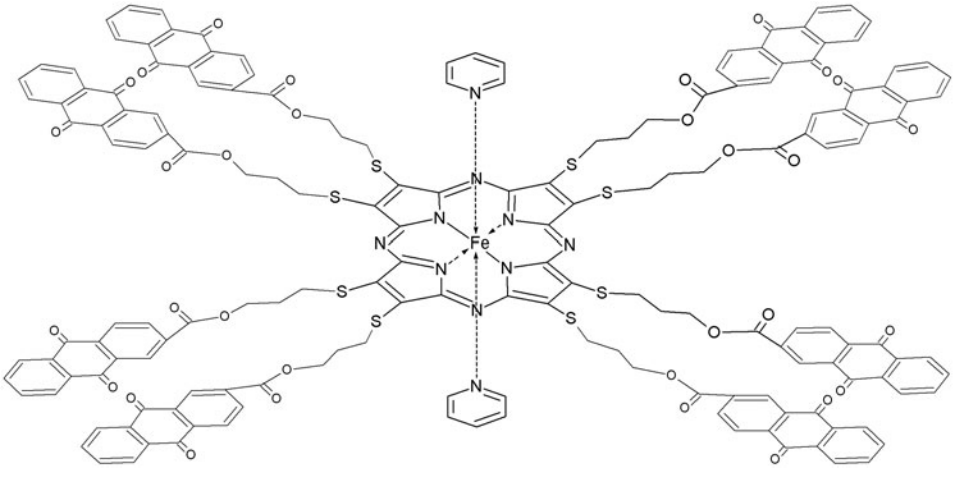


Figure 3. Bis(pyridine)[octakis(3-thiopropyl anthraquinone-2-carboxylate) porphyrazinato] iron(II) [FePz(py)$_2$] (**10**).

peak at 3330 cm^{-1} for **3** and the NH stretching vibrations of the inner core observed at 3310 cm^{-1} for the metal-free porphyrazine (**4**) [58], together with high solubility in chloroform and THF after this reaction, are all evidence of the formation of **3–7**. In the FT-IR spectrum of **9**, the vibration at 1580 cm^{-1} was observed which is characteristic of pyrazine [62]. In the FT-IR spectrum of **10**, bands at 1588 and 1228 cm^{-1} are likely because of the breathing mode of axial pyridine groups [63].

Table 1. Elemental analyses of **3–10***.

Compound	C	H	N	S
3	65.67 (65.56)	3.46 (3.58)	3.94 (3.82)	8.87 (8.75)
4	66.19 (66.06)	3.55 (3.67)	3.97 (3.85)	8.70 (8.82)
5	64.90 (64.79)	3.41 (3.53)	3.89 (3.78)	8.53 (8.65)
6	64.58 (64.69)	3.41 (3.53)	3.88 (3.77)	8.52 (8.64)
7	64.76 (64.65)	3.64 (3.53)	3.65 (3.77)	8.51 (8.63)
8	64.22 (64.09)	3.63 (3.50)	3.61 (3.74)	8.42 (8.56)
9	64.60 (64.73)	3.70 (3.58)	4.48 (4.60)	8.56 (8.43)
10	65.53 (65.41)	3.54 (3.68)	4.61 (4.49)	8.34 (8.22)

*Required values are given in parentheses.

In the ^{1}H NMR spectra of **3**, five different types of protons are clearly seen: two multiplets at 7.88–7.28 ppm corresponding to aromatic protons, a triplet at 4.68 ppm belonging to O–CH_2, a triplet at 4.12 ppm belonging to S–CH_2, and a multiplet at 2.58 ppm belonging to –CH_2–. The ^{1}H NMR spectrum of **4** showed a chemical shift of porphyrazine ring protons (singlet) at −1.05 ppm [38–45, 58]. The ^{1}H NMR spectra of **9** and **10** show an octahedrally coordinated Fe(II) structure. The chemical shift of the axially coordinated ligands has been considerably affected by the 18-π electrons of the porphyrazine center, i.e. the peaks at 8.59, 7.75, and 7.38 ppm in the free pyridine shift to 6.88, 4.82, and 2.30 ppm, respectively, after binding axially to form [$FePz(py)_2$]. Similarly, there is only a single peak at 2.26 ppm for pyrazine protons in the bridged structure $[FePz(pyz)]_n$ [64–67]. In the ^{13}C NMR spectra of diamagnetic porphyrazines **3**, **4**, and **7**, fourteen different chemical shifts of carbons were clearly seen.

Mass spectrometry data of anthraquinone-2-carboxylate-substituted magnesium, metal-free, cobalt, copper, zinc, and iron porphyrazines (**3–8**, **10**) confirmed the characteristic molecular ion peaks at *m/z*: 2931.9 $[M]^+$, 2909.8 $[M]^+$, 2966.8 $[M]^+$, 2970.1 $[M]^+$, 2973.1 $[M]^+$, 2998.9 $[M]^+$ and 3121.1 $[M]^+$, respectively, approving the target structures.

Porphyrazines (**3–10**) show typical electronic spectra with three strong absorption regions (table 2). One is in the UV region at 284–288 nm, the other is at 340–354 nm (B-band) arising from the deeper π-levels/LUMO transition, and the last one is in the visible part of the spectrum at 596–648 nm (Q-band) attributed to the π–π* transition from the highest occupied molecular orbital to the lowest unoccupied molecular orbital (LUMO) of the porphyrazine ring [68]. The characteristic Q-band transition of metallo-porphyrazines with D_{4h} symmetry is observed as a single band of high intensity in the visible region. The D_{2h} symmetry of **4** is verified by two absorptions in the visible region (620 and 676 nm). The

Table 2. UV–vis data for porphyrazines (**3–10**) in chloroform.

Compound	λ/nm (log ε/dm^3 M^{-1} cm^{-1})				
3	288 (4.97)	344 (4.88)		644 (4.65)	
4	284 (4.97)	348 (4.78)		620 (4.10)	676 (4.20)
5	284 (4.99)	340 (4.83)		632 (4.50)	
6	288 (4.98)	344 (4.87)		640 (4.57)	
7	288 (4.95)	344 (4.85)		644 (4.60)	
8	284 (4.93)	348 (4.91)	540 (4.26)	584 (4.12)	648 (3.92)
9	284 (4.96)	354 (4.81)		630 (4.46)	715 (4.38)
10	288 (4.95)	352 (4.94)		596 (4.64)	

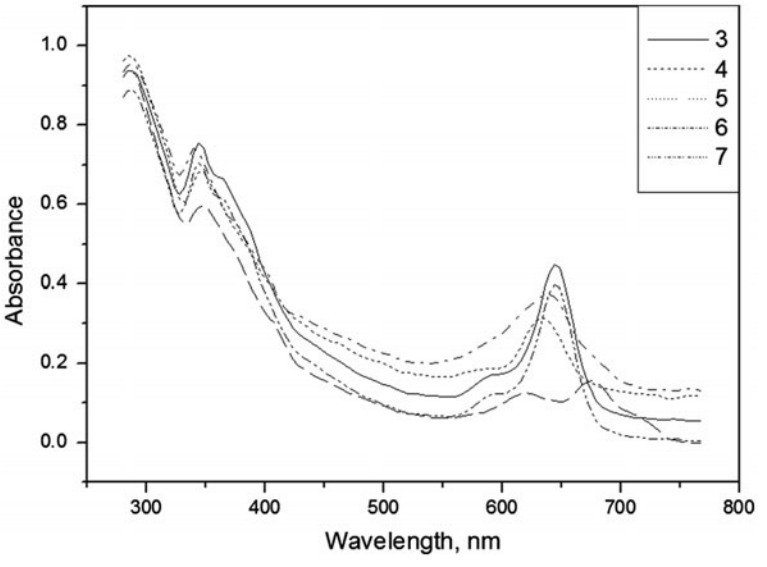


Figure 4. UV–vis spectra of **3–7** in chloroform at 1×10^{-5} M concentration.

UV–vis spectra of the porphyrazine complexes (**3–7** in $CHCl_3$, 1×10^{-5} M dm^{-3}) are given in figure 4. The Q-bands at 630 and 596 nm in the UV–vis spectra of $[FePz(pyz)]_n$ (**9**) and $[FePz(py)_2]$ (**10**) confirm coordination of the pyridine and pyrazine ligands to Fe(II).

The aggregation behavior of **6** was investigated at different concentrations in chloroform (figure 5). As the concentration was increased, the intensity of the Q-band absorption

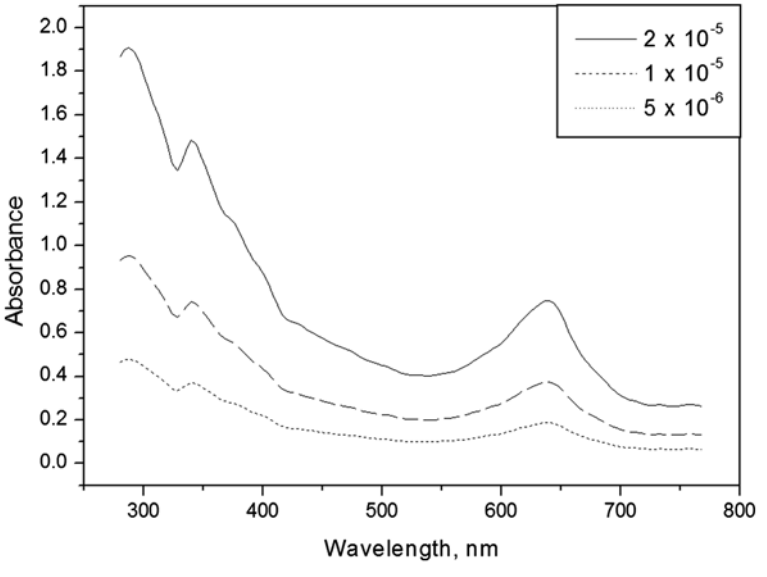


Figure 5. UV–vis spectra of **6** in chloroform at various concentrations (M).

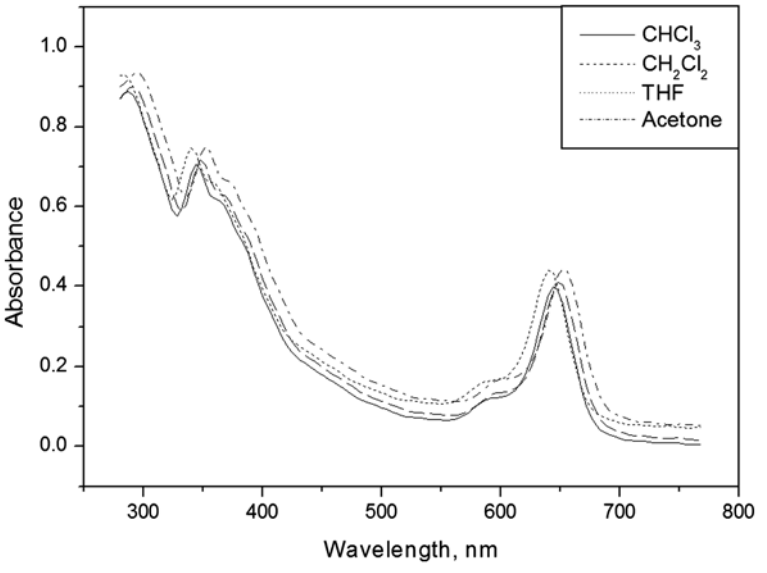


Figure 6. UV–vis spectra of **7** in different solvents at 1×10^{-5} M concentration.

increased in parallel, and there were no new bands because of aggregation [42]. The Beer–Lambert law was obeyed for **6** for concentrations ranging from 5×10^{-6} M dm^{-3} to 2×10^{-5} M dm^{-3} (figure 5). UV–vis spectra of **7** in solvents of different polarities (chloroform, dichloromethane, tetrahydrofuran, and acetone) at 1×10^{-5} M dm^{-3} concentration are given in figure 6. There is almost no difference with changes in the nature of the solvent.

Many characteristics arise in the oxidation state of the metal ion when a bidentate ligand such as pyrazine is used in place of pyridine. In addition, bidentate ligands place a bridge between the metal centers and formed a shish kebab type oligomer [22, 69]. In the UV–vis spectrum of **9**, the Q-band absorption at 630 nm shifted to a shorter wavelength (ca. 34 nm) when compared with the monomeric structure (**10**) obtained with pyridine. After oligomer formation, there was also a shoulder about 715 nm in UV–vis spectra of **9**.

4. Conclusion

We have described the synthesis, spectral, and structural properties of planar porphyrazine cores peripherally substituted with eight (anthraquinone-2-carboxylate) moieties through flexible bridges. The oligomeric complex, shish kebab-type, $[FePz(pyz)]_n$ and the monomeric compound $[FePz(py)_2]$ were formed as stable complexes by reacting FePzCl with pyrazine and pyridine, respectively. As a result, this study showed that the Fe(II) porphyrazine macrocycle reacts in excess liquid pyrazine to form exclusively a polymeric compound as was the case for most tetraaza annulenes. The anthraquinone-substituted porphyrazine derivatives showed high solubility in solvents of different polarities from chloroform to acetone.

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