Journal of Fluorine Chemistry 131 (2010) 1322–1326

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis, structural and spectral properties of novel octakis(3,5-bis-trifluoromethyl-benzylthio) substituted porphyrazine derivatives

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ARTICLE INFO

Article history:
Received 29 July 2010
Received in revised form 2 September 2010
Accepted 4 September 2010
Available online 21 September 2010

Keywords:
3,5-Bis-trifluoromethyl-benzylthio
Porphyrazine
^{19}F NMR spectroscopy
Zinc
Cobalt

ABSTRACT

[Octakis(3,5-bis-trifluoromethyl-benzylthio)porphyrazinato] magnesium carrying eight (3,5-bis-trifluoromethyl-benzylthio) groups on the peripheral positions have been synthesized by cyclotetramerization of 1,2-bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile in the presence of magnesium butanolate. Its demetalation by the treatment with trifluoroacetic acid resulted in the metal-free derivative. Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate have led to the metallo derivatives *M* = Cu(II), Zn(II), Co(II). These novel complexes were characterized by elemental analysis, together with FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, UV–vis and mass spectral data.
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1. Introduction

Peripherally functionalized porphyrazines (tetraazaporphyrins) and related macrocycles have been a subject of great interest due to various high synthetic possibilities, numerous technological applications, and biological importance in coordination chemistry [1–4]. Porphyrazines may be considered to be structural hybrids of the well-studied porphyrins and phthalocyanines. As such, they provide an excellent opportunity to explore the subtle effects of ligand structure on the properties of coordinated metal ions in porphyrinic complexes. In addition, tetraazaporphyrins reveal various unique properties (optical, electrochemical, and catalytic) which make them of interest in their own right [5–7].

When symmetrical octakis functionalization of the main core is demanded, planar tetrapyrrole derivatives with eight peripheral positions are the common starting substances [8–10]. The metal ions that have been incorporated into porphyrazine centrally and peripherally express new ways to induce, modify and control molecular properties [11,12]. It is well-known that there are long-range interactions between different parts of the molecule because of the diffuse nature of porphyrazine's π electronic structure. Thus, the electronic and magnetic properties of these molecular compounds should be very reactive to the nature of substituent ions and peripheral complexes.

Starting with eight alkylthio substituents appending to porphyrazine derivatives by Hoffman and co-workers [13], in which the presence of soft S donor atoms perform an important function in affecting the solid-state interactions, a large series of derivatives with physical and chemical properties comparable to those of phthalocyanines have been assigned. Metalloporphyrazines have also been investigated to show optical limiting effects comparable with phthalocyanines and naphthalocyanine derivatives [14]. Substitution of various units on the peripheral positions of porphyrazines has been performed either starting with an unsaturated dinitrile precursor with this unit attached at the beginning (e.g., dimethylaminoethylthio [13], tosylaminoethylthio [15]) or a porphyrazine that has been prepared at first with reactive functional groups and then additional groups (e.g., ferrocene [16], benzo-15-crown-5 [9,10], pyridine [17]) that have been incorporated by further condensation reactions.

More recently our group has been mainly interested in the preparation of new soluble phthalocyanine and porphyrazine derivatives. Among these, phthalocyanines with fused to or attached through bridges to macrocyclic structures and porphyrazines with long chains or functional groups such as quaternizable amino groups [18], crown ethers [19], ferrocenes [20], triphenylphosphine [21], 4-*tert*-buthylphenylthio [22] and tosylaminoethylthio [23] can be cited. Moreover, we have synthesized novel *seco*-porphyrazines substituted with (1-naphthyl) [24], (4-biphenyl) groups [25] on the peripheral positions as encountered by Barrett and co-workers, with peripheral amino derivatives [26]. We have also reported new porphyrazines with bulky electron rich

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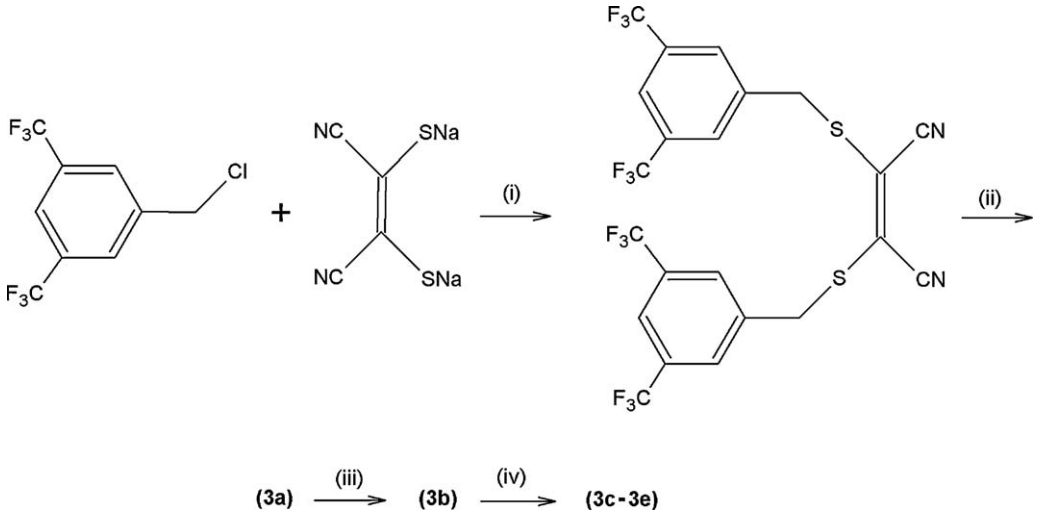
doi:10.1016/j.jfluchem.2010.09.002



Scheme 1. (i) Methanol; (ii) Mg turnings, I_2, *n*-BuOH; (iii) CF_3CO_2H; (iv) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.

substituents such as 1-naphthylmethylthio [27], 9-anthracenylmethylthio units [28].

Fluorinated metallo tetrapyrrol compounds form a class of coordination compounds which have currently been receiving a great deal of attention owing to their interesting electron transport characteristics [29–31]. Furthermore, fluorocarbons display enhanced thermal stability, hydrophobicity, chemical resistance, and lipophobicity in comparison to their hydrocarbon counterparts [32,33].

In this study, we have synthesized novel soluble porphyrazines with eight (3,5-bis-trifluoromethyl-benzylthio) substituents appended to the peripheral positions. Magnesium porphyrazinate has been synthesized for the first time by cyclotetramerization of 1,2-bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile in the presence of magnesium butanolate. The conversion of magnesium porphyrazinate into the metal-free derivative was achieved by the treatment with relatively strong acids (e.g., trifluoroacetic acid). Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate has led to the metal porphyrazinates (M = Cu, Zn, Co). These novel compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, UV–vis and mass spectral data.

2. Results and discussion

The starting material for these novel porphyrazine structures with eight (3,5-bis-trifluoromethyl-benzylthio) units bound to the periphery through flexible methylthio chains is 1,2-bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile (**2**) which was obtained from the disodium salt of dithiomaleonitrile (**1**) and 3,5-bis(trifluoromethyl)benzyl chloride (Scheme 1). The orange colored product (**2**) was obtained in 58% yield. The presence of electron-donating S-groups is expected to give porphyrazines absorbing electromagnetic radiation just in the same range as phthalocyanines [18,35,36]. The conversion of 1,2-bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile into porphyrazine was achieved by the template effect of magnesium butanolate (Scheme 1). The cyclotetramerization gave the blue-green [octakis(3,5-bis-trifluoromethyl-benzylthio) porphyrazinato]magnesium (**3a**) (Fig. 1). It is soluble in chloroform, dichloromethane, toluene and acetone, but insoluble in polar hydrocarbon solvents such as *n*-hexane. The conversion of **3a** into **3b** was achieved by the treatment with relatively strong acids (e.g., trifluoroacetic acid). The mass spectral results have clearly indicated the change of the structure from magnesium porphyrazinate (**3a**) to the demetalated porphyrazine (**3b**). Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate has led to the metal porphyrazinates (M = Cu, Zn, Co) (**3c**–**3e**) (Fig. 1).

All new compounds were identified through several spectroscopic techniques such as FT-IR, ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, UV–vis, mass and elemental analysis. The spectroscopic data of desired products were in accordance with the assigned structures.

Elemental analyses correspond closely with the values calculated for (2, **3a**–**3e**) (Table 1).

In the FT-IR spectrum of 1,2-bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile (**2**) stretching vibration of C≡N is observed at 2227 cm^{-1}, the aromatic and aliphatic C–H peaks are around 2865–3085 cm^{-1} and the aromatic C=C peak is at 1619 cm^{-1}. These values comply with those reported in the literature for similar compounds [27]. After the conversion of dinitrile derivative (**2**) to porphyrazine (**3a**), the sharp C≡N vibration around 2227 cm^{-1} disappeared. The N–H stretching absorption of the inner core of the metal-free porphyrazine (**3b**) was observed around 3330 cm^{-1}. FT-IR spectra of all porphyrazines derivatives (**3a**–**3e**) showed the aromatic and aliphatic C–H peaks are in the range 2850–3085 cm^{-1} and the aromatic C=C peak is at 1605–1667 cm^{-1} [27].

The N–H protons of the metal-free porphyrazine (**3b**) were also identified in the ^{1}H NMR spectrum with a broad peak at $\delta = -0.95$ ppm, presenting the typical shielding of inner core protons, which is a common feature of the ^{1}H NMR spectra of metal-free porphyrazines [15,18–20,23,27]. In the ^{1}H NMR spectra of diamagnetic porphyrazines **3a**, **3b** and **3d**, three different types of protons are clearly seen: two singlets around 7–8 ppm corresponding to aromatic protons and a singlet at 4.65 ppm (**3a**), 5.12 ppm (**3b**) or 4.86 ppm (**3d**) for methylene protons. The ratio of the integral values 3:2 also confirms the proposed structure. In the ^{13}C NMR spectra of diamagnetic porphyrazines **3a**, **3b** and **3d**, eight different single chemical shifts for carbon atoms are clearly seen. ^{19}F NMR spectra of diamagnetic porphyrazines **3a**, **3b** and **3d** show a single chemical shift for trifluoromethyl groups at −63.44, −63.42 and −63.40 ppm, respectively.

Electronic spectra were very useful to establish the structure of the porphyrazines (**3a**–**3e**). UV–vis spectra of porphyrazine core are dominated by two intense bands, the Q-band around 670 nm and the B-band in the near UV region around 350 nm, both correlated to $\pi \rightarrow \pi^*$ transitions [12,15]. The presence of an electron-donating group on the periphery causes a bathochromic shift on Q-bands. UV–vis spectra of metalloporphyrazines (**3a**, **3c**–

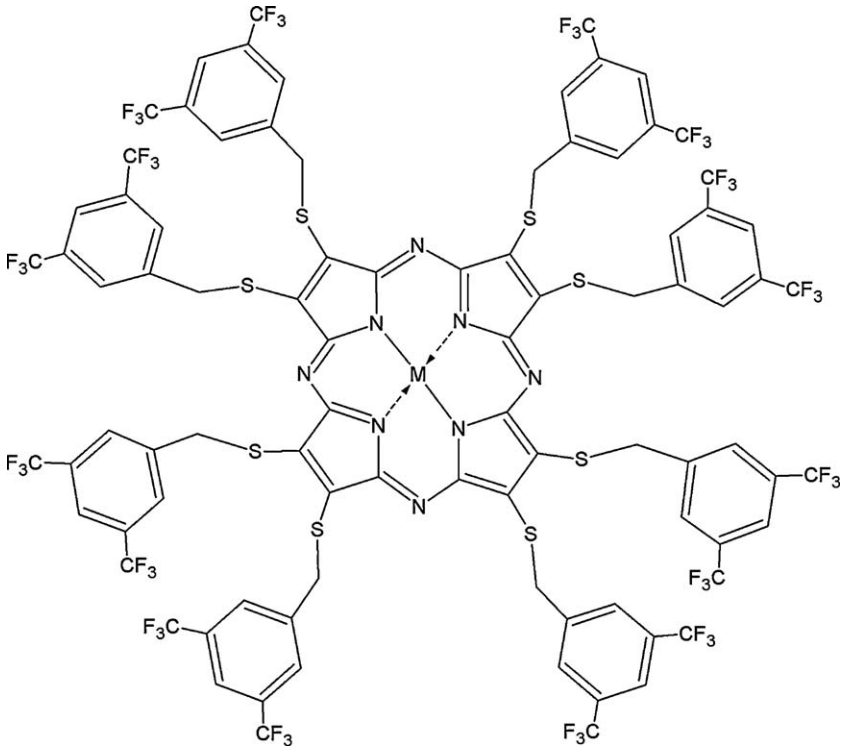


Fig. 1. Octakis (3,5-bis-trifluoromethyl-benzylthio) substituted porphyrazines.

Table 1
Elemental analyses results of **2** and **3a–3e**.[a]

Compound	C	H	N
2	44.57 (44.45)	1.82 (1.70)	4.60 (4.71)
3a	44.15 (44.00)	1.80 (1.68)	4.53 (4.66)
3b	44.55 (44.41)	1.91 (1.78)	4.61 (4.71)
3c	43.18 (43.29)	1.74 (1.65)	4.70 (4.59)
3d	43.38 (43.26)	1.76 (1.65)	4.47 (4.59)
3e	43.50 (43.38)	1.54 (1.65)	4.71 (4.60)

[a] Required values are given in parentheses.

Table 2
UV–vis data for the porphyrazines in chloroform.

Compound	λ (/nm) (log ε/dm^3 mol^{-1} cm^{-1})		
3a	378 (4.71)	668 (4.70)	
3b	336 (4.65)	652 (4.45)	715 (4.48)
3c	364 (4.64)	664 (4.49)	
3d	348 (4.40)	680 (4.36)	
3e	344 (4.33)	678 (4.38)	

3e in $CHCl_3$) prepared in the present work exhibited intense single Q-band absorptions around 668–680 nm and B bands in the near UV region around 344–378 nm (Table 2). For metal-free derivative (**3b**), Q-band is split into two peaks at 652 and 715 nm as a consequence of the change in the symmetry of porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h}. UV–vis spectra of **3a** and **3b** in chloroform are shown in Fig. 2. An absorbance *vs.* concentration study indicated that due to (3,5-bis-trifluoromethyl-benzylthio) units, the aspect of the UV–vis spectrum of the free ligand in Fig. 2, with broad and low intensity Q-bands does not exclude the presence of aggregation. UV–vis spectra of **3c** in solvents of different polarity (dichloromethane, ethanol, chloroform and pyridine) are given in Fig. 3. There is almost no difference with respect to the changes in the nature of the solvent.

3. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 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) and fluorotrichloromethane (^{19}F NMR) as the internal standards. Mass spectra were recorded on a Bruker Daltonics Micro-TOF and MALDI-TOF mass spectrometer using the electrospray ionisation (ESI) method. The instrument was operated in positive ion mode. All starting materials were purchased

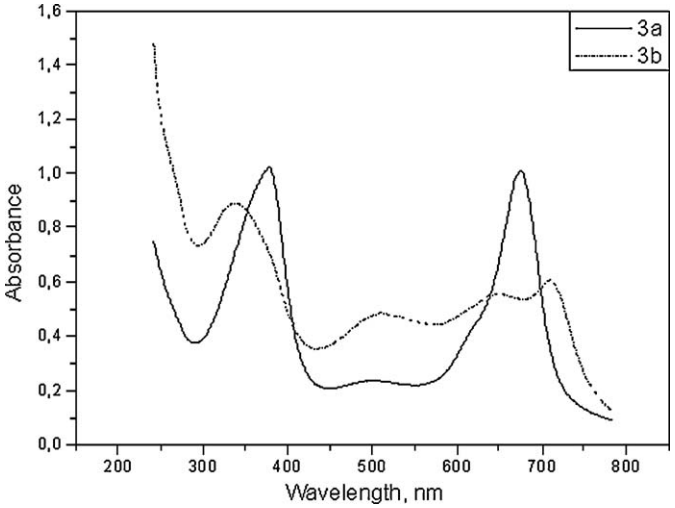


Fig. 2. UV–vis spectra of **3a** and **3b** in chloroform.

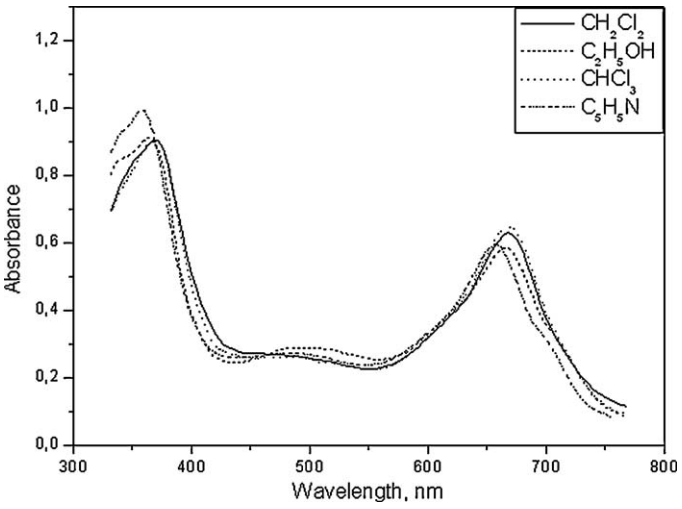


Fig. 3. UV–vis spectra of **3c** in various solvents.

from major suppliers and used without any further purification. The homogeneity of the products was tested in each step by TLC.

The disodium salt of dithiomaleonitrile (**1**) was prepared according to the previously reported procedures [34].

3.1. Synthesis of 2,3-bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile (2)

Disodium salt of dithiomaleonitrile (**1**) (1.12 g, 6.00 mmol) was mixed with 3,5-bis(trifluoromethyl)benzyl chloride (3.94 g, 15.0 mmol) in methanol (50.0 mL) and refluxed under nitrogen for about 18 h. When MeOH was evaporated, the remaining product was treated with $CHCl_3$ to remove insoluble salts by filtration. The $CHCl_3$ solution was extracted several times with 15% Na_2SO_4 solution and then dried over anhydrous Na_2SO_4 overnight. After evaporation of the solvent the colored product was extracted with refluxing *n*-hexane to remove any excess 3,5-bis(trifluoromethyl)benzyl chloride. The product was an orange colored and was very soluble in chloroform, dichloromethane and acetone, but insoluble in *n*-hexane. Yield: 2.07 g (58%). FT-IR, $\nu_{max}/(cm^{-1})$: 3085–3040 (CH, aromatic), 2935–2865 (CH, aliphatic), 2227 (C≡N), 1667, 1619 (C=C, aromatic), 1590, 1510, 1412, 1350, 1303, 1276, 1180, 1118, 1059, 901, 845, 705, 681, 585. ^{1}H NMR (δ, ppm) 7.58 (s, 2H, Ar–H), 7.32 (s, 4H, Ar–H), 4.68 (s, 4H, S–CH_2). ^{13}C NMR (δ, ppm) 40.2, 113.7, 115.8, 121.8, 124.5, 129.2, 131.0, 140.4. ^{19}F NMR (δ, ppm) −63.40. MS (ESI): (*m*/*z*): 594.9 $[M]^+$.

3.2. [2,3,7,8,12,13,17,18-Octakis(3,5-bis-trifluoromethyl-benzylthio) porphyrazinato] Mg(II) (3a)

Mg turnings (6 mg, 0.25 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20.0 mL) for about 8 h to obtain $Mg(BuO)_2$. 1,2-Bis(3,5-bis-trifluoromethyl-benzylthio)maleonitrile (**2**) (297 mg, 0.50 mmol) was added to this solution and the mixture was refluxed for about 12 h. The dark green product was filtered, washed with ethanol and water and dried in a vacuum. The crude product was dissolved in $CHCl_3$ and filtered. The $CHCl_3$ solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, a colored product was obtained. Finally, pure porphyrazine was obtained by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:50, v/v). The blue-green colored product was soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in *n*-hexane. Yield: 219 mg (73%). FT-IR, $\nu_{max}/(cm^{-1})$: 3075–3035 (CH, aromatic), 2925–2855 (CH, aliphatic), 1665, 1608 (C=C, aromatic), 1580, 1505, 1408, 1345, 1300, 1273, 1184, 1120, 1064, 905, 848, 708, 684, 588. ^{1}H NMR (δ, ppm) 7.64 (s, 8H, Ar–H), 7.35 (s, 16H, Ar–H), 4.65 (s, 16H, CH_2–S). ^{13}C NMR (δ, ppm) 40.0, 113.4, 115.6, 121.6, 124.6, 129.1, 131.2, 140.2. ^{19}F NMR (δ, ppm) −63.44. MS (ESI): (*m*/*z*): 2402.5 $[M]^+$.

3.3. [2,3,7,8,12,13,17,18- Octakis(3,5-bis-trifluoromethyl-benzylthio) H^{21}, H^{23} porphyrazine] (3b)

3a (120 mg, 0.05 mmol) was dissolved in the minimum amount of trifluoroaceticacid (∼4.00 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 it was filtered. The precipitate was extracted into the chloroform and the chloroform solution was extracted with water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a violet colored metal-free porphyrazine. **3b** was obtained by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:30, v/v). Yield: 76 mg (64%). FT-IR, $\nu_{max}/(cm^{-1})$: 3330 (N–H), 3070–3030 (CH, aromatic), 2930–2850 (CH, aliphatic), 1660, 1612 (C=C, aromatic), 1584, 1508, 1412, 1348, 1304, 1278, 1186, 1124, 1066, 903, 844, 704, 686, 582. ^{1}H NMR (δ, ppm) 7.66 (s, 8H, Ar–H), 7.33 (s, 16H, Ar–H), 5.12 (s, 16H, CH_2–S), −0.95 (br s, 2H, NH). ^{13}C NMR (δ, ppm) 40.2, 113.2, 115.4, 121.7, 124.5, 129.0, 131.3, 140.4. ^{19}F NMR (δ, ppm) −63.42. MS (ESI): (*m*/*z*): 2379.1 $[M]^+$.

3.4. General procedure for metalloporphyrazines (3c–3e)

3b (119 mg, 0.05 mmol) in $CHCl_3$ (10.0 mL) was stirred with the metal salt [$Cu(OAc)_2$ (91 mg, 0.5 mmol), $Zn(OAc)_2$ (92 mg, 0.5 mmol) or $Co(OAc)_2$ (89 mg, 0.5 mmol)] in ethanol (15.0 mL) and refluxed under nitrogen for about 4 h. Then, the precipitate composed of the crude product and the 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 minimum volume under reduced pressure and then added into *n*-hexane (150 mL) drop by drop to realize the precipitation. Finally, pure porphyrazine derivatives (**3c**–**3e**) were obtained by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:50, v/v).

3.4.1. [2,3,7,8,12,13,17,18-Octakis(3,5-bis-trifluoromethyl-benzylthio) porphyrazinato] Cu(II) (3c)

Yield: 51 mg (42%). FT-IR, $\nu_{max}/(cm^{-1})$: 3070–3030 (CH, aromatic), 2920–2850 (CH, aliphatic), 1660, 1605 (C=C, aromatic), 1584, 1508, 1408, 1346, 1302, 1275, 1184, 1122, 1066, 906, 846, 706, 682, 586. MS (ESI): (*m*/*z*): 2441.9 $[M]^+$.

3.4.2. [2,3,7,8,12,13,17,18-Octakis(3,5-bis-trifluoromethyl-benzylthio) porphyrazinato] Zn(II) (3d)

Yield: 46 mg (38%). FT-IR, $\nu_{max}/(cm^{-1})$: 3075–3035 (CH, aromatic), 2928–2852 (CH, aliphatic), 1662, 1606 (C=C, aromatic), 1580, 1502, 1408, 1344, 1302, 1275, 1182, 1122, 1066, 905, 848, 706, 685, 588. ^{1}H NMR (δ, ppm) 7.65 (s, 8H, Ar–H), 7.33 (s, 16H, Ar–H), 4.86 (s, 16H, CH_2–S). ^{13}C NMR (δ, ppm) 40.0, 113.3, 115.8, 121.4, 124.6, 129.0, 131.1, 140.1. ^{19}F NMR (δ, ppm) −63.40. MS (ESI): (*m*/*z*): 2443.6 $[M]^+$.

3.4.3. [2,3,7,8,12,13,17,18-Octakis(3,5-bis-trifluoromethyl-benzylthio) porphyrazinato] Co(II) (3e)

Yield: 55 mg (45%). FT-IR, $\nu_{max}/(cm^{-1})$: 3072–3032 (CH, aromatic), 2928–2857 (CH, aliphatic), 1664, 1608 (C=C, aromatic), 1582, 1503, 1408, 1344, 1300, 1275, 1184, 1122, 1066, 903, 846, 708, 682, 584. MS (ESI): (*m*/*z*): 2436.1 $[M]^+$.

Acknowledgement

This work was supported by the Scientific Research Fund of Fatih University under the project number P50020901_1.

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