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Synthesis and characterization of novel polyfluorinated porphyrazines

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ABSTRACT

By cyclotetramerization of 2,3-bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile in the presence of magnesium butanolate, magnesium porphyrazinate carrying eight (2,3,4,5,6-pentafluorobenzylthio) functional groups on the periphery positions has been synthesized. Conversion of the magnesium porphyrazinate into the metal-free derivative was achieved by treatment with trifluoroacetic acid. 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.

1. Introduction

Porphyrazines and their structural analogs belong to a wide class of macro heterocyclic tetrapyrrole systems that are constitutionally tetra-aza analogues of porphyrins. These porphyrins are of considerable interest because their representatives are components of the most important natural compounds (hemoglobin, myoglobin, cytochromes, chlorophylls, and others) and are included in such living processes including cell respiration, photosynthesis, and electron transport. Recently, heteroatomic substitutions directly fusing to the macrocyclic periphery have brought an increasing consideration to the porphyrazine works [1–5]. Relative ease of their synthetic preparation, and also the strong correlation between the nature of the substituent and the electronic and optical properties of the macro cyclic ring system play roles on this recent interest. Comparing to the phthalocyanine analogues, direct fusion of heteroatomic substituents onto the porphyrazine β-positions results in an evident effect; on the other hand, there is no such available analogous derivatives for the porphyrins. In comparison to the phthalocyanine counterparts, the porphyrazines also often display an extensively increased solubility in organic solvents. Thus, they maintain a unique position among the tetrapyrrolic macrocycles, and their straightforward synthesis coupled with their tunable electronic and optical properties, renders them exciting candidates for a whole range of applications [6].

Porphyrazines are considerably less studied than phthalocyanines. There have been several positive properties of porphyrazines, specifically those closest to synthetic analogs of phthalocyanines and their high stability against oxidation favoring their use in wide practical application as dyes and pigments. Porphyrazines have found several applications in new areas such as bleachable dyes in laser technique, discotic liquid crystals, constituents of electrochromic and electrophotographic materials, radiation protectors, gas sensors, catalysts of several methods (in particular, electrochemical), antimicrobial drugs, in luminescent diagnostics and photodynamic therapy of cancer tumors [7–12].

The main problem limiting applications of porphyrazines (Pzs) in many areas is still their limited solubility. Their solubility can be increased, on the other hand, by introducing electron-withdrawing (–F, –Cl, –Br) and electron-donating (–NH_2, Ar–S–, RO–, RS–) bulky or long chain alkyl groups into the peripheral places [13–17]. The formation of constitutional isomers and the higher dipole moment of the tetra-substituted Pzs resulting from the unsymmetrical grouping of the substituents on the periphery leads to higher solubility of Pzs in many organic solvents [18].

Metallo-porphyrazines substituted with fluorine atoms are currently receiving a great deal of attention because of their high thermal stability, hydrophobicity, lipophobicity and chemical resistance; they also have interesting electron-transporting characteristics [19]. By placing stronger electron-withdrawing fluorine atoms on the Pz ring results in both the valence and conduction band energies being further lowered. Thus, $MPzF_n$ (n: number of fluorine atoms) exhibits n-type behavior, while unsubstituted porphyrazines have p-type because of doping with electron accepting molecules [20]. These unexpected properties of

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$MPzF_n$ have led scientists to expose their chemistry to be used in a number of different industrial applications [21].

Our group has been deeply interested in the preparation of novel soluble porphyrazine derivatives. Among these, we have synthesized novel *seco*-porphyrazines substituted with 1-naphthyl [22], *o*-tolyl and *p*-tolyl [23], 4-tertbutylphenyl [24] and 4-biphenyl groups [25] on the peripheral positions, as encountered by Barrett, Hoffman and coworkers with peripheral amino derivatives [26]. Recently, we have also synthesized Pzs with peripheral functional groups such as quaternizable amino groups [27], crown ethers [28], ferrocenes [29], triphenylphosphine [30], 4-tert-buthylphenylthio [31], *o*-tolylthio and *p*-tolylthio [32], tosylaminoethylthio [33], 3-methylbutylthio [34], 1-naphthylmethylthio [35] and 9-anthracenylmethylthio [36] units can be cited.

In our previous study, we have reported the synthesis, structural and spectral properties of symmetric metallo-porphyrazines [37]. In this step, our aim has been to design new molecules with polyfluoro-substituents, enhancing their solubility in common solvents and at the same time prohibiting their aggregation. We report herein the synthesis, and characterization of new readily soluble metallo-porphyrazines with up to 40 fluorine-containing substituents on the periphery for the first time, and we also report on the effects of the substituents on the spectroscopic and aggregation properties of the porphyrazines derivatives in different solvents and at different concentrations in chloroform. By using different spectroscopic methods such as elemental analysis, FT-IR, ^{1}H NMR, ^{19}F NMR, UV–vis. and mass spectrometry, new compounds have been characterized.

2. Results and discussion

As proposed by Linstead, unsaturated 1,2-dinitrile derivative should be prepared as the starting material [38,39]. Disodium salt of dithiomaleonitrile (**1**) obtained from simple reactants sodium cyanide and carbondisulfide in two steps was referred as the starting point. Alkylation of disodium salt of maleonitrile with 2,3,4,5,6-pentafluorobenzyl bromide in methanol gave 2,3-bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile (**2**) which was in *cis*-form and easily soluble in chloroform, dichloromethane and acetone (Scheme 1). The orange colored product (**2**) was obtained in 58% yield. The presence of bulky electron-donating S-groups is expected to enhance the chemical stability and optical properties of porphyrazines [27,40,41]. Cyclotetramerization of 2,3-bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile into porphyrazine was realized by making use of the template effect of magnesium ions. The optimum condition was to accomplish the reaction in *n*-butanol at reflux temperature for 12 h (Scheme 1). Octakis(2,3,4,5,6-pentafluorobenzylthio) porphyrazinato magnesium (**3**) was very soluble in most of the common solvents except methanol and ethanol (Fig. 1). The conversion of **3** into **4** 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 (**3**) to the metal-free porphyrazine (**4**). Further reaction of **4** with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate has led to the metal porphyrazinates (M = Cu, Zn, Co) (**5–7**) (Fig. 1).

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

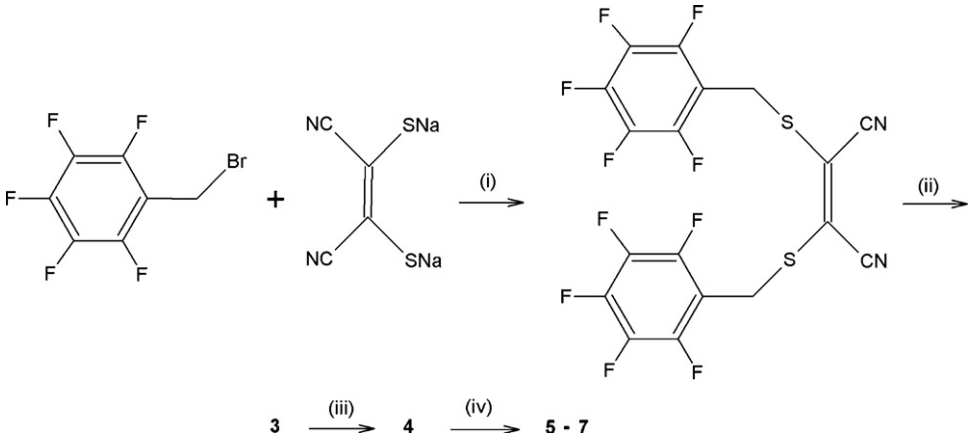
Elemental analyses agree closely with the values calculated for (**2–7**).

In the FT-IR spectrum of 2,3-bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile (**2**) stretching vibration of C≡N is observed at 2220 cm^{-1}, the aliphatic C–H peaks are around 2985–2855 cm^{-1}, aromatic C=C stretching vibrations are at 1650 cm^{-1} and C–F stretching vibrations are around 1355–1114 cm^{-1}. After the conversion of dinitrile derivative (**2**) to porphyrazine (**3**), the sharp C≡N vibration around 2220 cm^{-1} disappeared. The N–H stretching absorption of the inner core of the metal-free porphyrazine (**4**) was observed around 3290 cm^{-1}. FT-IR spectra of all porphyrazines derivatives (**3–7**) showed the aliphatic C–H peaks are in the range of 2988–2850 cm^{-1} and the aromatic C=C peak is at 1615–1648 cm^{-1}.

^{1}H NMR investigations of porphyrazines have provided the characteristic chemical shifts for the structures expected. In the ^{1}H-NMR spectra of 2,3-bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile (**2**) one type of proton is clearly seen: a singlet at 4.66 ppm for methylene protons. The NH protons in the inner core of the metal-free porphyrazine (**4**) are also very well characterized by the ^{1}H NMR which shows a peak at $\delta = -1.10$ ppm as a result of the 18 π-electron system of the porphyrazine ring [27–29,33,35,42].

In the ^{13}C NMR spectra of diamagnetic porphyrazines **3**, **4** and **6,** seven different single chemical shifts for carbon atoms are clearly seen.

^{19}F NMR spectroscopy has been a very useful technique for investigating the fluorinated compound. ^{19}F NMR spectrum of MgPz (**3**) showed three different peaks at −142.4 ppm, −152.6 ppm and −161.6 ppm, respectively, relative to the fluorine atoms in the *ortho*, *para* and *meta* positions of the phenyl substituents and the spectrum showed the expected signals of



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 $Co(OAc)_2$.

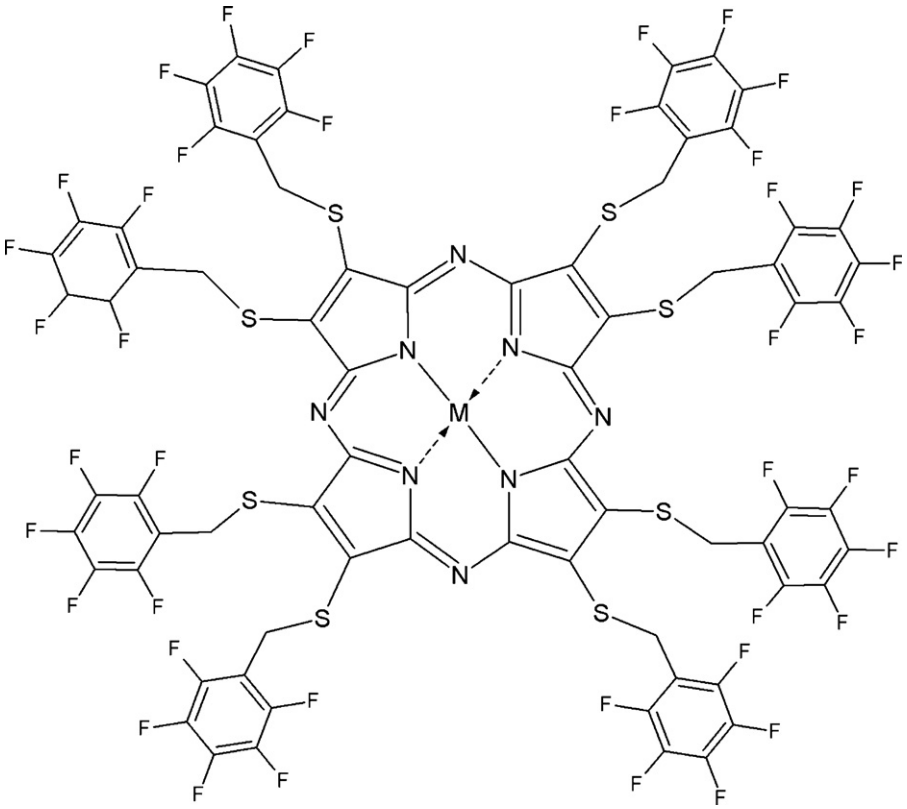


Fig. 1. Octakis (2,3,4,5,6-pentafluorobenzylthio) substituted porphyrazines (**3–7**).

the five fluorine atoms attached to the aromatic ring. Integration of the peaks gave a 2:1:2 ratio as expected.

In addition to these verifying results for the structures, the mass spectra of compounds (**3–7**) gave the characteristic molecular ion peaks at *m/z*: 2033.9 $[M]^+$, 2011.8 $[M]^+$, 2072.1 $[M]^+$, 2074.2 $[M]^+$ and 2068.8 $[M]^+$, respectively, confirming the proposed structures.

The UV–vis spectra of the porphyrazine complexes exhibited characteristic of absorptions in the Q-band region at around 664–680 nm for MPzs (**3**, **5–7**) in chloroform, attributed to the $\pi \rightarrow \pi^*$ transition from the HOMO to the LUMO of the Pz^{-2} ring, and in the B band region (UV region) at around 340–356 nm in chloroform, arising from the deeper $\pi \rightarrow \pi^*$ transitions (Table 1) [42,43]. The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. For metal-free derivative (**4**), Q band is split into two peaks at 654 and 712 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 **4–7** in chloroform are shown in Fig. 2.

Aggregation, which is usually described as a coplanar association, is dependent on the concentration, type of the solvent, type of the substituents, complexed metal ions and temperature [44–46]. The aggregation treatment of **3** was worked at different concentrations in chloroform (Fig. 3). 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 the aggregated ones [34]. It is seen that the Beer-Lambert law was corrected for compound **3** for concentrations ranging from 2×10^{-5} to 5×10^{-6} mol dm^{-3} (Fig. 3). And also the aggregation treatments of **3** were worked in different solvents such as DCM, THF and acetone at different concentrations ranging from 2×10^{-5} to 5×10^{-6} mol dm^{-3}. There were only slight differences in B and Q bands as nm and because of the aggregated ones there were no new bands.

It is expected that the substitution of polyfluorinated groups into the peripheral position of porphyrazines imparts high solubility in organic solvents such as chloroform, dichloromethane, and acetone. The increased solubility might be because

Table 1
UV–vis data for the porphyrazines in chloroform.

Compound	λ/nm (log ε/dm^3 mol^{-1} cm^{-1})		
3	356 (4.97)	664 (4.93)	
4	338 (4.77)	654 (4.47)	712 (4.50)
5	340 (4.95)	678 (4.99)	
6	352 (4.91)	680 (4.97)	
7	346 (4.83)	674 (4.88)	

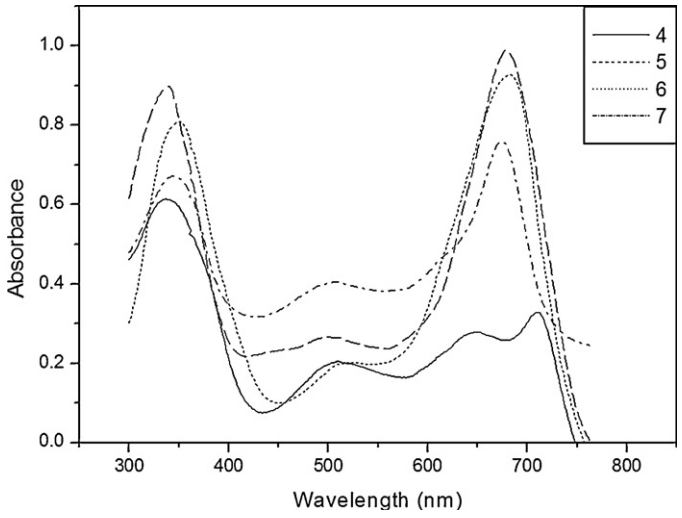


Fig. 2. UV–vis spectra of **4–7** in chloroform.

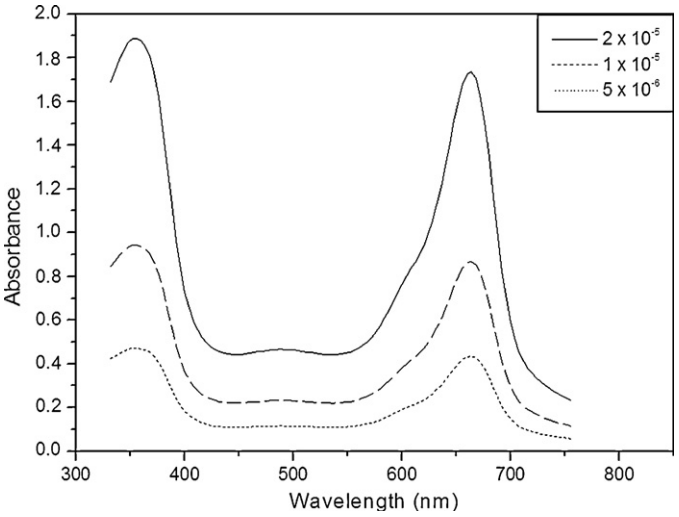


Fig. 3. UV–vis spectra of **3** in chloroform at various concentrations.

of the higher solubility of pentafluorobenzyl-substituted groups in organic polar solvents. The solubility of **3** in chloroform, DCM, THF, and acetone was determined as 45, 55, 61, and 63 mg/mL, respectively. When the polarities of the solvents are increasing, the solubility of **3** is also increasing as anticipated.

In our previous paper [32], non-fluorinated groups into the peripheral position such as *o*-tolyl and *p*-tolyl groups were synthesized and the solubility of MgPz in chloroform, DCM, THF, and acetone was determined as 29, 35, 38, and 39 mg/mL, respectively. As a result of these solubility data of fluorinated and non-fluorinated counterparts, it is clear that the main effect of solubility is due to fluorinated groups.

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 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) 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 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 [38].

3.1. Synthesis of 2,3-bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile (2)

Disodium salt of dithiomaleonitrile (**1**) (1.12 g, 6.00 mmol) was mixed with (2,3,4,5,6-pentafluorobenzyl bromide) (3.92 g, 15.0 mmol) in methanol (50.0 mL) and refluxed under nitrogen for about 18 h. After evaporation of MeOH, the remaining oil 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. When $CHCl_3$ was evaporated the colored product was dissolved in a minimum amount of chloroform and then added drop-wise into cold *n*-hexane to precipitate the product, which was filtered off and dried in vacuum. The orange colored product was very soluble in chloroform, dichloromethane and acetone, but insoluble in *n*-hexane. Yield: 2.29 g (76%). FT-IR, $\nu_{max}/(cm^{-1})$: 2985–2872 (CH, aliphatic), 2220 (C≡N), 1665, 1650 (C=C, aromatic), 1593, 1512, 1418, 1355, 1308, 1274, 1182, 1114, 1055, 903, 846, 705, 681, 555. ^{1}H NMR (δ, ppm): 4.66 (s, 4H, S-CH_2). ^{13}C NMR (δ, ppm): 18.6, 113.7, 113.9, 115.5, 137.2, 137.4, 141.8. ^{19}F NMR (δ, ppm): −144.6 (*o*-fluoro), −154.4 (*p*-fluoro), −163.6 (*m*-fluoro). MS (ESI) *m*/*z*: 502.9 $[M]^+$. Calcd. for $C_{18}H_4N_2S_2F_{10}$: C 43.04; H 0.80; N 5.58; S 12.77. Found: C 43.11; H 0.86; N 5.52; S 12.65.

3.2. [2,3,7,8,12,13,17,18-octakis(2,3,4,5,6-pentafluorobenzylthio) porphyrazinato] Mg(II) (3)

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 $Mg(BuO)_2$. 2,3-Bis(2,3,4,5,6-pentafluorobenzylthio)maleonitrile (**2**) (251 mg, 0.50 mmol) was added to this solution and the mixture was refluxed for about 12 h. The colored 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 $CHCl_3$ was evaporated, the dark green colored product was obtained. Purification of the product was accomplished by column chromatography with silica gel using methanol/chloroform (1:20) as eluent. **3** was soluble in chloroform, dichloromethane, acetone and THF, but insoluble in *n*-hexane. Yield: 198 mg (78%). FT-IR, $\nu_{max}/(cm^{-1})$: 2988–2850 (CH, aliphatic), 1660, 1615 (C=C, aromatic), 1595, 1515, 1415, 1358, 1310, 1276, 1180, 1112, 1058, 905, 848, 702, 680, 553. ^{1}H NMR (δ, ppm): 4.62 (s, 16H, S-CH_2). ^{13}C NMR (δ, ppm) 18.9, 113.4, 114.0, 115.8, 137.0, 137.4, 141.5. ^{19}F NMR (δ, ppm): −142.4 (*o*-fluoro), −152.6 (*p*-fluoro), −161.6 (*m*-fluoro). MS (ESI) *m*/*z*: 2033.9 $[M]^+$. Calcd. for $C_{72}H_{16}N_8S_8F_{40}Mg$: C 42.52; H 0.79; N 5.51; S 12.61. Found: C 42.61; H 0.86; N 5.44; S 12.73.

3.3. [2,3,7,8,12,13,17,18-octakis(2,3,4,5,6-pentafluorobenzylthio) H^{21}, H^{23} porphyrazine] (4)

3 (102 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. **4** was obtained by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:50, v/v). Yield: 67 mg (66%). FT-IR, $\nu_{max}/(cm^{-1})$: 3295 (N–H), 2987–2855 (CH, aliphatic), 1662, 1622 (C=C, aromatic), 1598, 1512, 1413, 1356, 1314, 1278, 1182, 1114, 1059, 906, 849, 705, 683, 556. ^{1}H NMR (δ, ppm): 4.62 (s, 4H, S-CH_2), −1.10 (br s, 2H, NH). ^{13}C NMR (δ, ppm): 18.8, 113.6, 113.9, 115.6, 137.2, 137.4, 141.6. ^{19}F NMR (δ, ppm): −142.3 (*o*-fluoro), −151.3 (*p*-fluoro), −154.4 (*m*-fluoro). MS (ESI) *m*/*z*: 2011.8 $[M]^+$. Calcd. for $C_{72}H_{18}N_8S_8F_{40}$: C 42.99; H 0.80; N 5.57; S 12.75. Found: C 42.89; H 0.75; N 5.64; S 12.62.

3.4. General procedure for metallo porphyrazines (5–7)

4 (101 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 6 h. Then, the precipitate composed of the crude product and the excess metal salt were 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 (**5–7**) were obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:20, v/v).

*3.4.1. [2,3,7,8,12,13,17,18-octakis(2,3,4,5,6-pentafluorobenzylthio) porphyrazinato] Cu(II) (**5**)*

Yield: 46 mg (44%). FT-IR, $\nu_{max}/(cm^{-1})$: 2985–2852 (CH, aliphatic), 1664, 1648 (C=C, aromatic), 1592, 1518, 1412, 1355, 1315, 1274, 1185, 1114, 1056, 902, 846, 704, 682, 550. MS (ESI) *m/z*: 2072.1 $[M]^+$. Calcd. for $C_{72}H_{16}N_8S_8F_{40}Cu$: C 41.72; H 0.78; N 5.41; S 12.37. Found: C 41.81; H 0.84; N 5.35; S 12.48.

*3.4.2. [2,3,7,8,12,13,17,18-octakis(2,3,4,5,6-pentafluorobenzylthio) porphyrazinato] Zn(II) (**6**)*

Yield: 50 mg (48%). FT-IR, $\nu_{max}/(cm^{-1})$: 2985–2858 (CH, aliphatic), 1665, 1636 (C=C, aromatic), 1598, 1512, 1410, 1355, 1310, 1274, 1184, 1110, 1056, 902, 846, 703, 681, 554. ^1H NMR (δ, ppm): 4.64 (s, 16H, S-CH_2). ^{13}C NMR (δ, ppm) 18.9, 113.4, 114.0, 115.8, 137.0, 137.4, 141.5. ^{19}F NMR (δ, ppm): −142.8 (*o*-fluoro), −152.4 (*p*-fluoro), −161.4 (*m*-fluoro). MS (ESI) *m/z*: 2074.2 $[M]^+$. Calcd. for $C_{72}H_{16}N_8S_8F_{40}Zn$: C 41.68; H 0.78; N 5.40; S 12.36. Found: C 41.61; H 0.85; N 5.48; S 12.23.

*3.4.3. [2,3,7,8,12,13,17,18-octakis(2,3,4,5,6-pentafluorobenzylthio) porphyrazinato] Co(II) (**7**)*

Yield: 54 mg (52%). FT-IR, $\nu_{max}/(cm^{-1})$: 2986–2850 (CH, aliphatic), 1666, 1644 (C=C, aromatic), 1590, 1514, 1410, 1353, 1312, 1276, 1180, 1112, 1058, 900, 844, 702, 684, 554. MS (ESI) *m/z*: 2068.8 $[M]^+$. Calcd. for $C_{72}H_{16}N_8S_8F_{40}Co$: C 41.81; H 0.78; N 5.42; S 12.40. Found: C 41.89; H 0.84; N 5.36; S 12.51.

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