

# The synthesis and spectral properties of novel porphyrazines with eight (*p*-tolylmethylthio) and (*o*-tolylmethylthio) units

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By cyclotetramerisation of 1,2-bis(*p*-tolylmethylthio) and 1,2-bis(*o*-tolylmethylthio) maleonitrile in the presence of magnesium butanolate, magnesium porphyrazines carrying eight (*p*-tolylmethylthio) and (*o*-tolylmethylthio) units on the peripheral positions have been synthesised. Conversion of the magnesium porphyrazines into the metal-free derivatives was achieved by treatment with trifluoroacetic acid. Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metal porphyrazines (M = Cu, Zn, Co).

**Keywords:** maleonitriles, thioethers, porphyrazines, magnesium, copper, cobalt, zinc complexes

On account of their catalytic properties, biological importance and possible technological applications, metal compounds with several tetrapyrrole ligands, specifically the porphyrins, porphyrazines (tetraazaporphyrins) and phthalocyanines, have attracted great interest.<sup>1–3</sup> Metal porphyrins are well known for their biological functions such as in photosynthesis and oxygen transfer. Metal phthalocyanines have found several applications in industry as semiconductors, in energy conversion, chemical and gas sensors, catalysis, electro photography, photosensitisers, laser technology, electrochromism, liquid crystals, and optical data collection.<sup>4–10</sup> Therefore, there have been many experimental studies of metal porphyrins and metal phthalocyanines, whereas metal porphyrazines have received much less consideration since their early synthesis, probably because of the lack of an efficient synthetic method for making soluble derivatives.<sup>11–13</sup> Recently, however, some different researches involving porphyrazines have been made, which presage an excellent future for their applications.<sup>14–16</sup>

Our group has been studying the preparation of new soluble phthalocyanine and porphyrazine derivatives. Among these, phthalocyanines fused to or attached through bridges to macrocyclic structures, and porphyrazines with long chains or functional units such as quaternisable amino groups,<sup>17</sup> crown ethers,<sup>18</sup> ferrocenes,<sup>19</sup> triphenylphosphine,<sup>20</sup> 4-*tert*-butylphenylthio<sup>21</sup> and tosylaminoethylthio<sup>22</sup> groups can be cited. Recently, we have synthesised novel *seco*-porphyrazines substituted with 1-naphthyl<sup>23</sup> and *p*-tolyl or *o*-tolyl units<sup>24</sup> on the peripheral positions, as encountered by Barrett, Hoffman and coworkers, with peripheral aminoporphyrazine derivatives.<sup>25</sup> We have also reported new porphyrazines with bulky electron-rich substituents such as 1-naphthylmethylthio,<sup>26</sup> 9-anthracenylmethylthio units<sup>27</sup> and (9-anthracenylmethylthio) iron derivatives.<sup>28</sup>

## Results and discussion

In the present study, we report novel soluble porphyrazines with eight (*p*-tolylmethylthio) and (*o*-tolylmethylthio) substituents appending to the peripheral positions. By cyclotetramerisation of 1,2-bis(*p*-tolylmethylthio)- and 1,2-bis(*o*-tolylmethylthio)-maleonitrile (**2**, **3**) in the presence of magnesium butanolate, magnesium porphyrazines have been synthesised. Their demetalation by treatment with trifluoroacetic acid produced the metal-free derivatives. Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metallo derivatives M(II) (M = Cu, Zn, Co). The new compounds were characterised by elemental analysis together with FT-IR, <sup>1</sup>H NMR, UV-Vis and mass spectral data.

The starting materials for these novel porphyrazine structures with eight (*p*-tolylmethylthio) or (*o*-tolylmethylthio) groups

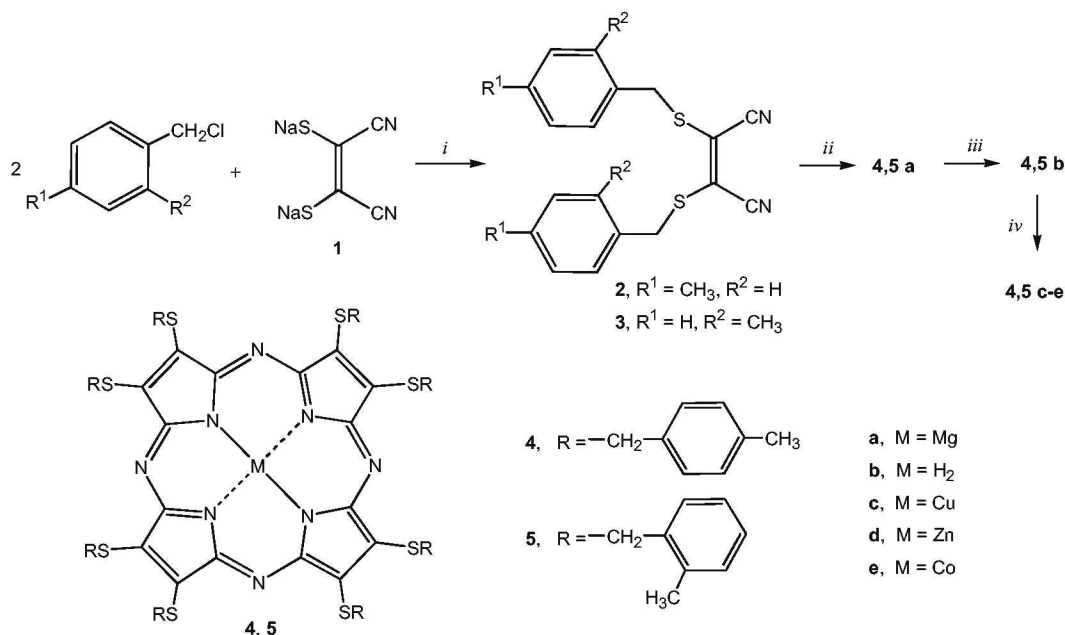
bound to the periphery are the 1,2-bis(*p*-tolylmethylthio) maleonitrile (**2**) and 1,2-bis(*o*-tolylmethylthio) isomer (**3**) which were obtained from  $\alpha$ -chloro-*p*-xylene and  $\alpha$ -chloro-*o*-xylene respectively and the disodium salt of dithiomaleonitrile (**1**) (Scheme 1). The yellow product **2** and the yellow-green product **3** were obtained in 78% and 83% yields, respectively. The conversion of **2** and **3** into **4a** and **5a** (Scheme 1) was achieved by the template effect of magnesium butanolate: cyclotetramerisation gave the dark green magnesium-porphyrazine **4a** in 63% yield and the blue-green **5a** in 58% yield. They were soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in apolar hydrocarbon solvents such as *n*-hexane. The conversion of **4a** and **5a** into the magnesium-free porphyrazines **4b** and **5b** was achieved by treatment with trifluoroacetic acid. Their mass spectra clearly show that the magnesium has been removed and replaced by hydrogen atoms. Proton-metal exchange in the metal-free porphyrazines (**4b**, **5b**) using metal salts gave the metalated species **4c–e**, **5c–e** (Scheme 1).

The precursors **2** and **3**, and the porphyrazines **4a–e** and **5a–e** were identified using spectroscopic techniques such as <sup>1</sup>H NMR, FT-IR, UV-Vis and MS, and elemental analysis. The elemental analyses correspond closely with the calculated values (see Experimental section).

In the FT-IR spectrum of **2**, the stretching vibration of C≡N is observed at 2215 cm<sup>-1</sup>, the aromatic and aliphatic C–H peaks are around 2876–3052 cm<sup>-1</sup>, and the characteristic substituted *p*-tolyl peak is at 803 cm<sup>-1</sup>; in the IR spectrum of **3**, the stretching vibration of C≡N is observed at 2212 cm<sup>-1</sup>, the aromatic and aliphatic C–H peaks are around 2863–3059 cm<sup>-1</sup> and the characteristic substituted (*o*-tolyl) peak is at 735 cm<sup>-1</sup>. These values are consistent with those reported elsewhere for similar compounds.<sup>23,26,27</sup> After the conversion of **2** and **3** into **4a** and **5a**, the C≡N vibrations around 2215 and 2212 cm<sup>-1</sup> disappeared. In the metal-free porphyrazines (**4b**, **5b**), the N–H stretching absorptions of the inner core were observed around 3339 and 3328 cm<sup>-1</sup>. The FT-IR spectra of all porphyrazine derivatives (**4a–e**, **5a–e**) showed the aromatic and aliphatic C–H peaks at around 2848–3059 cm<sup>-1</sup>, the characteristic C=C aromatic peaks around 1605–1675 cm<sup>-1</sup>; the characteristic *p*-disubstituted benzene peaks showed at around 805–848 cm<sup>-1</sup> in **4** and the *o*-disubstituted benzene peaks around 735–766 cm<sup>-1</sup> in **5**.

In the <sup>1</sup>H NMR spectra of the diamagnetic porphyrazines (**4a**, **4b**, **4d**, **5a**, **5b**, **5d**), three different types of proton are clearly seen: a multiplet around 7.20–7.35 ppm corresponding to the phenyl protons, a singlet around 4.33–4.39 ppm corresponding to the S–CH<sub>2</sub>, and a singlet around 2.40–2.44 ppm for the methyl protons. The ratio of the integral values 4:2:3 confirms the proposed assignments. The N–H protons of the metal-free porphyrazines (**4b**, **5b**) were also identified in the <sup>1</sup>H NMR spectra with broad peaks at  $\delta = -1.15$  and

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Reagents: i, heat, MeOH; ii,  $\text{Mg}(\text{OBU})_2$ ; iii,  $\text{CF}_3\text{CO}_2\text{H}$ ; iv, heat in EtOH,  $\text{Cu}(\text{OAc})_2$ ,  $\text{Zn}(\text{OAc})_2$ , or  $\text{Co}(\text{OAc})_2$

Scheme 1

-1.05 ppm, presenting the typical shielding of inner core protons, which is a common feature of the  $^1\text{H}$  NMR spectra of metal-free porphyrazines.<sup>18,19,26,29</sup>

Electronic spectra are especially useful to establish the structure of the porphyrazines **4a–e** and **5a–e**. The UV-Vis spectrum of the porphyrazine core is dominated by two intense bands, the Q band in the visible region around 650 nm and the B band in the near UV around 350 nm, both correspond to  $\pi \rightarrow \pi^*$  transitions.<sup>30,31</sup> The presence of electron-donating units on the periphery causes a bathochromic shift of Q bands. The UV-Vis spectra in chloroform of porphyrazines **4a**, **4c–e**, **5a**, **5c–e** prepared in the present work exhibited intense single Q band absorptions around 642–675 nm and B bands in the near UV region around 345–378 nm (Table 1). As a consequence of the change in the symmetry of the porphyrazine core from  $D_{4h}$  in the case of the metallo-derivatives) to  $D_{2h}$ , the electronic absorption spectra of **4b** and **5b** display a split in the Q band, to 634 and 706 nm and 638 and 715 nm, respectively. The UV-Vis spectra of **4a** and **4b** in chloroform are shown in Fig. 1. An absorbance vs. concentration study indicated that, due to the bulky tolylmethylthio substituents, no aggregation occurred in **4a**, **4b**, **5a** or **5b**.

In conclusion, we describe the synthesis and the spectral characterisation of novel porphyrazines surrounded by eight bulky *p*- or *o*-tolylmethylthio units on the periphery.

## 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. Proton NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using TMS and  $\text{CDCl}_3$  as the reference and solvent, respectively. Mass spectra were recorded on a Bruker Daltonics MicrOTOF LC-MS spectrometer using the electro spray 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 disodium salt of dithiomaleonitrile (**1**) was prepared according to the previously reported procedure.<sup>32</sup> **1,2-Bis(p-tolylmethylthio)maleonitrile (2)**: The disodium salt of dithiomaleonitrile (**1**)<sup>32</sup> (1.12 g, 6 mmol) was mixed with ( $\alpha$ -chloro-*p*-xylene) (2.11 g, 15 mmol) in methanol (50 ml) and heated to reflux under nitrogen for *ca* 8 h. Then MeOH was evaporated off, and

Table 1 UV-Vis data for **4a–e** and **5a–e** in chloroform

Compound	$\lambda/\text{nm}$ (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )
<b>4a</b>	378 (4.71) 675 (4.70)
<b>4b</b>	378 (4.89) 634 (4.74) 706 (4.81)
<b>4c</b>	377 (4.79) 652 (4.84)
<b>4d</b>	368 (4.78) 644 (4.88)
<b>4e</b>	366 (4.84) 646 (4.89)
<b>5a</b>	345 (4.53) 675 (4.58)
<b>5b</b>	354 (4.51) 638 (4.18) 715 (3.85)
<b>5c</b>	358 (4.41) 642 (4.38)
<b>5d</b>	350 (4.45) 646 (4.42)
<b>5e</b>	356 (4.49) 650 (4.40)

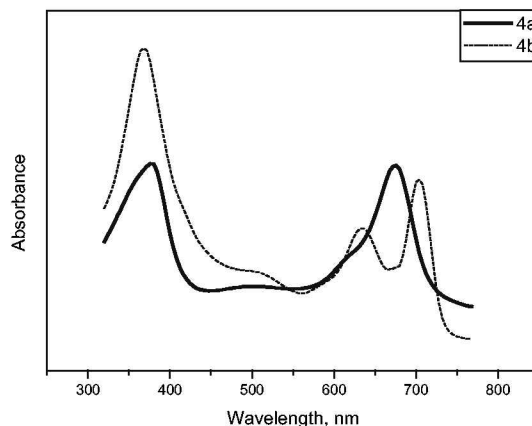


Fig. 1 UV-Vis spectra of **4a** and **4b** in chloroform.

the residue was treated with chloroform to remove insoluble salts by filtration. The chloroform solution was extracted several times with 15% aqueous  $\text{Na}_2\text{SO}_4$  and then dried over anhydrous  $\text{Na}_2\text{SO}_4$  overnight. After evaporation of the solvent the residual solid was extracted with refluxing *n*-hexane to remove any excess of  $\alpha$ -chloro-*p*-xylene. The yellow dinitrile **2** was very soluble in chloroform and dichloromethane, but insoluble in *n*-hexane. Yield: 1.64 g (78%). IR:  $\nu_{\text{max}}$  3052, 2974–2876, 2215, 1651, 1517, 1452, 1380, 1269, 1201, 1168, 1087, 1041, 848, 803, 747, 721  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.30–7.17 (m, 8H, ArH), 4.31 (s, 4H, S- $\text{CH}_2$ ), 2.39 (s, 6H,  $\text{CH}_3$ ). MS (ESI):  $m/z$  350.2  $[\text{M}]^+$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}_2$  (350.09): C, 68.53; H, 5.18; N, 7.99. Found: C, 68.65; H, 5.07; N, 7.85%.



**1,2-Bis(o-tolylmethylthio)maleonitrile (3):** The synthetic procedure was identical to that of **2** above, but using  $\alpha$ -chloro-*o*-xylene in place of the *p*-xylene. The dinitrile **3** was yellow-green and very soluble in chloroform and dichloromethane, but insoluble in *n*-hexane. Yield: 1.75 g (83%). IR:  $\nu_{\max}$  3059, 2974–2863, 2212, 1605, 1494, 1461, 1380, 1261, 1222, 1170, 1093, 1036, 875, 838, 766, 735  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.32&7.19 (m, 8H, ArH), 4.36 (s, 4H, S–CH<sub>2</sub>), 2.41 (s, 6H, CH<sub>3</sub>). MS (ESI):  $m/z$  350.7 [M]<sup>+</sup>. Anal. Calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub> (350.09): C, 68.53; H, 5.18; N, 7.99. Found: C, 68.68; H, 5.26; N, 8.09%.

**The octakis(tolylmethylthio)porphyrzinato]magnesium(II) complexes 4a, 5a**

Mg turnings (24.3 mg, 1 mmol) and a small I<sub>2</sub> crystal were refluxed in *n*-BuOH (20 ml) for about 8 h to obtain Mg(OBu)<sub>2</sub>. To this solution the dinitrile (701 mg, 2 mmol) was added and the mixture was refluxed for about 8 h. The crude coloured product was filtered off, washed with ethanol and water and dried in a vacuum. The solid was dissolved in chloroform and filtered from insoluble salts. The chloroform solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent the green or blue-green solid residue was purified by column chromatography on silica (eluent CH<sub>3</sub>OH: CHCl<sub>3</sub>, 1:50 v/v). The products were soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in *n*-hexane.

**[2,3,7,8,12,13,17,18-Octakis(p-tolylmethylthio)porphyrzinato]Mg(II) (4a):** Prepared using the dinitrile **2**, as a dark green solid (450 mg, 63%). IR:  $\nu_{\max}$  3050, 2978–2880, 1614, 1519, 1465, 1366, 1271, 1184, 1126, 1090, 1044, 847, 805, 750, 725  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.34–7.21 (m, 4H, ArH), 4.33 (s, 2H, S–CH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>). MS (ESI):  $m/z$  1426.6 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>MgN<sub>8</sub>S<sub>8</sub> (1426.32): C, 67.37; H, 5.09; N, 7.86. Found: C, 67.49; H, 5.20; N, 7.71%.

**[2,3,7,8,12,13,17,18-Octakis(o-tolylmethylthio)porphyrzinato]Mg(II) (5a):** From the dinitrile **3**, a blue-green solid (414 mg, 58%). IR:  $\nu_{\max}$  3055, 2980–2870, 1625, 1495, 1465, 1355, 1265, 1220, 1148, 1095, 1040, 878, 818, 758, 735  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.35–7.22 (m, 4H, ArH), 4.39 (s, 2H, S–CH<sub>2</sub>), 2.44 (s, 3H, CH<sub>3</sub>). MS (ESI):  $m/z$  1426.2 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>MgN<sub>8</sub>S<sub>8</sub> (1426.32): C, 67.37; H, 5.09; N, 7.86. Found: C, 67.52; H, 5.18; N, 7.73%.

**The octakis(tolylmethylthio)porphyrzines 4b, 5b:** The porphyrzinato–magnesium complex **4a** or **5a** (143 mg, 0.1 mmol) was dissolved in the minimum amount of trifluoroacetic acid (*ca* 4 ml) and stirred for 3 h at room temperature. When the reaction mixture was added to ice drop by drop, and then neutralised with 25% aqueous ammonia, precipitation occurred and the solid was separated and dissolved in chloroform, and the chloroform solution was extracted with water twice. After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated to obtain the metal-free porphyrzine, which was purified by column chromatography (SiO<sub>2</sub>; CH<sub>3</sub>OH: CHCl<sub>3</sub>, 1:50 v/v).

**2,3,7,8,12,13,17,18-Octakis(p-tolylmethylthio)-H<sup>21</sup>,H<sup>23</sup>-porphyrzine (4b):** Green solid (62 mg, 44%). IR:  $\nu_{\max}$  3339, 3053, 2928–2862, 1618, 1515, 1452, 1328, 1275, 1172, 1125, 1085, 1040, 847, 803, 753, 723  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.35–7.21 (m, 4H, ArH), 4.34 (s, 2H, S–CH<sub>2</sub>), 2.42 (s, 3H, CH<sub>3</sub>), –1.15 (br s, 2H, NH). MS (ESI):  $m/z$  1404.3 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>74</sub>N<sub>8</sub>S<sub>8</sub> (1404.04): C, 68.44; H, 5.31; N, 7.98. Found: C, 68.32; H, 5.44; N, 7.86%.

**2,3,7,8,12,13,17,18-Octakis(o-tolylmethylthio)-H<sup>21</sup>,H<sup>23</sup>-porphyrzine (5b):** Green powder (73 mg) (52%). IR:  $\nu_{\max}$  3328, 3045, 2924–2852, 1628, 1491, 1441, 1332, 1260, 1215, 1185, 1088, 1038, 885, 820, 762, 738  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.34–7.20 (m, 4H, ArH), 4.38 (s, 2H, S–CH<sub>2</sub>), 2.43 (s, 3H, CH<sub>3</sub>), –1.05 (br s, 2H, NH). MS (ESI):  $m/z$  1404.5 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>74</sub>N<sub>8</sub>S<sub>8</sub> (1404.04): C, 68.44; H, 5.31; N, 7.98. Found: C, 68.30; H, 5.38; N, 7.83%.

**General procedure for metallo-porphyrzines (4c–e):** The metal-free porphyrzine (**4b** or **5b**) (140 mg, 0.1 mmol) in CHCl<sub>3</sub> (10 ml) was stirred with the metal salt (1 mmol) [Cu(OAc)<sub>2</sub> (182 mg), Zn(OAc)<sub>2</sub> (183 mg) or Co(OAc)<sub>2</sub> (177 mg)] in ethanol (15 ml) and heated to reflux under nitrogen for about 4 h. After cooling, the precipitate, consisting of the crude product and the excess of metal salt, was filtered off and dried. 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 (100 ml) drop by drop to precipitate the product. The porphyrzine derivatives (**4c–e** or **5c–e**) were purified by column chromatography (SiO<sub>2</sub>; CH<sub>3</sub>OH: CHCl<sub>3</sub>, 1:20 v/v).

**[2,3,7,8,12,13,17,18-Octakis(p-tolylmethylthio)porphyrzinato]Cu(II) (4c):** Blue powder (66 mg, 45%). IR:  $\nu_{\max}$  3055, 2928–2885, 1642, 1513, 1448, 1380, 1276, 1191, 1123, 1083, 1042, 838, 802, 758, 725  $\text{cm}^{-1}$ . MS (ESI):  $m/z$  1465.2 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>CuN<sub>8</sub>S<sub>8</sub> (1465.57): C, 65.56; H, 4.95; N, 7.65. Found: C, 65.43; H, 4.82; N, 7.79%.

**[2,3,7,8,12,13,17,18-Octakis(p-tolylmethylthio)porphyrzinato]Zn(II) (4d):** Green powder (56 mg, 38%). IR:  $\nu_{\max}$  3048, 2925–2875, 1675, 1510, 1440, 1355, 1265, 1184, 1128, 1080, 1038, 830, 805, 767, 728  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.35–7.19 (m, 4H, ArH), 4.35 (s, 2H, S–CH<sub>2</sub>), 2.44 (s, 3H, CH<sub>3</sub>). MS (ESI):  $m/z$  1467.6 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>N<sub>8</sub>S<sub>8</sub>Zn (1467.41): C, 65.48; H, 4.95; N, 7.64. Found: C, 65.55; H, 4.83; N, 7.75%.

**[2,3,7,8,12,13,17,18-Octakis(p-tolylmethylthio)porphyrzinato]Co(II) (4e):** Blue powder (63 mg, 43%). IR:  $\nu_{\max}$  3056, 2936–2848, 1668, 1518, 1438, 1361, 1262, 1174, 1135, 1081, 1044, 845, 803, 758, 727  $\text{cm}^{-1}$ . MS (ESI):  $m/z$  1460.7 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>CoN<sub>8</sub>S<sub>8</sub> (1460.95): C, 65.77; H, 4.97; N, 7.67. Found: C, 65.88; H, 4.86; N, 7.79%.

**[2,3,7,8,12,13,17,18-Octakis(o-tolylmethylthio)porphyrzinato]Cu(II) (5c):** Blue powder (70 mg, 48%). IR:  $\nu_{\max}$  3052, 2928–2868, 1621, 1493, 1458, 1355, 1258, 1212, 1188, 1091, 1041, 888, 828, 759, 735  $\text{cm}^{-1}$ . MS (ESI):  $m/z$  1465.4 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>CuN<sub>8</sub>S<sub>8</sub> (1465.57): C, 65.56; H, 4.95; N, 7.65. Found: C, 65.62; H, 5.05; N, 7.54%.

**[2,3,7,8,12,13,17,18-Octakis(o-tolylmethylthio)porphyrzinato]Zn(II) (5d):** Green powder (65 mg, 44%). IR:  $\nu_{\max}$  3055, 2922–2864, 1631, 1495, 1448, 1352, 1260, 1214, 1193, 1094, 1038, 885, 825, 756, 736  $\text{cm}^{-1}$ . NMR:  $\delta_{\text{H}}$  7.33–7.21 (m, 4H, ArH), 4.35 (s, 2H, S–CH<sub>2</sub>), 2.40 (s, 3H, CH<sub>3</sub>). MS (ESI):  $m/z$  1467.1 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>N<sub>8</sub>S<sub>8</sub>Zn (1467.41): C, 65.48; H, 4.95; N, 7.64. Found: C, 65.57; H, 5.06; N, 7.53%.

**[2,3,7,8,12,13,17,18-Octakis(o-tolylmethylthio)porphyrzinato]Co(II) (5e):** Blue powder (75 mg (51%)). IR:  $\nu_{\max}$  3040, 2935–2874, 1632, 1498, 1437, 1342, 1271, 1236, 1192, 1098, 1035, 889, 823, 759, 735  $\text{cm}^{-1}$ . MS (ESI):  $m/z$  1460.6 [M]<sup>+</sup>. Anal. Calcd for C<sub>80</sub>H<sub>72</sub>CoN<sub>8</sub>S<sub>8</sub> (1460.95): C, 65.77; H, 4.97; N, 7.67. Found: C, 65.85; H, 4.83; N, 7.77%.

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