

# Synthesis of antipodal $\beta$ -trisubstituted *meso*-tetraphenylporphyrins and the crystal structure of hexaphenylporphinatozinc(II) bispyridinate complex

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**Abstract.** A series of antipodal  $\beta$ -trisubstituted *meso*-tetraphenylporphyrins, H<sub>2</sub>TPP(R)<sub>3</sub> (R = CH<sub>3</sub>, Ph, PE, and 2'-thienyl) derivatives and their metal (Cu(II) and Zn(II)) complexes were synthesised and characterised by electronic absorption, <sup>1</sup>H NMR spectroscopy and mass spectrometry. The magnitude of the red-shift in absorption bands in these free-base porphyrins depend on the nature of the substituent and follow the general trend: PE > 2'-thienyl > Br > Ph > CH<sub>3</sub>. Synthesis, characterisation and crystal structure of 2,5,10,12,15,20-hexaphenylporphinato zinc(II) bispyridinate, ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub> complex is also reported. It shows planar geometry of the porphyrin ring with two  $\beta$ -phenyls located at the antipodal 2,12-pyrrole positions. The two axially coordinated pyridine ring planes are oriented almost parallel to each other and they are in staggered conformation relative to opposite pyrrolic nitrogens. The normal-coordinate structural decomposition analysis of the ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub> complex revealed slight *wave* distortion of the macrocycle.

**Keywords.** Synthesis;  $\beta$ -pyrrole trisubstituted porphyrins; substituted porphyrins; metalloporphyrins; hexaphenylporphyrin; crystal structure.

## 1. Introduction

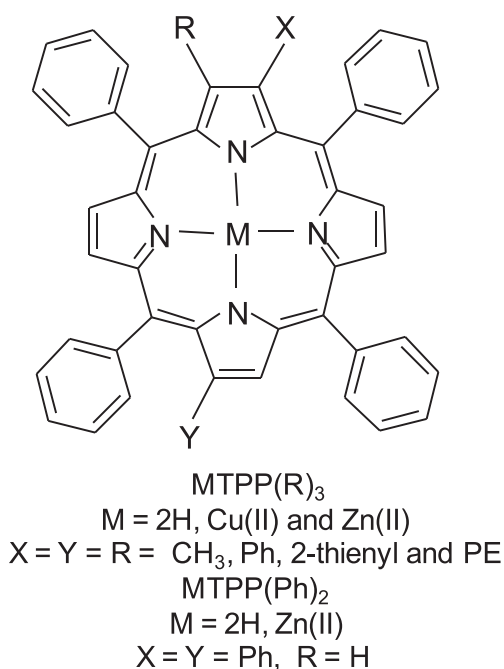
Synthesis of functionalised porphyrins and metalloporphyrins are of remarkable interest because of their use as model compounds of biological significance.<sup>1,2</sup> The highly substituted tetrarylporphyrins exhibited distorted structures owing to the repulsive interaction among the substituents. These porphyrins were employed as model compounds of non-planar distortions of hemes in heme proteins.<sup>3,4</sup> The introduction of appropriate substituents at the periphery of the porphyrin macrocycle provide altered properties and have been found to be potentially useful in a variety of material applications.<sup>5</sup> Many *meso*-tetraarylporphyrins and their metal complexes find use in applications such as supramolecular network-solids<sup>6,7</sup> catalysts,<sup>8–10</sup> liquid crystals,<sup>5</sup> non-linear optics,<sup>11</sup> dye-sensitised solar cells<sup>12</sup> and others.<sup>2</sup>

The presence of electron donating or withdrawing groups at the  $\beta$ -pyrrole positions of the porphyrin ring induces significant changes in optical absorption, electrochemical redox and stereochemical properties.<sup>2,13–15</sup> Notably, the MTPPs with fewer (1–4) or more brominated porphyrins have been useful precursors to the

synthesis of a variety of other porphyrins that are preparatively difficult.<sup>16–28</sup> The reaction of stoichiometric amounts of NBS with H<sub>2</sub>TPP in CHCl<sub>3</sub> at ambient conditions produced regioselective product, H<sub>2</sub>TPPBr<sub>4</sub>.<sup>29,30</sup> It is a useful precursor in the preparation of other tetra-substituted MTPPs with interesting physicochemical properties.<sup>21,23,28</sup> The regioselective synthesis of  $\beta$ -pyrrole brominated H<sub>2</sub>TPPBr<sub>n</sub> (n = 1–3) are difficult to synthesise which often lead to mixture of products. In our previous work, we reported the synthesis and separation of dibromo and tribromo-H<sub>2</sub>TPP derivatives.<sup>22</sup> Further, crystal structure of the ZnTPP(Ph)<sub>3</sub>(1,4-dioxane) complex showed antipodal  $\beta$ -pyrrole substitution of phenyl groups.<sup>22</sup> Although, the preparation of  $\beta$ -dibromo-H<sub>2</sub>TPP from N-bromosuccinimide induced bromination of H<sub>2</sub>TPP is reported in the literature,<sup>22,31–35</sup> the regioselectivity has remained largely unexamined. Crystal structure of the H<sub>2</sub>TPPBr<sub>2</sub> showed antipodal distribution of bromo groups with disorder over all the four pyrrole rings.<sup>31</sup> The regioselective synthesis of 2,3-dibromo-H<sub>2</sub>TPP was achieved by bromination of H<sub>2</sub>TPP(NO<sub>2</sub>) followed by denitration reaction.<sup>36</sup>

In the present work, we report the synthesis and characterisation of a series of unsymmetrically

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**Figure 1.** Chemical structures of  $\beta$ -trisubstituted MTPPs.

$\beta$ -trisubstituted MTPP(R)<sub>3</sub> derivatives (figure 1). Such unsymmetrically substituted porphyrins could be useful in non-linear optical applications. Furthermore, to determine the distribution of bromo groups in H<sub>2</sub>TPPBr<sub>2</sub>, the diphenyl-H<sub>2</sub>TTP and its Zn(II) complex were synthesised and characterised. Single crystal XRD analysis of ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub> complex showed interesting structural features.

## 2. Experimental

### 2.1 Materials

5,10,15,20-tetraphenylporphyrin, H<sub>2</sub>TTP was prepared using reported procedure.<sup>37</sup> The brominated precursor porphyrin, H<sub>2</sub>TPPBr<sub>n</sub> (n = 2 and 3) were synthesised by literature method.<sup>22</sup> All the solvents employed in this study were of analytical grade and distilled prior to use. Propionic acid, benzaldehyde, pyrrole and N-bromosuccinimide were procured from Sigma-Aldrich (India). N-bromosuccinimide (NBS) was recrystallised from hot water and dried at 70°C for 12 h under vacuum (8.0 mbar) before use. CDCl<sub>3</sub>, benzene-*d*<sub>6</sub>, DMSO-*d*<sub>6</sub>, superbases (2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3] undecane), phenylboronic acid, methylboronic acid, tributyl(2-thienyl)tin, (Bu)<sub>3</sub>Sn(2-thienyl), tributyl(phenylethynyl)tin, (Bu)<sub>3</sub>Sn(PE) and tetrakis(triphenylphosphine) palladium(0) were purchased from Sigma-Aldrich (India) and used as received. Metal acetates, copper(II) acetate monohydrate and zinc(II) acetate dihydrate were procured

from SRL (India) and used without further purification. Silica gel (100–200 mesh) for column chromatography were purchased from Rankem (India) and used as such. Precoated aluminum plates with silica gel for chromatography were purchased from E. Merck (Germany) and used as such.

### 2.2 Instrumentation and methods

Electronic absorption spectra of porphyrins were recorded on a JASCO V-550 model UV-Visible spectrophotometer using a pair of quartz cells of 1 cm path length in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. <sup>1</sup>H NMR spectra of porphyrins were recorded on a Bruker Avance 400 MHz FT-NMR spectrometer in CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> and benzene-*d*<sub>6</sub> using tetramethylsilane as an internal reference at 298 K. The mass spectra of the porphyrins were carried out on an electro-spray ionization (ESI) mass spectrometer model Micromass Q-TOF micro™ in CH<sub>2</sub>Cl<sub>2</sub> solvent of the porphyrin containing 5% formic acid. The metalloporphyrins were analyzed by matrix assisted laser desorption time-of-flight (MALDI-TOF) on a Voyager DE-PRO model mass spectrometer using  $\alpha$ -cyano-4-hydroxycinnamic acid as the matrix under positive ion mode condition. Elemental analysis of the samples was performed on a Perkin Elmer CHNO/S analyzer model 2400 series. Single crystal X-ray diffraction data collection was performed at 173 K on a Bruker Apex-II CCD diffractometer equipped with a liquid nitrogen cryostat.

SIR92 (WINGX) program was used to solve the structure by direct methods.<sup>38</sup> The structure was performed on F<sup>2</sup> using SHELXL97 software<sup>39</sup> (Sheldrick, 1997). Structure was refined using full matrix least squares technique. The ORTEPs were generated using ORTEP-3<sup>40</sup> program and intermolecular interactions were calculated using Platon program.<sup>41</sup> Single crystals of ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub>, **1** were grown by slow diffusion of vapours of hexane to a saturated solution of the porphyrin in 1,2-dichloroethane containing few drops of distilled pyridine over a period of week.

Crystallographic information file of ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub> structure, **1** has been deposited to the Cambridge Crystallographic Data Centre as supplementary material with the publication number CCDC 737939.

### 2.3 Synthesis of H<sub>2</sub>TTP(R)<sub>3</sub> (R = CH<sub>3</sub> and Ph) derivatives and their metal (Cu(II) and Zn(II)) complexes

H<sub>2</sub>TTP(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>TTP(Ph)<sub>3</sub> were prepared using reported procedures<sup>20</sup> using six equivalent of RB(OH)<sub>2</sub>

(R = CH<sub>3</sub> or Ph). The yield of H<sub>2</sub>TPP(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>TPP(Ph)<sub>3</sub> were found to be 45% and 80%, respectively. The MTPP(CH<sub>3</sub>)<sub>3</sub> (M = Cu(II) and Zn(II)) were prepared using conventional reported procedure in almost quantitative yields. **H<sub>2</sub>TPP(CH<sub>3</sub>)<sub>3</sub>**: <sup>1</sup>H NMR in CDCl<sub>3</sub>  $\delta$  ppm, 8.65 (d, 1H, *J* = 4.4 Hz,  $\beta$ -pyrrole-H), 8.61 (s, 1H,  $\beta$ -pyrrole-H), 8.57 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.55, 8.53 (ABq, 2H,  $\beta$ -pyrrole-H), 8.20 (m, 2H, *o*-Ph-H), 8.08 (m, 6H, *o*-Ph-H), 7.72 (m, 12H, *m* and *p*-Ph-H), 2.59 (s, 3H), 2.46 (s, 3H), 2.45 (s, 3H, CH<sub>3</sub>-H), -2.65 (s, 1H, NH), -2.95 (s, 1H, NH). HR ESI MS calcd. for C<sub>47</sub>H<sub>36</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 657.3018 (found: 657.3030). **CuTPP(CH<sub>3</sub>)<sub>3</sub>**: MALDI-TOF MS calcd. for CuC<sub>47</sub>H<sub>34</sub>N<sub>4</sub>: 717.207 (found 718.36). **ZnTPP(CH<sub>3</sub>)<sub>3</sub>**: <sup>1</sup>H NMR (400 MHz) in CDCl<sub>3</sub>: 8.84 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.74 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.68 (m, 2H,  $\beta$ -pyrrole-H), 8.61 (s, 1H,  $\beta$ -pyrrole-H), 8.19 (d, 2H, *J* = 7.2 Hz, *o*-Ph-H), 8.07 (m, 6H, *o*-Ph-H), 7.73 (m, 12H, *m* and *p*-Ph-H), 2.55 (s, 3H, CH<sub>3</sub>-H), 2.41 (s, 6H, CH<sub>3</sub>-H). MALDI-TOF MS calcd. for ZnC<sub>47</sub>H<sub>34</sub>N<sub>4</sub>: 718.207 (found: 720.06). CuTPP(Ph)<sub>3</sub> and ZnTPP(Ph)<sub>3</sub> were isolated in almost quantitative yields. **H<sub>2</sub>TPP(Ph)<sub>3</sub>**: <sup>1</sup>H NMR in CDCl<sub>3</sub>:  $\delta$ <sub>H</sub> (ppm), 8.70 (s, 1H,  $\beta$ -pyrrole-H), 8.66 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.52 (d, 2H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.42 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.25 (m, 2H, *meso-o*-Ph-H), 7.95 (d, 2H, *J* = 6.8 Hz, *meso-o*-Ph-H), 7.83 (d, 4H, *J* = 7.2 Hz, *meso-o*-Ph-H), 7.74 (m, 3H, *meso-m* and *p*-Ph-H), 7.36 (m, 2H,  $\beta$ -Ph-H), 7.20 (m, 12H, *m* & *p*-Ph-H &  $\beta$ -Ph-H), 6.95 (d, 4H, *J* = 7.2 Hz,  $\beta$ -Ph-H), 6.88 (m, 6H,  $\beta$ -Ph-H), -2.22 (s, 2H, NH). HR ESI-MS calcd. for C<sub>62</sub>H<sub>42</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 843.3487 (found: 843.3486). **CuTPP(Ph)<sub>3</sub>**: MALDI-TOF MS calculated for CuC<sub>62</sub>H<sub>40</sub>N<sub>4</sub>: 903.254 (found: 902.9). **ZnTPP(Ph)<sub>3</sub>**: <sup>1</sup>H NMR in CDCl<sub>3</sub>: 8.82 (m, 2H,  $\beta$ -pyrrole-H), 8.67 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.63 (d, 1H, *J* = 4.4 Hz,  $\beta$ -pyrrole-H), 8.54 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.22 (m, 2H, *meso-o*-Ph-H), 7.88 (m, 2H, *meso-o*-Ph-H), 7.77 (m, 4H, *meso-o*-Ph-H), 7.71 (m, 3H,  $\beta$ -Ph-H), 7.36 (m, 2H,  $\beta$ -Ph-H), 7.18 (m, 12H, *meso-m* & *p*-Ph and  $\beta$ -Ph-H), 6.98 (m, 4H,  $\beta$ -Ph-H), 6.87 (m, 6H,  $\beta$ -Ph-H). MALDI-TOF MS calcd. for ZnC<sub>62</sub>H<sub>40</sub>N<sub>4</sub>: 904.254 (found: 905.5).

#### 2.4 Synthesis of 2,3,12-triphenylethynyl-5,10,15,20-tetraphenylporphyrin, H<sub>2</sub>TPP(PE)<sub>3</sub> and its metal (Cu(II) and Zn(II)) complexes

H<sub>2</sub>TPPBr<sub>3</sub> (0.12 g, 0.15 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 g, 0.036 mmol) were dissolved in 20 mL of 1,4-dioxane and allowed to stir at room temperature. To this

solution, (Bu)<sub>3</sub>Sn(PE) (0.32 ml, 0.84 mmol) was added in 10 mL dioxane dropwise over a period of 15 min. Then, the resultant mixture was stirred and refluxed for 3 h. At the end of this period, the reaction mixture was rotary evaporated to dryness. The crude product was redissolved in CHCl<sub>3</sub> and purified through silica gel column chromatography using CHCl<sub>3</sub> as the eluant. The purified product was dried at 85°C for 6 h under vacuum (8 mbar). Yield of the product: 0.1 g (77%). **H<sub>2</sub>TPP(PE)<sub>3</sub>**: <sup>1</sup>H NMR (400 MHz) in CDCl<sub>3</sub>: 8.97 (s, 1H,  $\beta$ -pyrrole-H), 8.84 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.76 (d, 1H, *J* = 5.2 Hz,  $\beta$ -pyrrole-H), 8.69 (d, 2H, *J* = 5.4 Hz,  $\beta$ -pyrrole-H), 8.26 (m, 8H, *meso-o*-Ph-H), 7.72 (m, 12H, *meso-m* and *p*-Ph-H), 7.33 (m, 15H,  $\beta$ -PE-H), -2.64 (s, 2H, NH). <sup>13</sup>C NMR (125 MHz) in CDCl<sub>3</sub>:  $\delta$  141.7, 141.4, 141.2, 140.8, 134.8, 134.8, 134.7, 134.5, 132.1, 132.0, 129.4, 128.8, 128.7, 128.5, 128.0, 127.9, 127.8, 127.0, 127.0, 126.9, 126.8, 124.0, 123.8, 120.4, 120.2, 120.1, 119.8, 104.7, 104.7, 99.1, 86.2, 86.0. HR ESI-MS calcd. for C<sub>68</sub>H<sub>43</sub>N<sub>4</sub> (M+H)<sup>+</sup>: 915.3488 (found 915.3483). **CuTPP(PE)<sub>3</sub>**: MALDI-TOF MS calcd. for CuC<sub>68</sub>H<sub>40</sub>N<sub>4</sub>: 975.254 (found 975.86). **ZnTPP(PE)<sub>3</sub>**: <sup>1</sup>H NMR (400 MHz) in CDCl<sub>3</sub>:  $\delta$  9.15 (s, 1H,  $\beta$ -pyrrole-H), 8.84 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.76 (d, 1H, *J* = 4.8 Hz,  $\beta$ -pyrrole-H), 8.69 (m, 2H,  $\beta$ -pyrrole-H), 8.18 (m, 8H, *meso-o*-Ph-H), 7.71 (m, 12H, *meso-m* and *p*-Ph-H), 7.34 (m, 15H,  $\beta$ -PE-H). MALDI-TOF MS calcd. for ZnC<sub>68</sub>H<sub>40</sub>N<sub>4</sub>: 976.254 (found 975.70).

H<sub>2</sub>TPP(2'-thienyl)<sub>3</sub> was prepared in 66% yield using (Bu)<sub>3</sub>Sn(2-thienyl) reagent by Stille coupling reaction as in the synthesis of H<sub>2</sub>TPP(PE)<sub>3</sub>. **H<sub>2</sub>TPP(2'-thienyl)<sub>3</sub>**: <sup>1</sup>H NMR in CDCl<sub>3</sub>: 8.70 (d, 1H, *J* = 5.2 Hz,  $\beta$ -pyrrole-H), 8.65 (s, 1H,  $\beta$ -pyrrole-H), 8.61 (d, 1H, *J* = 5.4 Hz,  $\beta$ -pyrrole-H), 8.57 (d, 1H, *J* = 5.2 Hz,  $\beta$ -pyrrole-H), 8.53 (d, 1H, *J* = 5.2 Hz,  $\beta$ -pyrrole-H), 8.28 (m, 2H, *meso-o*-Ph-H), 8.09 (m, 2H, *meso-o*-Ph-H), 7.97 (m, 4H, *meso-o*-Ph-H), 7.75 (m, 3H, *meso-m* & *p*-Ph-H), 7.37 (m, 9H, *meso-m* & *p*-Ph-H), 7.13 (dd, 1H, *J* = 5.13 Hz, thienyl-H), 6.98 (m, 1H, thienyl-H), 6.73 (m, 1H, thienyl-H), 6.60 (m, 6H, thienyl-H). -2.20 (s, 2H, NH). HR ESI-MS calcd. for C<sub>56</sub>H<sub>37</sub>N<sub>4</sub>S<sub>3</sub> [M+H]<sup>+</sup>: 861.2180 (found 861.2194). **CuTPP(2'-thienyl)<sub>3</sub>**: MALDI-TOF MS calcd. for CuC<sub>56</sub>H<sub>34</sub>N<sub>4</sub>S<sub>3</sub>: 921.124 (found: 921.52). **ZnTPP(2'-thienyl)<sub>3</sub>**: <sup>1</sup>H NMR (400 MHz) in CDCl<sub>3</sub>: 8.89 (s, 1H,  $\beta$ -pyrrole-H), 8.79 (d, 2H, *J* = 7.2 Hz,  $\beta$ -pyrrole-H), 8.66 (m, 2H,  $\beta$ -pyrrole-H), 8.57 (d, 2H, *J* = 7.4 Hz, *meso-o*-Ph-H), 8.21 (m, 2H, *meso-o*-Ph-H), 7.95 (m, 4H, *meso-o*-Ph-H), 7.86 (m, 2H, *meso-m* & *p*-Ph-H), 7.72 (m, 4H, *meso-m* & *p*-Ph-H), 7.34 (m, 6H, *m* & *p*-Ph-H), 7.18 (m, 1H, thienyl-H), 7.04 (m, 1H, thienyl-H), 6.76 (m, 1H, thienyl-H), 6.60 (m, 6H,

thienyl-H). MALDI-TOF MS calcd. for  $\text{ZnC}_{56}\text{H}_{34}\text{N}_4\text{S}_3$ : 924.50 (found: 924.61).

### 2.5 Synthesis of 2,5,10,12,15,20-hexaphenylporphyrin, $\text{H}_2\text{TPP}(\text{Ph})_2$ and its zinc(II) complex

The Suzuki cross-coupling reaction of  $\text{H}_2\text{TPPBr}_2$  with five equivalent of phenylboronic acid was carried out using the reported procedure.<sup>20</sup>  $\text{H}_2\text{TPP}(\text{Ph})_2$  was isolated in 71% yield. The product was obtained as a single major fraction along with the 10–15% of other minor mixture of phenylated products.  $^1\text{H}$  NMR in  $\text{CDCl}_3$ : 8.73 (s, 1H,  $\beta$ -pyrrole-H), 8.70 (s, 2H,  $\beta$ -pyrrole-H), 8.64 (d, 1H,  $J = 7.5$  Hz,  $\beta$ -pyrrole-H), 8.60 (d, 1H,  $J = 7.5$  Hz,  $\beta$ -pyrrole-H), 8.49 (s, 1H,  $\beta$ -pyrrole-H), 8.19 (m, 4H, *meso-o*-Ph-H), 7.86 (m, 4H, *meso-o*-Ph-H), 7.76 (m, 6H, *meso-m* & *p*-Ph-H), 7.31 (m, 6H, *meso-m* & *p*-Ph-H), 7.19 (m, 4H,  $\beta$ -Ph-H), 7.09 (m, 6H,  $\beta$ -Ph-H),  $-2.43$  (s, 1H, NH),  $-2.53$  (s, 1H, NH).  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ : 142.7, 142.2, 140.5, 140.2, 138.3, 136.1, 135.8, 134.7, 134.6, 134.5, 130.3, 127.7, 127.3, 127.2, 127.1, 126.8, 126.7, 126.6, 126.1, 125.8, 125.8, 121.5, 121.1, 119.9, 119.6. HR ESI-MS calcd. for  $\text{C}_{56}\text{H}_{38}\text{N}_4$   $[\text{M}+\text{H}]^+$ : 767.3176 (found 767.3175). Elemental analysis calcd. for  $\text{C}_{56}\text{H}_{38}\text{N}_4 \cdot 0.5\text{H}_2\text{O}$ : C, 86.68; H, 5.07; N, 7.22%. Found: C, 86.26; H, 4.57; N, 7.05%.  **$\text{ZnTPP}(\text{Ph})_2$** :  $^1\text{H}$  NMR in  $\text{CDCl}_3$ : 8.89 (s, 1H,  $\beta$ -pyrrole-H), 8.81 (m, 3H,  $\beta$ -pyrrole-H), 8.77 (d, 1H,  $\beta$ -pyrrole-H), 8.67 (s, 1H,  $\beta$ -pyrrole-H), 8.23 (m, 4H, *meso-o*-Ph-H), 7.87 (m, 4H, *meso-o*-Ph-H), 7.70 (m, 6H, *meso-m* and *p*-Ph-H), 7.35 (m, 4H, *meso-m* and *p*-Ph-H), 7.20 (m, 4H,  $\beta$ -Ph-H), 7.13 (m, 6H,  $\beta$ -Ph-H). HR ESI-MS calcd. for  $\text{ZnC}_{56}\text{H}_{36}\text{N}_4$   $[\text{M}+\text{H}]^+$ : 829.2310 (found 829.2325).

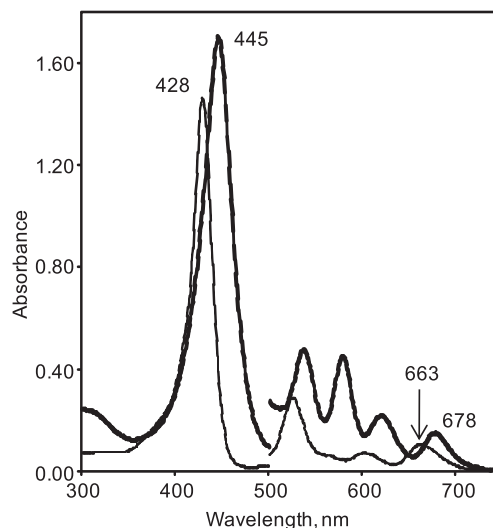
## 3. Results and Discussion

### 3.1 Synthesis and characterisation

A mixture of antipodal  $\text{H}_2\text{TPPBr}_2$  and  $\text{H}_2\text{TPPBr}_3$  were prepared in moderate yields of 30% and 40% respectively, using controlled amount of N-bromosuccinimide (2.8 equivalent) with  $\text{H}_2\text{TPP}$  in  $\text{CHCl}_3$  at an ambient temperature using the reported procedure.<sup>22</sup> A direct synthesis of  $\text{MTPPR}_3$  (R =  $\text{CH}_3$ , Ph, 2-thienyl and PE) from  $\text{H}_2\text{TPPBr}_3$  was achieved using appropriate C-C coupling reaction. The Suzuki cross-coupling reaction of  $\text{H}_2\text{TPPBr}_3$  with methylboronic acid and phenylboronic acid was carried out using slightly modified procedure<sup>20</sup> which yielded corresponding  $\text{H}_2\text{TPP}(\text{CH}_3)_3$  and  $\text{H}_2\text{TPP}(\text{Ph})_3$  in 45% and 85%, respectively. Previous synthesis of  $\text{H}_2\text{TPP}(\text{CH}_3)_3$

was reported using Heck reaction of  $\text{H}_2\text{TPPBr}_4$ .<sup>42</sup> Similarly, synthesis of  $\text{H}_2\text{TPP}(2\text{-thienyl})_3$  was reported as a minor side product of the Stille coupling reaction of  $\text{H}_2\text{TPPBr}_4$  with  $(\text{Bu})_3\text{Sn}(2\text{-thienyl})$ .<sup>21</sup> Here the  $\text{H}_2\text{TPP}(\text{PE})_3$  (yield, 77%) and  $\text{H}_2\text{TPP}(2\text{-thienyl})_3$  (yield, 66%) were selectively prepared by Stille coupling reaction of  $(\text{Bu})_3\text{Sn}(\text{R})$  (R = PE and 2-thienyl) with  $\text{H}_2\text{TPPBr}_3$  as the precursor using modified reported procedure.<sup>21</sup> The corresponding metal (Cu(II) and Zn(II)) complexes of  $\text{MTPP}(\text{X})_4\text{s}$  were isolated in almost quantitative yields using conventional procedures. The Suzuki cross-coupling reaction of dibromo- $\text{H}_2\text{TPP}$  with phenylboronic acid yielded mostly one isomer 2,5,10,12,15,20-hexaphenylporphyrin as the product. Its Zn(II)-complex was prepared by conventional procedures. All the synthesised porphyrins were characterized by electronic absorption,  $^1\text{H}$  NMR spectroscopy and mass spectrometry.

Electronic absorption spectra of  $\text{H}_2\text{TPPBr}_3$  and its Stille coupled product,  $\text{H}_2\text{TPP}(\text{PE})_3$  are shown in figure 2. The absorption spectral data of all the synthesised porphyrins are listed in table 1. For comparison, the data of  $\text{H}_2\text{TPPBr}_3$  are also listed in the table 1. Generally, all the free-base derivatives showed a 'B' band and four visible 'Q' bands. Among the porphyrins examined,  $\text{H}_2\text{TPP}(\text{PE})_3$  showed the highest red-shift in both B and Q bands relative to other free-base porphyrins. The magnitude of the red-shift in longest wavelength ( $\text{Q}_x(0,0)$ ) is  $\sim 12$  nm and B band is  $\sim 8$  nm per PE group relative to  $\text{H}_2\text{TPP}(\text{CH}_3)_3$ . This is possibly due to conjugation of PE groups with the porphyrin  $\pi$ -system. Similar behaviour was reported for  $\text{H}_2\text{TPP}(\text{CHO})(\text{PE})_2$ <sup>25</sup> and  $\text{H}_2\text{TPP}(\text{PE})_8$ <sup>27</sup> derivatives.



**Figure 2.** Optical absorption spectra of  $\text{H}_2\text{TPP}(\text{PE})_3$  (heavy line) and  $\text{H}_2\text{TPPBr}_3$  (thin line) in  $\text{CH}_2\text{Cl}_2$  at 298 K. The intensity of Q bands are magnified by three times.

**Table 1.** Electronic absorption spectral data<sup>a</sup> of H<sub>2</sub>TPP(R)<sub>3</sub> and their metal complexes in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

Porphyrin	B band, nm	Q bands, nm
H <sub>2</sub> TPPBr <sub>3</sub>	428 (5.44)	525 (4.27), 602 (3.57), 663 (3.75)
H <sub>2</sub> TPP(CH <sub>3</sub> ) <sub>3</sub>	333 (4.36), 419 (5.59)	518 (4.31), 547 (sh), 587 (3.84), 641 (3.66)
H <sub>2</sub> TPP(Ph) <sub>3</sub>	429 (5.42)	525 (4.19), 561 (3.85), 598 (3.75), 662 (3.45)
H <sub>2</sub> TPP(2'-thienyl) <sub>3</sub>	436 (5.30)	532 (4.24), 564 (sh), 607 (3.70), 680 (3.66)
H <sub>2</sub> TPP(PE) <sub>3</sub>	445 (5.34)	537 (4.32), 579 (4.29), 620 (3.96), 678 (3.81)
H <sub>2</sub> TPP(Ph) <sub>2</sub>	425 (5.47)	522 (4.25), 557 (3.90), 596 (3.78), 652 (3.51)
CuTPP(CH <sub>3</sub> ) <sub>3</sub>	417 (5.53),	541 (4.20), 575 (sh)
CuTPP(Ph) <sub>3</sub>	425 (5.54)	549 (4.30), 584 (sh)
CuTPP(2'-thienyl) <sub>3</sub>	429 (5.45)	556 (4.31), 592 (4.02)
CuTPP(PE) <sub>3</sub>	445 (5.41)	531 (3.98), 565 (4.32), 611 (4.51)
ZnTPP(CH <sub>3</sub> ) <sub>3</sub>	345 (4.24), 420 (5.67)	549 (4.30), 581 (sh)
ZnTPP(Ph) <sub>3</sub>	355 (4.23), 428 (5.49)	555 (4.23), 601 (sh)
ZnTPP(2'-thienyl) <sub>3</sub>	435 (5.46)	561 (4.30), 597 (3.93)
ZnTPP(PE) <sub>3</sub>	450 (5.44)	536 (3.98), 573 (4.32), 617 (4.51)
ZnTPP(Ph) <sub>2</sub> <sup>b</sup>	426 (100)	553 (6.0), 590 (sh)

<sup>a</sup>values in parentheses refers to log  $\epsilon$ <sup>b</sup>values in parentheses indicates normalized absorbance.

Interestingly, the extent of red-shift in both 'B' and longest wavelength (Q<sub>x</sub> (0,0)) band in H<sub>2</sub>TPP(X)<sub>3</sub>s depend on the nature of the substituent 'X' and follow the general trend: CH<sub>3</sub> < Ph ~ Br < 2-thienyl < PE. Moreover, the red-shift of the 'B' and 'Q' bands increase with an increase in the number of phenyl, thienyl, CH<sub>3</sub> and PE groups. The metal complexes revealed a decrease in the number of absorption bands relative to their free-base porphyrins.<sup>43</sup> All the free-base porphyrins and their metal complexes exhibited comparable molar absorption coefficients relative to their corresponding MTPP(X)<sub>4</sub> (X = CH<sub>3</sub>, Br, 2-thienyl and Ph) derivatives.<sup>16,21,30</sup>

A comparison of <sup>1</sup>H NMR data of H<sub>2</sub>TPPX<sub>3</sub> with other substituted porphyrins showed interesting features. H<sub>2</sub>TPP(CH<sub>3</sub>)<sub>3</sub> feature two independent singlets at 2.45 ppm (6 protons) and 2.60 ppm (3 protons) for CH<sub>3</sub> groups while a singlet at 2.39 ppm was reported for H<sub>2</sub>TPP(CH<sub>3</sub>)<sub>4</sub> in CDCl<sub>3</sub>.<sup>44</sup> It is of interest to note that the proton adjacent to 'X' in one of the  $\beta$ -pyrrole show a downfielded resonance for X = 2-thienyl or PE while it was an upfield signal for X = CH<sub>3</sub> or Ph. The imino protons in H<sub>2</sub>TPP(CH<sub>3</sub>)<sub>3</sub> showed two singlets (−2.67 ppm and −2.94 ppm) while only one singlet was reported for H<sub>2</sub>TPP(Ph)<sub>3</sub> (−2.23 ppm), H<sub>2</sub>TPP(2-thienyl)<sub>3</sub> (−2.21 ppm) and H<sub>2</sub>TPP(PE)<sub>3</sub> (−2.64 ppm) derivatives. The observed <sup>1</sup>H NMR spectral data is consistent with the reported H<sub>2</sub>TPP(X)<sub>3</sub> (X = CH<sub>3</sub>, Ph

and 2-thienyl) derivatives.<sup>21,22,42</sup> Zn(II)-porphyrins featured slightly down-fielded resonances relative to their corresponding free base porphyrins.<sup>44</sup>

MTPP(Ph)<sub>2</sub> (M = 2H, and Zn(II)) showed blue-shifted electronic absorption bands relative to the corresponding MTPP(R)<sub>3</sub> derivatives (table 1). <sup>1</sup>H NMR of H<sub>2</sub>TPP(Ph)<sub>2</sub> shows less number of downfielded proton resonances relative to H<sub>2</sub>TPP(Ph)<sub>3</sub> in CDCl<sub>3</sub> at 298 K. The H<sub>2</sub>TPP(Ph)<sub>2</sub> shows proton resonances of the phenyls upto 7.07 ppm while H<sub>2</sub>TPP(Ph)<sub>3</sub> shows resonances upfielded to a value of 6.8 ppm. Imino protons of H<sub>2</sub>TPP(Ph)<sub>3</sub> and H<sub>2</sub>TPP(Ph)<sub>2</sub> appear as one singlet and two singlets, respectively. The complexity of the proton resonances are more for the phenyls in H<sub>2</sub>TPP(Ph)<sub>3</sub> relative to H<sub>2</sub>TPP(Ph)<sub>2</sub> and this is perhaps due to the decrease in symmetry of the former than the latter. The ZnTPP(Ph)<sub>2</sub> shows marginal change in <sup>1</sup>H NMR relative to its free base porphyrin. <sup>1</sup>H NMR spectra of H<sub>2</sub>TPP(X)<sub>4</sub> (X = Ph, Br and CH<sub>3</sub>) derivatives exhibited singlet for the antipodal  $\beta$ -pyrrole protons.<sup>16,30,42</sup>

### 3.2 Crystal structure of ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub>, **1** complex

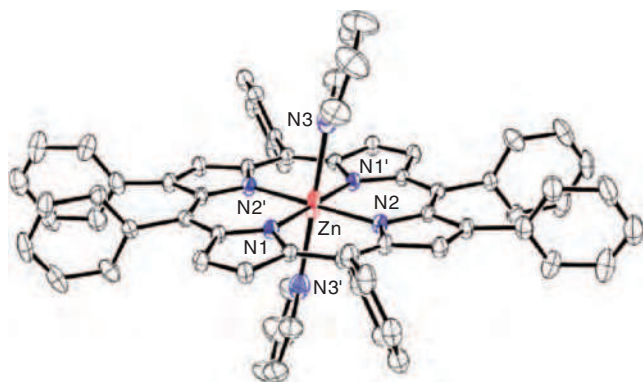
To determine the distribution of the two phenyl groups at the  $\beta$ -pyrrole positions of the ZnTPP(Ph)<sub>2</sub>, its structure **1** was determined by single crystal XRD analysis. Crystallographic data of the complex, **1** is listed in

**Table 2.** Crystallographic data of ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub>, **1**.

Structure	<b>1</b>
Chemical formula	C <sub>66</sub> H <sub>46</sub> N <sub>6</sub> Zn
Formula weight	988.46
Crystal system	P-1
Space group	Triclinic
a (Å)	9.6100(19)
b (Å)	11.400(2)
c (Å)	11.750(2)
α (°)	93.51(3)
β (°)	103.50(3)
γ (°)	96.66(3)
Volume (Å <sup>3</sup> )	1238.0(4)
Z	1
D <sub>calcd.</sub> (g/cm <sup>3</sup> )	1.326
F 000	514
Crystal size (mm <sup>3</sup> )	0.29 × 0.24 × 0.20
θ range (°)	2.23–26.43
Reflections collected	13445
Independent reflections	4239
GOF on F <sup>2</sup>	0.997
R <sub>1</sub> [I > 2σ(I)]	0.0865
wR <sub>2</sub> [I > 2σ(I)]	0.2315
Residual (e Å <sup>-3</sup> )	−0.723–1.159

table 2. The molecule crystallizes in triclinic P-1 with half the porphyrin unit and a coordinated pyridine in the asymmetric unit. The unit cell has one porphyrin unit (Z = 1). Molecular structure of the complex is shown in figure 3. It can be seen that the Zn(II)-centre shows unusual six-coordination geometry having two axially coordinated pyridines with planar macrocycle. The stereochemistry of the 24-atom core is comparable to six-coordinated ZnTPP(THF)<sub>2</sub> complex.<sup>45</sup>

The structure **1** is compared with the reported six-coordinated ZnTPP(THF)<sub>2</sub>,<sup>45</sup> **2** to determine the influence of coordination and porphyrin macrocycle on the



**Figure 3.** ORTEP of ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub> complex (thermal ellipsoids at 30% probability level). Hydrogens are not shown for clarity. Selected atoms are labelled for clarity. Colour scheme: C, black; N, blue and Zn, red.

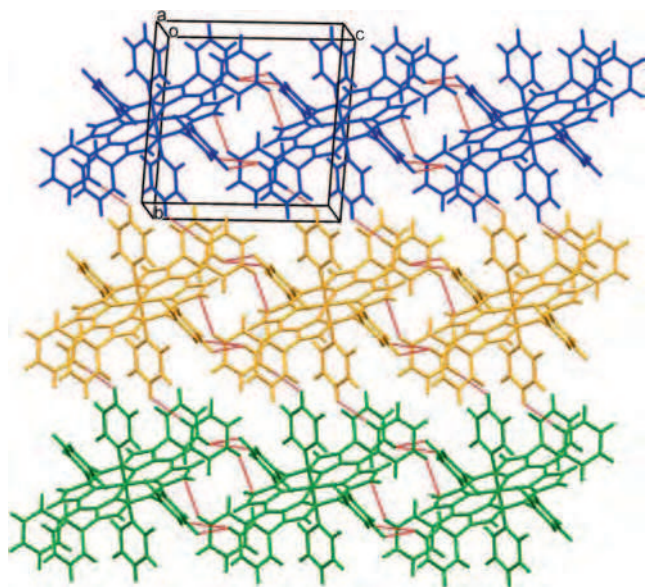
**Table 3.** Some selected mean bond lengths and geometrical parameters of six-coordinated Zn(II)-porphyrin structures.

	ZnTPP(Ph) <sub>2</sub> (Py) <sub>2</sub> , <b>1</b>	ZnTPP(THF) <sub>2</sub> , <b>2</b>
Bond distance (Å)		
Zn–N	2.055(6)	2.057(1)
Zn–X <sub>axial</sub>	2.459(5)	2.380(2)
C <sub>b</sub> –C <sub>b</sub>	1.355(9)	1.349(3)
N–C <sub>a</sub>	1.377(9)	1.371(3)
C <sub>a</sub> –C <sub>m</sub>	1.397(8)	1.403(4)
Angle (°)		
C <sub>a</sub> –N–C <sub>a</sub>	106.9(4)	107.0(2)
N–C <sub>a</sub> –C <sub>m</sub>	125.3(6)	125.8(3)
N–C <sub>a</sub> –C <sub>b</sub>	109.3(6)	109.3(4)
C <sub>a</sub> –C <sub>b</sub> –C <sub>b</sub>	107.3(5)	107.2(1)
C <sub>a</sub> –C <sub>m</sub> –C <sub>a</sub>	126.6(6)	125.0(2)
ΔZn(II), (Å)	± 0.060(3)	–
r.m.s. (Å)	0.031(5)	–
Mean dihedral angle (°)		
Meso-phenyl	76.4(5)	63.2
Pyrrole	1.9(2)	–

<sup>a</sup>from ref.<sup>45</sup>. Δ (Zn(II)), deviation of Zn(II) ion from porphyrin mean plane; r.m.s. refers to average deviation of the 24-atoms core from their least-squares plane.

selected mean bond lengths and geometrical parameters in these complexes (table 3). The (Zn–N<sub>por</sub>)<sub>av</sub> for the substituted pyrrole in ZnTPP(Ph)<sub>2</sub>(Py)<sub>2</sub> is almost similar to ZnTPP(THF)<sub>2</sub> but marginally longer than four-coordinated ZnTPP (2.036(6) Å).<sup>46</sup> As anticipated, the axially bonded two pyridine nitrogens are fairly longer Zn–N<sub>py</sub> in **1** than Zn–O<sub>thf</sub> in **2**. Similar distances are reported for the five-coordinated ZnTPP(Ph)<sub>4</sub>(Py) complex (2.239(8) Å)<sup>47</sup> and other Zn(II)-porphyrins.<sup>23,28,48</sup> The Zn(II) is almost in plane with the four nitrogens in **1** but they are displaced towards the axial ligand in five coordinated structures. The comparison of selected mean bond lengths of pyrrole and the macrocyclic geometric parameters of **1** and **2** are quite similar in these structures. These features are also quite comparable to four coordinated ZnTPP structure.

In the case of structure of **1**, axially coordinated pyridines are in eclipsed configuration relative to each other. Further, the pyridine ring plane is in staggered orientation relative to opposite pyrrolic nitrogens. The angle between the plane of the pyridine ring relative to the porphyrin ring mean plane is 71.4°. Moreover, the



**Figure 4.** Molecular packing diagram of **1** showing the layer-like structure oriented parallel to unit cell 'bc' plane. One-dimensional chains aligned parallel to unit cell 'c' axis are shown in different colours. The inter-porphyrin short contacts are indicated in dotted red lines.

$N_{py}$  of the axial pyridines are not exactly perpendicular but  $Zn-N_{py}$  makes a tilt angle of  $5.6^\circ$  relative to the porphyrin mean plane. The mean  $N_{py}\dots N_{por}$  (pair of nitrogens N1 and N2) distance is shorter ( $3.082 \text{ \AA}$ ) when compared to the distance of  $3.321 \text{ \AA}$  for the nitrogens (N1' and N2') from the opposite side of the porphyrin ring plane (figure 3). The pyrrole rings in **1** are almost planar within  $0.02 \text{ \AA}$ .

The molecular packing may be visualized as one-dimensional array of porphyrins oriented along unit cell 'c' axis. In the array, the interporphyrin interactions<sup>49</sup> are dominated by weak  $C-H\dots\pi$  [(Ph)C-H...C(Ph), (Ph)C-H... $\pi$ (pyr)] with short contact distances in the range  $2.86\text{--}2.89 \text{ \AA}$  and dihydrogen (Ph)H...H(Ph) ( $2.30 \text{ \AA}$ ).<sup>50,51</sup> These one-dimensional arrays are interacting *via* dihydrogen (H...H) short contacts ( $2.30 \text{ \AA}$ ) to form a layer-like structure (figure 4) oriented parallel to unit cell 'bc' plane. Further, layers are held by weak inter-porphyrin (Ph)C-H... $\pi$ (Ph) and (Pyr)C-H... $\pi$ (Ph) short contacts in the range  $2.76\text{--}2.83 \text{ \AA}$  and stack on each other, along the unit cell 'a' axis to form three dimensional packing.

Normal-coordinate structural decomposition analysis<sup>52</sup> of the macrocycle was performed to delineate the magnitude of in-plane and out-of-plane deformations in **1** and it showed essentially very *negligible* distortion as evidenced from minimum basis set for the out-of-plane displacement,  $D_{oop}$  ( $0.184 \text{ \AA}$ ). The *wave* ( $E_g(x)$ ,  $53.6\%$  and  $E_g(y)$ ,  $46.1\%$ ) deformations contribute mostly to the distortion of the macrocycle.

Furthermore, a small in-plane displacement ( $D_{ip} = 0.2307 \text{ \AA}$ ) value was observed with contributions from  $B_{2g}$  (*m-str*,  $4\%$ ),  $B_{1g}$  (*N-str*,  $23.6\%$ ),  $A_{1g}$  (*bre*,  $60\%$ ) and  $A_{2g}$  (*rot*,  $12.6\%$ ) deformations. Similar trend in distortion of the macrocycle was reported for the planar porphyrin ring in  $ZnTPP(R)_4$  ( $R = Ph$  and 2-thienyl).<sup>21,47</sup>

#### 4. Conclusions

Synthesis and characterization of some  $\beta$ -tri-substituted *meso*-tetraphenylporphyrins and their metal complexes have been reported. The MTPP(PE)<sub>3</sub>s showed more red-shift in both B and Q transitions when compared to other trisubstituted porphyrins examined in this study. The synthesis and crystal structure of the  $ZnTPP(Ph)_2(Py)_2$  complex was carried out and it revealed six coordination geometry around the Zn(II) ion. The Zn(II) ion is situated almost in-plane with the porphyrin ring. The normal-coordinate structural decomposition analysis of **1** shows mainly a very small *wave* type of deformation of the porphyrin macrocycle.

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