

## Synthesis and crystal structure of 5-(4'-carboxyphenyl)-10,15,20-tri(4'-*t*-butylphenyl)porphinato zinc(II) complex

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**Abstract.** Synthesis and crystal structure of 5-(4'-carboxyphenyl)-10,15,20-tri(4'-*t*-butylphenyl)porphinato zinc(II) have been presented. The title complex shows interesting hydrogen-bonded dimeric structure in the solid state.

**Keywords.** Metalloporphyrins; hydrogen-bonding; self-assembly; crystal structure; carboxy porphyrins.

### 1. Introduction

Substituted porphyrins are of considerable importance owing to their use as model compounds of various tetrapyrrole pigments of nature.<sup>1–3</sup> These porphyrins are of increasing interest for their possible material applications<sup>4</sup> and also for their unique physico-chemical properties.<sup>5,6</sup> 5,10,15,20-Tetraphenylporphyrin (H<sub>2</sub>TPP) and its phenyl-substituted derivatives are widely explored systems due to their ease of synthesis and facile functionalisation. The introduction of substituents at the *b*-pyrrole positions greatly alters the properties of the porphyrin *p*-system relative to that observed for meso-phenyl-substituted TPPs.<sup>7</sup> Numerous reports are available on the synthesis and properties of functionalised porphyrins and metalloporphyrins.<sup>1</sup>

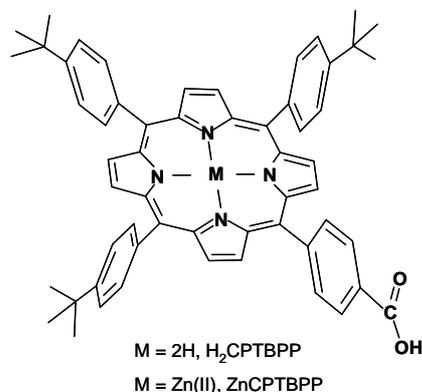
In recent years, many functionalised meso-tetraphenylporphyrins have been employed in material applications.<sup>4</sup> Notably, various meso-phenyl-substituted MTTPs were used in the construction of supra-molecular network solids.<sup>4</sup> Such solid-state networks are formed via intermolecular interactions arising from peripheral functional groups. Among the various porphyrinic network solids, the hydrogen-bonded carboxy groups and metal-bridged systems show high thermal stability.<sup>8–10</sup> Such robust network solids have been employed in shape-selective sorption of amines in heterogeneous media.<sup>8</sup> Further, the substituted porphyrin self-assemblies have been used as versatile models for light-harvesting antenna chlorophylls.<sup>11,12</sup>

In this article, we present the synthesis of a mono-carboxy tetraarylporphinato zinc(II) complex (figure 1) and its crystal structure. The complex shows interesting dimeric self-assembly through complementary hydrogen-bonding between the peripheral carboxy groups.

### 2. Experimental

#### 2.1 Materials

5-(4'-Carboxymethylesterphenyl)-10,15,20-tri(4'-*t*-butylphenyl)porphyrin (H<sub>2</sub>CMeTBPP) was synthesised using the reported procedure.<sup>13,14</sup> Pyrrole, 4-methylformyl benzoate and 4-*t*-butylbenzaldehyde were procured from Aldrich (USA) and used as received. Zinc(II) acetate dihydrate and potassium hydroxide procured from CDH (India) were also used as received. Silica gel (100–200 mesh) for column



**Figure 1.** Molecular structure of mono-*p*-carboxytetra-arylporphyrins.

Dedicated to the memory of the late Professor Bhaskar G Maiya

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chromatography was purchased from Acmes (India) and used as received, while the solvents dichloromethane, chloroform and tetrahydrofuran (THF) obtained from Sisco Research Labs (India) were refluxed and distilled over CaH<sub>2</sub>.

## 2.2 Instrumentation

Electronic absorption spectra of porphyrins were recorded on a Jasco V-550 UV–Vis absorption spectrophotometer using matched quartz cells of 1 cm path length at ambient temperature. <sup>1</sup>H NMR spectra of samples were performed on a Bruker 400 MHz FT-NMR spectrometer in CDCl<sub>3</sub> using tetramethylsilane as the internal standard at 298 K. Crystal structure data collection of the 5-(4'-carboxy phenyl)-10,15,20-tri(4'-*t*-butylphenyl)porphinato zinc(II) (ZnCPTBPP) complex was performed on a Bruker SMART CCD diffractometer with a Mo K<sub>α</sub> (0.71073 Å), *T* = 223 K. Mass spectra of the samples were recorded on a Voyager-DE™ PRO Biospectrometry instrument using *α*-cyano-4-hydroxycinnamic acid.

## 2.3 Synthesis of 5-(4'-carboxyphenyl)-10,15,20-tri(4'-*t*-butylphenyl)porphyrin (H<sub>2</sub>CPTBPP)

Aqueous KOH (20%) in THF (10 ml) was added to a THF (5 ml) solution containing 0.110 g of H<sub>2</sub>CmeTBPP and the resulting solution was refluxed for 36 h. At the end of this period, the solvent was evaporated to dryness. The residue was then taken in water (10 ml) and filtered to obtain a purple-coloured residue. The residue was treated with 10 ml of dilute aq. HCl (5%) followed by aq. saturated NaHCO<sub>3</sub> solution. It was then dissolved in 2% THF in CHCl<sub>3</sub> and the solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. It was then concentrated and chromatographed on a silica gel column using THF/CHCl<sub>3</sub> (1:9, v/v) as the eluant. The product was dried under vacuum (0.01 torr) at 120°C; the yield of the product was 0.093 g (91%). Electronic absorption spectral data in THF: *I*<sub>max</sub>, nm (log *e*): 420 (5.76), 515 (4.39), 550 (4.17), 593 (3.90), 650 (3.90). <sup>1</sup>H NMR in CDCl<sub>3</sub>: *d*<sub>H</sub> in ppm (400 MHz, TMS): 8.82 (*m*, 8H, pyrrole-H), 8.51 (*d*, 2H, carboxyphenyl-H<sub>o</sub>), 8.35 (*d*, 2H, carboxyphenyl-H<sub>m</sub>), 8.16 (*d*, 6H, 4'-*t*-butylphenyl-H<sub>o</sub>), 7.77 (*d*, 6H, 4'-*t*-butylphenyl-H<sub>m</sub>), 1.55 (*s*, 27H, 4'-*t*-butyl-H), -2.65 (*s*, 2H, NH-H). MALDI-TOF spectrum (*m/z*): 827.28 (calcd., 827.08). Elemental analysis: Calcd., for C<sub>57</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub> - C, 82.78; H, 6.58; N, 6.77%. Found: C, 82.51; H, 6.52; N, 6.55%.

The Zn(II)-complex of the porphyrin, H<sub>2</sub>CPTBPP, was prepared using conventional procedure.<sup>15</sup> Electronic absorption spectral data of ZnCPTBPP in THF: *I*<sub>max</sub>, nm (log *e*): 425 (5.66), 557 (4.27), 597 (3.95). <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>: *d*<sub>H</sub> (400 MHz, TMS): 13.26 (*bs*, 1H, carboxylic acid-H), 8.77 (*m*, 8H, pyrrole-H), 8.36 (*d*, 2H, carboxyphenyl-H<sub>o</sub>), 8.30 (*d*, 2H, carboxyphenyl-H<sub>m</sub>), 8.12 (*d*, 6H, 4'-*t*-butylphenyl-H<sub>o</sub>), 7.82 (*d*, 6H, 4'-*t*-butylphenyl-H<sub>m</sub>), 1.58 (*s*, 27H, 4'-*t*-butyl-H). MALDI-TOF spectrum (*m/z*): 890.97 (calcd. 890.45).

## 2.4 Methods

2.4a *Crystal structure of ZnCPTBPP (THF)·0.5 cyclohexane complex*: C<sub>64</sub>H<sub>66</sub>N<sub>4</sub>O<sub>3</sub>Zn, *M<sub>r</sub>* = 1004.58. Crystal dimensions: 0.35 × 0.35 × 0.18 mm<sup>3</sup>, purple, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.1723(8) Å, *b* = 17.0218(11) Å, *c* = 25.9807(17) Å, *g* = 90°, *b* = 97.243(2)°, *g* = 90°, *V* = 5778.8(6) Å<sup>3</sup>, *Z* = 4, *r*<sub>calcd</sub> = 1.155 Mg/m<sup>3</sup>, *F*(000) = 2128. Diffractometer: Bruker Smart CCD diffractometer with Mo K<sub>α</sub> (0.71073 Å), *T* = 223 K. Data collection [*2θ* = 50°, range of *hkl*: *h* = -15 to 14, *k* = -14 to 20, *l* = -30 to 30. Number of reflections collected, 31983, 10184 independent reflections (*R* = 0.0759), Refinement on *F*<sup>2</sup> with the results *R*1 = 0.0840, *wR*2 = 0.2412. The program SMART<sup>16</sup> was used for collecting frames of data, indexing reflection and determination of lattice parameters, and program SAINT<sup>16</sup> for integration of the intensity of reflections and scaling. SADABS<sup>16</sup> was used for absorption correction and SHELXL<sup>17</sup> for space group and structure determination and least-squares refinements on *F*<sup>2</sup>. The Fourier difference routine indicated the presence of 0.5 molecule of cyclohexane in the lattice.

## 3. Results and discussion

In an effort to determine the role of the carboxy group at the periphery of the porphyrin in the molecular self-assembly, we have examined the crystal structure of monocarboxyporphyrin, ZnCPTBPP complex. The precursor monocarboxyester porphyrin was prepared using the reported procedure and its deesterified carboxy porphyrin H<sub>2</sub>CPTBPP derivative was obtained by base hydrolysis. The Zn(II)-complex, ZnCPTBPP, was prepared by conventional metallation procedures<sup>15</sup>. The synthesised porphyrins were characterised by UV–Vis, <sup>1</sup>H NMR, and mass spectroscopy and also by elemental analysis. Monocarboxy porphyrins, MCPTBPP (*M* = 2H, Zn(II)) were examined

for their self-assembly in the solid state. These porphyrins are moderately soluble in halogenated solvents and highly soluble in polar solvents (DMSO, THF, DMF).

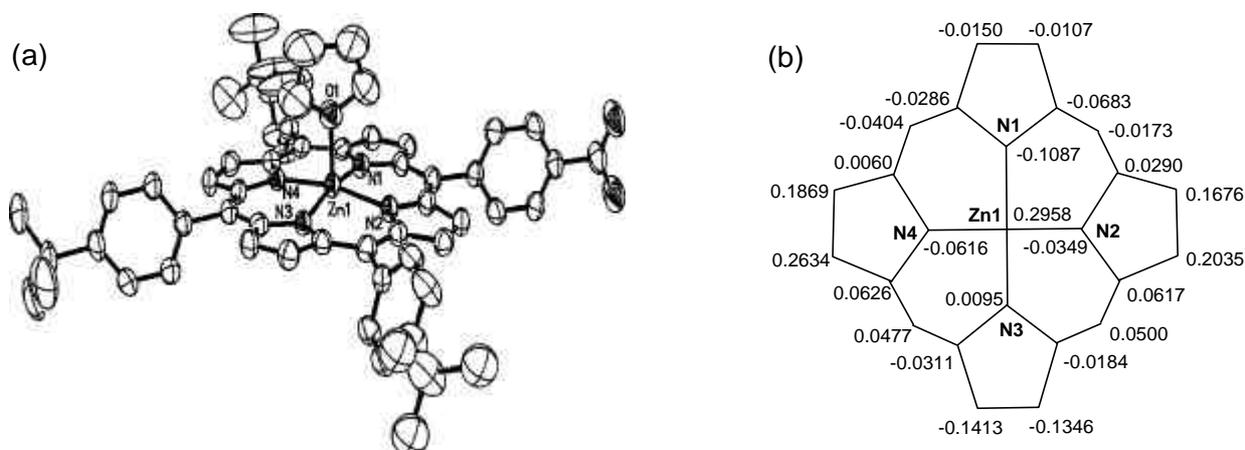
Free-base carboxymethylester ( $\text{H}_2\text{CMePTBPP}$ ) and its carboxy derivative ( $\text{H}_2\text{CPTBPP}$ ) exhibit typical four-banded visible and a Soret band with marginal red-shift in their absorption spectral bands relative to that observed for  $\text{H}_2\text{TPP}$ .<sup>18</sup>  $^1\text{H}$  NMR spectral features of  $\text{H}_2\text{CPTBPP}$  show resonances arising from meso-phenyl, *p-t*-butyl, *b*-pyrrole protons and imino hydrogens, while its Zn(II)-complex shows absence of imino hydrogen resonances. The integrated intensities of the resonances are in conformity with the expected structures.

Crystals of the  $\text{ZnCPTBPP}$  complex were grown by slow diffusion of cyclohexane solvent to a porphyrin solution in THF over a period of three days. The unit cell has four porphyrin units with five-coordination around the Zn(II)-centre. The ORTEP diagram of the complex is shown in figure 2a. The selected bond lengths and angles of the complex are shown in table 1. For comparison, the data of six-coordinated ( $\text{ZnTPP}(\text{THF})_2$ )<sup>19</sup> and four-coordinated ( $\text{ZnTPP}$ )<sup>20</sup> complexes are also incorporated in table 1. The average Zn–N distance (2.052(4) Å) in  $\text{ZnCPTBPP}(\text{THF})$  is relatively higher than that reported for four coordinated  $\text{ZnTPP}$  (2.037(2) Å) and is quite similar to that found for  $\text{ZnTPP}(\text{THF})_2$  complexes (2.057(4) Å). In the  $\text{ZnCPTBPP}(\text{THF})$  complex, the Zn(II) ion is situated 0.2958 Å above the four nitrogen atoms which is quite common for five-coordinated Zn(II)-

porphyrins.<sup>21</sup> In the case of six-coordinate  $\text{ZnTPPs}$ , the Zn(II) ion lies almost in the plane of the four nitrogen atoms.<sup>21–23</sup> The fifth ligand, THF shows a short Zn–O bond length of 2.151(4) Å relative to that reported for the  $\text{ZnTPP}(\text{THF})_2$  complex (2.380(2) Å) and 2.1643(2) Å for the  $\text{ZnTPPBr}_4(\text{THF})$ <sup>24</sup> complex. The bound-THF solvate shows envelope confirmation as observed in case of the  $\text{ZnTPP}(\text{THF})_2$  or  $\text{ZnTPPBr}_4(\text{THF})$  complexes.

The average N–Zn–O1 angle is found to be 96.89 (20)° showing some 6.89° deviation from the plane of the porphyrin core. Upon examination, the Zn–N4 core shows significant variation from 180° for N1–Zn1–N3 and N2–Zn1–N4 angles (av. 166.17(19)°) a value of 88–90° for the N1–Zn1–N2 and N3–Zn1–N4 angles. An examination of the deviation of core atoms from the mean plane formed by the 24-atom macrocyclic ring shows interesting core-conformational features. The displacement of atoms from the mean plane is shown in figure 2b. The opposite pyrrole rings show up and down displacement from the mean plane with a maximum deviation of 0.26 Å of the *b*-pyrrole carbon. The average displacement of *b*-pyrrole carbons from the mean plane formed by the 24 atom core is  $\pm 0.017$  Å. The displacement of the *b*-pyrrole carbons and meso-carbons from planarity suggest saddle-like geometry of the porphyrin ring and such conformational features are known for very sterically crowded porphyrins.<sup>7</sup>

Interestingly, the porphyrins exhibit dimeric self-assembly (figure 3) through hydrogen-bonding interactions and are aligned almost parallel to the unit cell

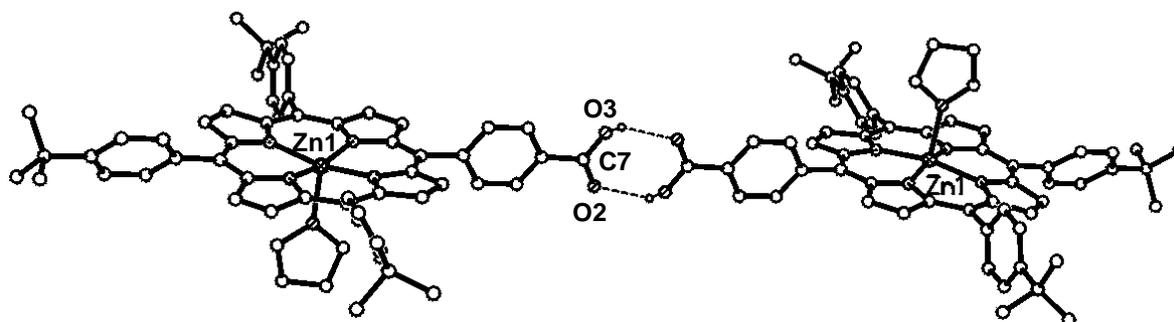


**Figure 2.** (a) ORTEP diagram of the  $\text{ZnCPTBPP}(\text{THF})\cdot 0.5$  cyclohexane complex (thermal ellipsoids at 50% probability level). Hydrogen atoms are not shown for clarity. (b) The mean plane deviation (in Å) of atoms from the mean plane formed by the 24-atom core. Only the core zinc and the nitrogen atoms are labelled for clarity.

**Table 1.** Selected geometric parameters for ZnCPTBPP(THF)·0.5 cyclohexane complex.

	ZnCPTBPP(THF)· 0.5 cyclohexane	ZnTPP(THF) <sub>2</sub> <sup>a</sup>	ZnTPP <sup>a</sup>
<i>Distances (Å)</i>			
(Zn–N) <sub>average</sub>	2.052(4)	2.057(2)	2.037(2)
Zn–O(THF)	2.151(4)	2.380(2)	–
Zn(II)-to-meso carbon	3.405(3)	–	3.447(2)
<i>Angles (°)</i>			
(N–Zn1–O1) <sub>average</sub>	96.89(18)	86.95(1)	–
<i>Dihedral angles (°)</i>			
Phenyl-to-core <sup>b</sup>	71.29(25)	72.0	62.0

<sup>a</sup>Data for ZnTPP(THF)<sub>2</sub> and ZnTPP structures were taken from references [19] and [20] respectively; <sup>b</sup>dihedral angle is defined with respect to the porphyrin 24-atom core

**Figure 3.** Dimeric self-assembled structure of ZnCPTBPP(THF)·0.5 cyclohexane complex. Only the core Zn(II) ion and the carboxylic group are labelled for clarity.

*a*-axis. The hydrogen-bonding distance (O...O) between the oxygens of the carboxylic acid moieties is found to be 2.628 Å indicating fairly strong intermolecular hydrogen-bonding between the porphyrins through the *p*-carboxy groups (figure 3). The observed hydrogen-bonding distance is quite similar to that reported for carboxy-bridged porphyrinic-network solids.<sup>25</sup> Hydrogen-bonded dimers are oriented in a slipped-stack orientation with vertical separation between the porphyrin plane being about 4.871 Å. The meso-phenyl groups in the ZnCPTBPP(THF) complex are more perpendicular to the porphyrin core relative to that observed for ZnTPP and are similar to that reported for ZnTPP(THF)<sub>2</sub> or ZnTPPBr<sub>4</sub>(THF) complexes. Further, hydrogen-bonded dimeric porphyrins show no significant interactions with adjacent dimers, since the close contact between the molecules in the lattice is greater than 3.45 Å.

#### 4. Summary

Synthesis and characterization of *p*-monocarboxy-porphyrin has been reported. *p*-Carboxy-substituted ZnCPTBPP shows five-coordination geometry with interesting dimeric structure in the solid state through molecular self-assembly. These carboxy-functionalised porphyrins may serve as versatile building blocks for the construction of molecular self-assemblies.

*Supplementary material:* Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 253385. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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