



# Quantitative crystal structure analysis of fluorinated porphyrins



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## ABSTRACT

Herein, we report a series of fluorinated porphyrins, 5,10,15,20-tetrakis(2',6'-difluorophenyl)porphyrin, MT(2',6'-DFP)P where M = 2H, **1**; Co(II)·(MeOH)<sub>2</sub>, **2**; Cu(II), **3**; Zn(II)·(MeOH)<sub>2</sub>, **4** and Zn(II)·(THF)<sub>3</sub>, **5** have been structurally characterized by single crystal X-ray diffraction analysis. All the compounds are crystallized in monoclinic crystal system and the crystal structures of **2**, **4** and **5** features octahedral geometry whereas **3** exhibits square planar geometry. The compounds **1**, **3** and **2**, **4** are isostructural, show similar molecular crystal packing and comparable intermolecular interactions. The supramolecular self assembly of compounds **1–5** is dominated by a variety of intermolecular interactions such as C–H···F, C–H···π, C–F···π and F···F. Furthermore, the role of weak intermolecular interactions in the crystal packing has been analysed and quantified using Hirshfeld surface analysis.

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## 1. Introduction

The well-known definition of crystal engineering is quoted by Desiraju as “the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in design of new solids with desired physical and chemical properties” [1]. Intermolecular interactions in organic/inorganic compounds play an important role in the crystal packing of molecules which attracts intense attention in various research fields including supramolecular chemistry [2–4]. Such interactions involving fluorine are of mainly three kinds, namely C–F···H, F···F and C–F···π which provides stability to form molecular self-assemblies especially in the absence of strong intermolecular forces [5–8]. Even though these individual interactions are energetically weak, the net result may become considerably strong due to the co-operative effect and thus may provide a higher stability to the crystalline lattice. In addition, supramolecular assembly is framed by suitable combination of various types of weak intermolecular interactions like C–H···π and the geometrical preference of the metal ion. Owing to the high electronegativity of fluorine, it renders the C–F bond highly polar and by introducing the fluorine atoms into the organic moieties result in significant changes in the physical properties and biological activities compared with non-fluorinated precursors [9–11]. It is well known that the fluorinated drugs are innumerable and the study of weak intermolecular interactions involving fluorine is essential in the field of medicinal

chemistry. Porphyrins and their metal derivatives have been widely studied due to their distinct spectral, electrochemical properties and novel biological activities. Synthetic porphyrin analogues are considered to be the ligands of choice to mimic natural processes, because of their close resemblance to natural systems in both structure and properties [12]. Study of weak interactions involving halogenated porphyrins offers an emerging field of research in crystal engineering [13]. A diverse range of self-assembly patterns of porphyrin have been discovered, held together by van der Waals interactions, hydrogen bonding, or metal coordination [14–16]. In order to explore the better understanding of intermolecular interactions to the supramolecular assembly, it is crucial to get quantitative measurements of these interactions. Hirshfeld surface analysis [17,18] is becoming a valuable tool for elucidating molecular crystal structures quantitatively and such quantitative measures of weak interactions in porphyrins are poorly documented in the literature [16,19]. In this context, we hereby report the crystal structures and Hirshfeld surface analysis of 5,10,15,20-tetrakis(2',6'-difluorophenyl) porphyrin, H<sub>2</sub>T(2',6'-DFP)P and its metal complexes (Fig. 1). And also, the effect of 2,6-difluorophenyl groups is discussed on the evaluation of intermolecular interactions.

## 2. Experimental

### 2.1. Materials and synthetic procedures

All the chemicals employed here for the synthesis were commercially available reagents of analytical grade and were used without further purification. Solvents used for the synthesis

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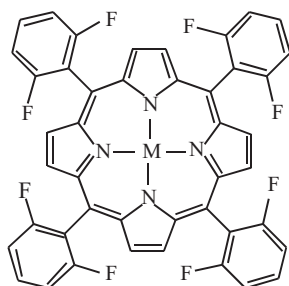
M = 2H, **1**; Co(II), **2**; Cu(II), **3** and Zn(II), **4**

Fig. 1. Molecular structure of porphyrins under study.

were purified using the available literature methods [20]. 5,10,15,20-Tetrakis(2',6'-difluorophenyl) porphyrin, H<sub>2</sub>T(2',6'-DFP)P ligand, **1**, was synthesized using the method reported by Lindsey et al. [21] and the metal complexes were prepared by the literature method [22] to afford the desired complexes yielded in 92–95%.

## 2.2. X-ray structure determination

Crystals of the porphyrin ligand and their metal complexes were grown at room temperature and single crystal X-ray structure data collections were performed on a Bruker AXS Kappa Apex II CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystals were coated with inert oil, mounted on a glass capillary, and crystal data were collected at 298 K. The reflections with  $I > 2\sigma(I)$  were employed for structure solution and refinement. The SIR92 [23] (WINGX32) program was used for solving the structure by direct methods. Successive Fourier synthesis was employed to complete the structures after full-matrix least squares refinement on  $|F|^2$  using the SHELXL97 [24] software. Fourier synthesis led to the location of all of the non-hydrogen atoms. For the structure refinement, all data were used including negative intensities. The criterion of  $F^2 > 2\sigma(F^2)$  was employed for calculating  $R_1$ .  $R$  factors based on  $F^2$  ( $wR_2$ ) are statistically about twice as large as those based on  $F$ , and  $R$  factors

based on all data will be even larger. Non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms in the porphyrin structure could be located in the difference map. However, the hydrogen atoms were geometrically relocated at chemically meaningful positions and were given riding model refinement. Single crystal X-ray diffraction data of **1–5** was collected by the selection of appropriate suitable single crystals which are formed by the vapour diffusion method using appropriate solvent systems (Table 1).

## 2.3. Hirshfeld surface analysis

Hirshfeld surfaces (HSs) and 2D fingerprint plots (FPs) were generated using *Crystal Explorer 3.1* [25] based on results of single crystal X-ray diffraction studies. The function  $d_{\text{norm}}$  is a ratio encompassing the distances of any surface point to the nearest interior ( $d_i$ ) and exterior ( $d_e$ ) atom and the van der Waals radii of the atoms [26–28]. The negative value of  $d_{\text{norm}}$  indicates the sum of  $d_i$  and  $d_e$  is shorter than the sum of the relevant van der Waals radii, which is considered to be a closest contact and is visualized as red colour in the HSs. The white colour denotes intermolecular distances close to van der Waals contacts with  $d_{\text{norm}}$  equal to zero whereas contacts longer than the sum of van der Waals radii with positive  $d_{\text{norm}}$  values are coloured with blue. A plot of  $d_i$  versus  $d_e$  is a 2D fingerprint plot which recognizes the existence of different types of intermolecular interactions.

## 3. Results and discussion

Synthesis of fluorinated porphyrins, 5,10,15,20-tetrakis(2',6'-difluorophenyl)porphyrin, MT(2',6'-DFP)P where M = 2H, **1**; Co(II)·(MeOH)<sub>2</sub>, **2**; Cu(II), **3**; Zn(II)·(MeOH)<sub>2</sub>, **4** and Zn(II)·(THF)<sub>3</sub>, **5** is reported and are structurally characterized by single crystal X-ray diffraction analysis. All the compounds are crystallized in monoclinic system with half a molecule in the asymmetric unit with space groups,  $P2_1/c$ ,  $P2_1/n$ ,  $P2_1/c$ ,  $P2_1/n$  and  $C2/c$ , respectively, for **1–5** (Table 1). The ORTEP and molecular crystal packing diagrams for compounds **1–5** are shown in Fig. 2. The compounds **1, 3** and **2, 4** are isostructural with a similar crystal packing pattern and the former pair crystallized without solvent molecules in the

Table 1

Crystal structure data of porphyrins under study. **1**, H<sub>2</sub>T(2',6'-DFP)P; **2**, CoT(2',6'-DFP)P·2(MeOH); **3**, CuT(2',6'-DFP)P; **4**, ZnT(2',6'-DFP)P·2(MeOH); **5**, ZnT(2',6'-DFP)P·3(THF).

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>44</sub> H <sub>22</sub> F <sub>8</sub> N <sub>4</sub>	C <sub>46</sub> H <sub>28</sub> CoF <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>44</sub> H <sub>20</sub> CuF <sub>8</sub> N <sub>4</sub>	C <sub>46</sub> H <sub>28</sub> ZnF <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>56</sub> H <sub>44</sub> ZnF <sub>8</sub> N <sub>4</sub> O <sub>3</sub>
fw	758.66	879.65	820.18	886.09	1038.32
Colour	Purple	Pink	Red	Red	Red
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$C2/c$
$a$ (Å)	12.5342(10)	12.426(5)	12.5477(7)	12.4217(18)	20.671(5)
$b$ (Å)	11.4384(9)	12.723(5)	11.3955(6)	12.529(2)	12.397(5)
$c$ (Å)	12.1720(10)	12.709(5)	12.1642(7)	12.6954(18)	20.865(5)
$\alpha$ (deg)	90.0	90.000(5)	90.0	90.0	90.000(5)
$\beta$ (deg)	97.080(3)	114.615(5)	96.391	114.092(17)	108.486(5)
$\gamma$ (deg)	90.0	90.000(5)	90.0	90.0	90.000(5)
Volume (Å <sup>3</sup> )	1731.8(2)	1826.7(13)	1728.52(17)	1803.7(5)	5071(3)
$Z$	2	2	2	2	4
$D_{\text{calcd}}$ (mg/m <sup>3</sup> )	1.455	1.599	1.576	1.632	1.360
Wavelength ( $\lambda$ ) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
$T$ (K)	293(2)	293(2)	293(2)	173(2)	293(2)
No. of unique reflections	2690	3583	5329	3165	3068
No. of parameters refined	258	278	259	351	328
GOF on $F^2$	1.026	1.055	1.013	1.059	0.996
$R_1^a$	0.0359	0.0488	0.0372	0.0766	0.0741
$wR_2^b$	0.0818	0.1445	0.0944	0.1685	0.1954

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $I_o > 2\sigma(I_o)$ .

<sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

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