

## **Location controlled symmetry reduction: Paradigm of Open Metalloporphyrin framework based on tetracarboxy porphyrin linker**

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## 1. Experimental Section

### 1.1. Materials and methods:

Unless otherwise specified all the chemicals were received as analytical grade reagents and used without further purification. 4-carboxydipyrromethane was prepared according to the literature procedure.<sup>1</sup> All reactions requiring anhydrous conditions were conducted under an atmosphere of argon in oven-dried glassware in dry solvents. Thin layer chromatography (TLC) was performed on silica gel plates Merck 60 F<sub>254</sub>. Flash column chromatography was carried out using alumina.

#### 1.1.1. Synthesis of 5,15-Bis(4'-carbomethoxyphenyl)-10,20-bis(3'-carbomethoxyphenyl) porphyrin (H<sub>4</sub>-TpmCPP):

To 500.0 ml of DCM in round bottomed flask, 3-carboxy benzaldehyde (0.30 g, 2.0 mmol,) and 4-carboxy dipyrromethane (0.56 g, 2.0 mmol) were added and degassed with N<sub>2</sub> for 10 min. To the resultant mixture TFA (0.30 ml, 4.04 mmol) was added slowly through syringe under inert atmosphere. The reaction mixture was stirred for two hours at room temperature and followed by the addition of the DDQ (0.448 g, 2.0 mmol) and continued to stir for another one hour. The final reaction mixture and washed thoroughly with solution of saturated NaHCO<sub>3</sub> and the organic phase was extracted by (3 X 100 mL) aliquots of DCM, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. Purification by column chromatography (Al<sub>2</sub>O<sub>3</sub>, DCM/PE, 1:1) gives the desired trans porphyrin in 30% yield. The metallation of the porphyrin ester with Zn(OAc)<sub>2</sub> followed by hydrolysis gives the Zn-H<sub>4</sub>-TpmCPP in quantitative yield.

#### 1.1.2. Synthesis of Gd-TpmCMPF:

To the solution of Zn-H<sub>4</sub>TpmCPP (2.6 mg, 3.0 μmol) in 300.0 μL DMF, a solution of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (6.8 mg, 20.0 μmol) in 100.0 μL of 1M HNO<sub>3</sub> was added and sealed in a screw cap vial followed by heating at 120°C in a bath reactor. After formation of a clear supernatant solution and pink precipitate, 275.0 μL of 1N NaOH was added to reaction mixture at same temperature and sonicated a while to obtain purple colored turbid solution. The resultant solution was then heated at the same temperature for 7-10 days to obtain a block shaped crystal of Gd-TpmCMPF and white precipitates. The crystals were separated by filtration, washed with DMF, acetone and water for several times to remove the white precipitates and air dried for further

characterizations. Yield: ~20 %. FTIR ( $\text{cm}^{-1}$ ): 3325, 2954, 2750, 2420, 1660, 1425, 1332, 1205, 1070, 980, 752.  $\lambda_{\text{em}}/\text{nm}$  (THF): 652, 716.

## 1.2. Physical measurements:

Solution state emission spectra were measured on Horiba Jobin Yvon FL3-11 spectrofluorometer at room temperature. Solid state emission was recorded through spin coating of the crystalline Gd-TpmCMPF in toluene solutions on a glass slide. The experiments were done on Horiba scientific FluorEssence spectrophotometer by placing the LnMPF-1 coated glass slide at  $0^\circ$  to the detector. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 system spectrophotometer in ATR mode. Powder X-ray diffraction (PXRD) data were recorded on Bruker D8 Advance diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) over a  $2\theta$  range of  $5\text{--}50^\circ$  at a scan rate of  $1^\circ \text{ min}^{-1}$ . Thermogravimetric analyses (TGA) were carried out on an STA 409 PC analyzer, and corresponding masses were analyzed by a QMS 403 C mass analyzer, under a flow of  $\text{N}_2$  gas with a heating rate of  $5^\circ \text{C min}^{-1}$  in the temperature range of  $40\text{--}600^\circ \text{C}$ .

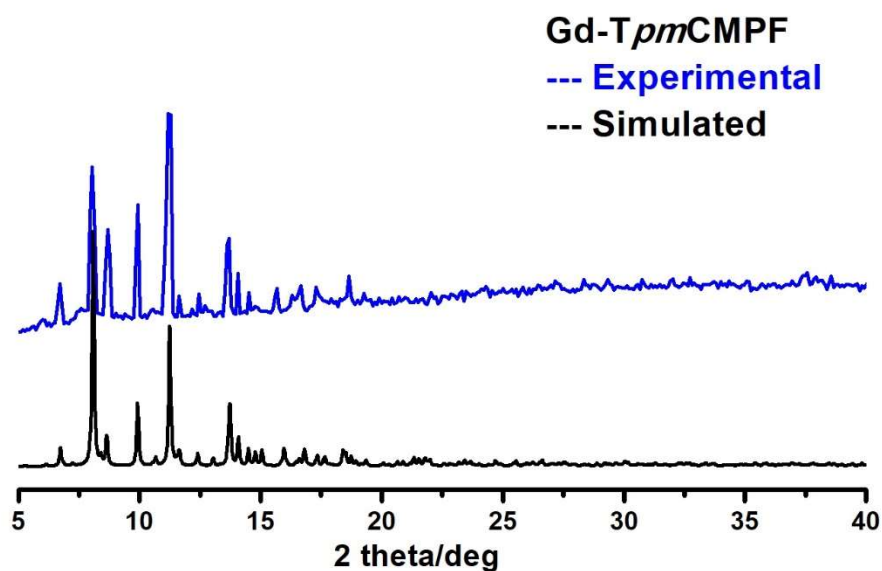
Single crystal X-ray diffraction (SCXRD) measurements [Bruker-Apex Duo diffractometer,  $\text{I}\mu\text{S}$  micro-focus  $\text{MoK}\alpha$  radiation] were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil. These structures were solved by direct and Fourier methods and refined by full-matrix least-squares (using standard crystallographic software (SHELXT-2014, SHELXL-2014)).<sup>2,3</sup> They were found to contain severely disordered crystallization solvents (usually an unknown combination of DMF and water) and dimethyl ammonium cations the dissociation products of the DMF solvent (hydrolyzed in the solvothermal conditions) within the intra-lattice voids. The solvent content could not be reliably identified and modeled by discrete atoms. Correspondingly, the contribution of the disordered solvent moieties and cations was subtracted from the diffraction pattern by the SQUEEZE procedure and PLATON software.<sup>4</sup> Due to the loose crystal packing in these compounds and the large amounts of disordered solvents contained therein they diffracted to low  $\theta$ -angles only. Due to the geometrical asymmetry of coordination groups observed in the employed linker the components of crystal structure were severely disordered, hence poor data was observed. The solvent accessible voids in all the structure is  $2823 \text{ \AA}^3$  (approximately 55% of the crystal volume with residual electron count of 796 e). Topological analysis was carried out by TOPOS software package was used to analyze the topological features

of the available framework solids.<sup>5</sup> Analysis of the coordination geometries around the metal centers was performed by using the SHAPE 2.1 program.<sup>6</sup>

**Crystal Data** for C<sub>49</sub>H<sub>25</sub>GdN<sub>4</sub>O<sub>10</sub>Zn (Framework only, *M<sub>r</sub>* = 1052.35 g/mol): monoclinic, space group P2/n (no. 13), *a* = 17.903(3) Å, *b* = 16.7851(16) Å, *c* = 21.149(2) Å, *β* = 96.467(4)°, *V* = 6315.0(13) Å<sup>3</sup>, *Z* = 4, *T* = 110(2) K, *μ*(MoKα) = 1.466 mm<sup>-1</sup>, *ρ<sub>calc</sub>* = 1.107 g/cm<sup>3</sup>, 26408 reflections measured (3.336° ≤ 2θ ≤ 46.76°), 9115 unique (*R<sub>int</sub>* = 0.0623, *R<sub>sigma</sub>* = 0.0951) which were used in all calculations. The final *R*<sub>1</sub> was 0.0892 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.2851 (all data).

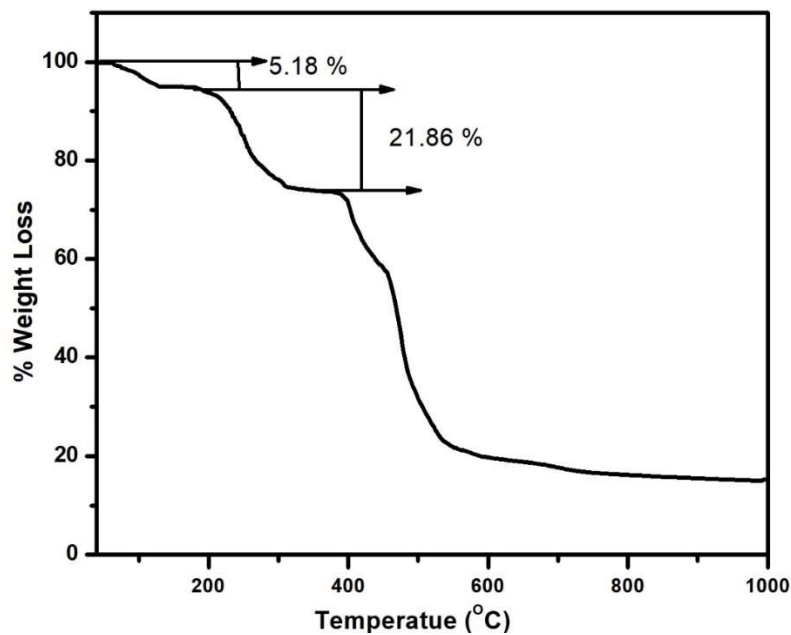
## 2. PXRD analyses

To ensure the phase purity of the compound presented in this study, X-ray diffraction patterns of powder sample have been recorded. The diffraction patterns for the simulated data (calculated from single crystal data) are matched with the observed data, which proves the bulk homogeneity of the crystalline solids. The experimental patterns have a few un-indexed diffraction peaks, and some peaks are slightly broadened and shifted in comparison to those simulated patterns. These slight differences between the experimental and calculated ones presumably stem from inadequate modelling of the solvent molecules.



**Fig.S1.** PXRD pattern of compound Gd-TpmCMPF

### 3. Thermogravimetric analysis (TGA):

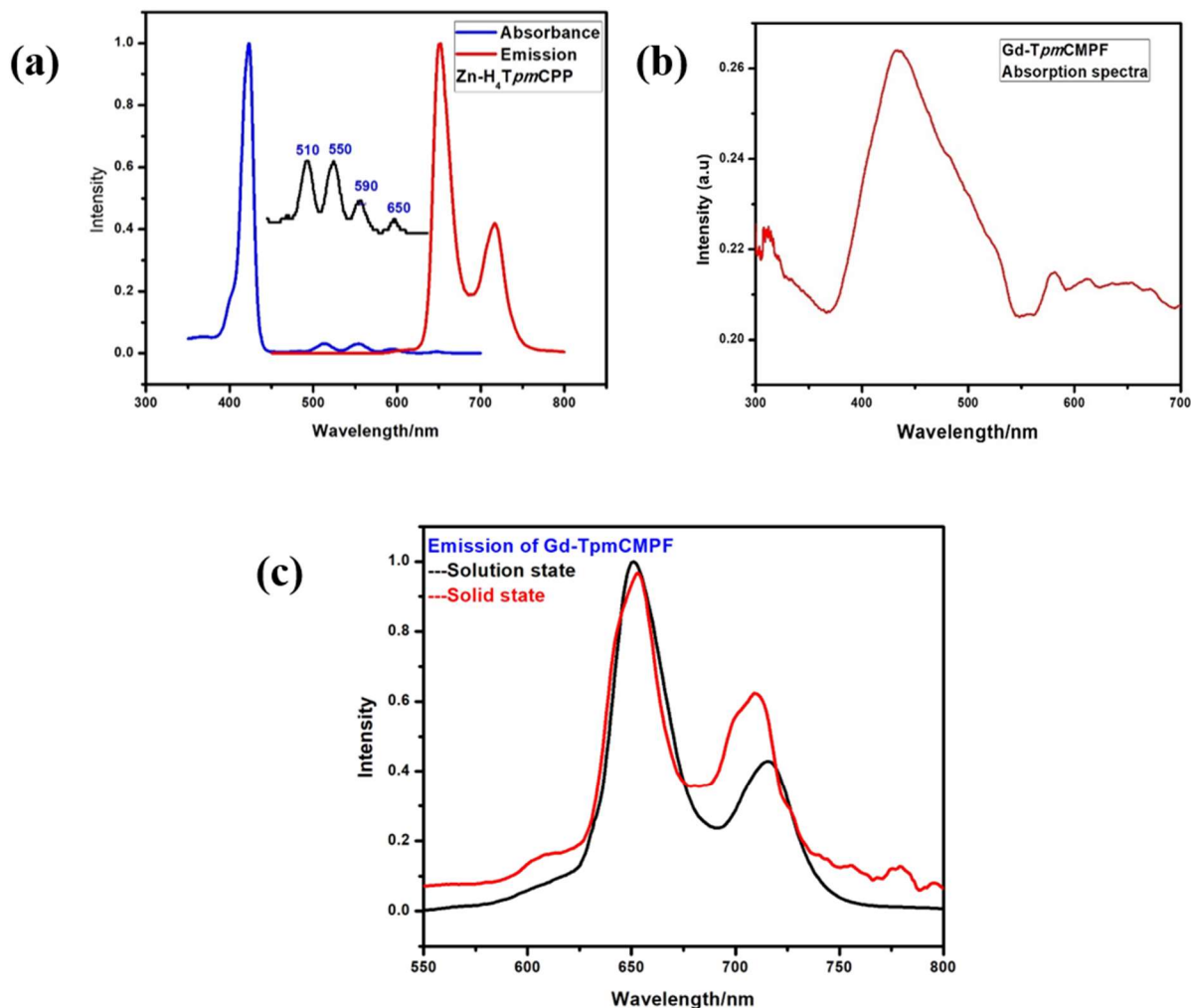


**Fig.S2.** Thermogravimetric curve of compound Gd-*TpmCMPF*

**Table S1:** Calculation of solvent molecules based on squeezed electrons and TGA

Squeezed electrons	Z	Squeezed electrons per Molecular formula	Estimated DMA cations	Estimated DMF	Estimated H <sub>2</sub> O	% Wt Loss from TGA till 350°C	Plausible Molecular formula
796	4	796/4=199	3 9.8 %	2 10.36%	4 5.11%	27.04 % (Experimental) 25.27% (Theoretical)	[Gd-(μ <sub>2</sub> -HCOO){Zn-(μ <sub>2</sub> -HCOO)( <i>TpmCPP</i> )}] .3MeNH <sub>2</sub> ·2DMF·4H <sub>2</sub> O

## 4. Optical Studies



**Fig. S3.** (a) Solution state absorption and emission spectra of Zn-H<sub>4</sub>TpmCPP (b) Solution state absorption spectra of Gd-TpmCMPF (c) Solid state and solution state emission spectra of the framework Gd-TpmCMPF

The solution state absorption and emission spectra of linker Zn-H<sub>4</sub>TpmCPP was shown in figure S3a. The absorption spectra of the linker Zn-H<sub>4</sub>TpmCPP displays sharp Soret band at 422 nm and four weak bands located at 510, 550, 590 and 650 nm. The emission spectra of Zn-H<sub>4</sub>TpmCPP after excitation at 422 nm shows two bands 650 [Q(0,0)] and 715 [Q(0,1)]. The solution state absorption spectra of the framework Gd-TpmCMPF displays strong broad absorption peak

centered at 435 nm and weak bands located in the region 550 to 650 nm (figure S3b). A slight blue shift of Soret band was observed for the framework compared to the linker. The emission spectra of the framework were recorded in both solid and solution by exciting the sample at 435 nm. As shown in figure S3c the emission spectra shows only the peaks related to the porphyrin building blocks due to their strong absorption in the UV region, whereas it does not contain any peaks related to the Gd(III) center. The emission of the Gd(III) centers located above the triplet of the organic linkers hence the emissions of this metal center cannot be observed.<sup>7</sup> Both solid and solution state emission spectra of the framework show similar peaks with slight shift from the linker as shown in the table S2. It appears that the optical properties of the linker remain intact even after its incorporation into the framework.

**Table S2.** Details of emission peaks of the linker and framework

Solution state emission spectra of linker		Solution state emission spectra of the framework		Solid state emission spectra of the framework	
<b>Q(0,0)</b>	<b>Q(0,1)</b>	<b>Q(0,0)</b>	<b>Q(0,1)</b>	<b>Q(0,0)</b>	<b>Q(0,1)</b>
650	715	651	716	653	710

## 5. Summary of SHAPE analysis for Gd(III) center in complex Gd-TpmCMPF.

**Table S3.** Various probable shapes / geometries for *coordination number 9*:

Vertices	Code	Label	Shape	Symmetry
9	1	EP-9	Enneagon	$D_{9h}$
	2	OPY-9	Octagonal pyramid	$C_{8v}$
	3	HBPY-9	Heptagonal bipyramid	$D_{7h}$
	4	JTC-9	Triangular cupola (J3) = trivacant cuboctahedron	$C_{3v}$
	5	JCCU-9	Capped cube (Elongated square pyramid, J8)	$C_{4v}$
	6	CCU-9	Capped cube	$C_{4v}$
	7	JCSAPR-9	Capped sq. antiprism (Gyroelongated square pyramid J10)	$C_{4v}$
	8	CSAPR-9	Spherical Capped square antiprism	$C_{4v}$
	9	JTCTPR-9	Tricapped trigonal prism (J51)	$D_{3h}$
	10	TCTPR-9	Spherical Tricapped trigonal prism	$D_{3h}$
	11	JTDIC-9	Tridiminished icosahedron (J63)	$C_{3v}$
	12	HH-9	Hula-hoop	$C_{2v}$
	13	MFF-9	Muffin	$C_s$

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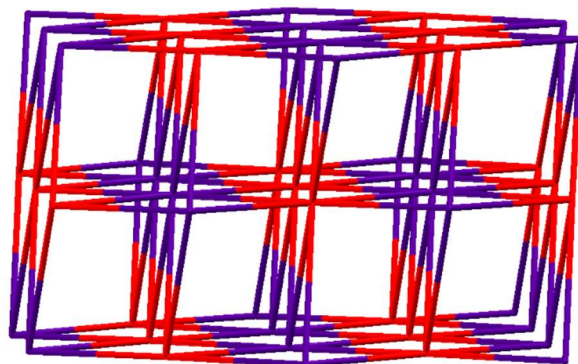
### Complex (Gd)

Structure [ML9 ] EP-9 OPY-9 HBPY-9 JTC-9 JCCU-9 CCU-9 JCSAPR-9  
**CSAPR-9** JTCTPR-9 TCTPR-9 JTDIC-9 HH-9 MFF-9

Gd , 34.861, 19.990, 15.940, 13.861, 7.648, 5.996, 3.896, **2.924**,  
 4.903, 3.395, 10.032, 10.611, 3.493.



## 6. Topological Analysis



**Fig.S4.** Topological representation of Gd-TpmCMPF

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#####
1:C49 H27 Gd N4 O10 Zn/intercluster bonds and atoms at rings>6
#####
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Topology for Sc1

-----  
Atom Sc1 links by bridge ligands and has

Common vertex with	R(A-A)					
Ti 1	-0.2500	0.9421	0.2500	(-1 0 0)	11.507A	1
Ti 1	0.7500	0.9421	0.2500	(0 0 0)	11.507A	1
Ti 1	0.2500	0.0579	-0.2500	(1 1 0)	13.029A	1
Ti 1	0.2500	0.0579	0.7500	(1 1 1)	13.029A	1
Ti 1	-0.2500	-0.0579	0.2500	(-1-1 0)	13.092A	1
Ti 1	0.7500	-0.0579	0.2500	(0-1 0)	13.092A	1
Ti 1	0.2500	1.0579	-0.2500	(1 2 0)	13.999A	1
Ti 1	0.2500	1.0579	0.7500	(1 2 1)	13.999A	1

Topology for Ti1

-----  
Atom Ti1 links by bridge ligands and has

Common vertex with	R(A-A)					
Sc 1	0.2500	0.5113	0.2500	(0 0 0)	11.507A	1
Sc 1	1.2500	0.5113	0.2500	(1 0 0)	11.507A	1
Sc 1	0.7500	0.4887	0.7500	(1 1 1)	13.029A	1
Sc 1	0.7500	0.4887	-0.2500	(1 1 0)	13.029A	1
Sc 1	1.2500	1.5113	0.2500	(1 1 0)	13.092A	1
Sc 1	0.2500	1.5113	0.2500	(0 1 0)	13.092A	1
Sc 1	0.7500	1.4887	0.7500	(1 2 1)	13.999A	1
Sc 1	0.7500	1.4887	-0.2500	(1 2 0)	13.999A	1

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Structural group analysis

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Structural group No 1

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Structure consists of 3D framework with TiSc  
Coordination sequences  
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Sc1: 1 2 3 4 5 6 7 8 9 10  
Num 8 26 56 98 152 218 296 386 488 602  
Cum 9 35 91 189 341 559 855 1241 1729 2331  
-----

Ti1: 1 2 3 4 5 6 7 8 9 10  
Num 8 26 56 98 152 218 296 386 488 602  
Cum 9 35 91 189 341 559 855 1241 1729 2331  
-----

TD10=2331  
Vertex symbols for selected sublattice  
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Sc1 Point symbol: {4<sup>24</sup>.6<sup>4</sup>}  
Extended point symbol:  
[4.4.4.4.4.4.4.4.4.4.4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).6(18).6(18).6(18).6(18)]  
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Ti1 Point symbol: {4<sup>24</sup>.6<sup>4</sup>}  
Extended point symbol:  
[4.4.4.4.4.4.4.4.4.4.4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).6(18).6(18).6(18).6(18)]  
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Point symbol for net: {4<sup>24</sup>.6<sup>4</sup>}  
8-c net; uninodal net  
Topological type: bcu body centered cubic; 8/4/c1; sqc3 (topos&RCSR.ttd) {4<sup>24</sup>.6<sup>4</sup>} - VS  
[4.4.4.4.4.4.4.4.4.4.4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).\*.\*.\*] (76154 types in 11 databases)

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