Supplementary Information

For

Control of the spatial arrangements of supramolecular networks based on saddle-distorted porphyrins by intermolecular hydrogen bonding

Tomoya Ishizuka, Muniappan Sankar and Takahiko Kojima*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Table S1. Crystallographic data for tetrahydroxy-dodecaphenylporphyrins.

compound	**2** [a]	**2**-THF_2 [a]	**2**-bpy-**2** [a]	**3**-bpy-**3** [a]
crystal system	tetragonal	monoclinic	triclinic	monoclinic
space group	$I4_1/a$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
T [K]		120		
formula	$C_{92}H_{60}N_4O_4Zn$ ·0.8$CHCl_3$	$C_{92}H_{60}N_4O_4Zn$ ·5C_4H_8O	$2C_{92}H_{60}N_4O_4Zn$ ·$C_{10}H_8N_2$·4C_4H_8O	$2C_{92}H_{60}N_4Zn$ ·$C_{10}H_8N_2$
FW	1446.30	1711.33	3146.27	2729.80
a [Å]	28.0259(19)	25.353(5)	21.250(8)	17.044(3)
b [Å]	28.0259(19)	11.688(3)	21.596(8)	36.306(6)
c [Å]	10.1867(7)	32.746(7)	22.033(8)	25.196(5)
α [°]	90	90	83.030(5)	90
β [°]	90	112.406(3)	79.946(6)	94.573(3)
γ [°]	90	90	89.807(6)	90
V [Å^3]	8001.2(12)	8970(3)	9881(6)	15541(5)
Z	4	4	2	4
λ (Mo $K\alpha$) [Å]		0.71073		
D_c [g cm^{-3}]	1.182	1.267	1.058	1.167
reflns measured	16393	31563	28400	45728
reflns unique	3812	11428	17931	14508
$R1$ ($I > 2\sigma(I)$)	0.0931	0.0731	0.0794	0.0565
$wR2$ ($I > 2\sigma(I)$)	0.3126	0.2164	0.2184	0.1357
GOF	1.081	1.065	0.925	0.873

[a] CCDC-941987 (**2**), -941988 (**2**-THF_2), -941989 (**2**-bpy-**2**) and -941990 (**3**-bpy-**3**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Summary for bond lengths (Å) and angles (°) for tetrahydroxy-dodecaphenylporphyrins

compound	**2**	**2**-THF_2	**2**-bpy-**2**		**3**-bpy-**3**	
Zn-N1 [Å]	2.024(4)	2.065(4)	2.043(6)	2.080(6)	2.060(5)	2.069(6)
Zn-N2 [Å]	—	2.042(4)	2.085(6)	2.023(6)	2.071(5)	2.042(6)
Zn-N3 [Å]	—	2.064(4)	2.070(6)	2.067(6)	2.055(5)	2.056(6)
Zn-N4 [Å]	—	2.047(4)	2.060(6)	2.042(6)	2.083(5)	2.048(6)
Zn-X_{axial} [Å]	—	2.411(6), 2.317(4)	2.106(6)	2.157(6)	2.161(5)	2.182(6)
N1-C1 [Å]	1.380(6)	1.355(6)	1.358(9)	1.363(9)	1.355(7)	1.383(9)
N1-C4 [Å]	1.369(6)	1.366(6)	1.369(9)	1.370(9)	1.352(7)	1.384(9)
N2-C6 [Å]	—	1.367(6)	1.385(9)	1.407(9)	1.373(7)	1.371(9)
N2-C9 [Å]	—	1.368(6)	1.366(9)	1.377(9)	1.371(7)	1.364(8)
N3-C11 [Å]	—	1.355(6)	1.361(9)	1.370(9)	1.363(7)	1.376(8)
N3-C14 [Å]	—	1.373(6)	1.381(9)	1.366(9)	1.366(7)	1.378(8)
N4-C16 [Å]	—	1.367(6)	1.375(9)	1.360(9)	1.368(7)	1.349(8)
N4-C19 [Å]	—	1.381(6)	1.348(10)	1.384(10)	1.356(7)	1.400(8)
C1-N1-C4 [°]	107.0(4)	107.3(4)	106.6(6)	108.6(6)	107.9(5)	108.2(7)
C6-N2-C9 [°]	—	108.3(4)	106.9(6)	105.1(6)	106.7(5)	107.0(7)
C11-N3-C14 [°]	—	108.4(4)	108.0(6)	107.7(6)	108.1(5)	108.0(6)
C16-N4-C19 [°]	—	107.6(4)	108.2(6)	107.0(6)	108.2(5)	108.9(6)
mean deviation [Å]	0.347	0.546	0.492	0.474	0.470	0.487
P1-P2 [°] [a]	—	—	11.4		13.6	
twist of bpy [°] [b]	—	—	26.7		49.5	
twist of Ps [°] [c]	—	—	7.2		44.2	

[a] Dihedral angles between porphyrin mean planes in dimeric structures. [b] Dihedral angles between two pyridine rings in bpy ligands. [c] Dihedral angles between planes consisting of N1-Zn1-N3 and N5-Zn2-N7 in dimeric structures.

Table S3. Summary for absorption maxima (λ_{max}) and half-height widths of solid-state absorption for **2** and **3**

	Soret band		Q bands					
	λ_{max} [nm]	$\nu_{1/2}$ [cm^{-1}]	$\lambda_{max}1$ [nm]	$\nu_{1/2}$ [cm^{-1}]	$\lambda_{max}2$ [nm]	$\nu_{1/2}$ [cm^{-1}]	λ_{max} [nm]	$\nu_{1/2}$ [cm^{-1}]
2	484	6360	609	4500	678	3060		
2-THF_2	476	3570	595	2010	648	1430		
2-bpy-**2**	479	4350	607	2350	651	2210		
3	459	2270	581	1810	626	720		
3-bpy-**3**	480	2550	602	2030	664	1320	860	2740

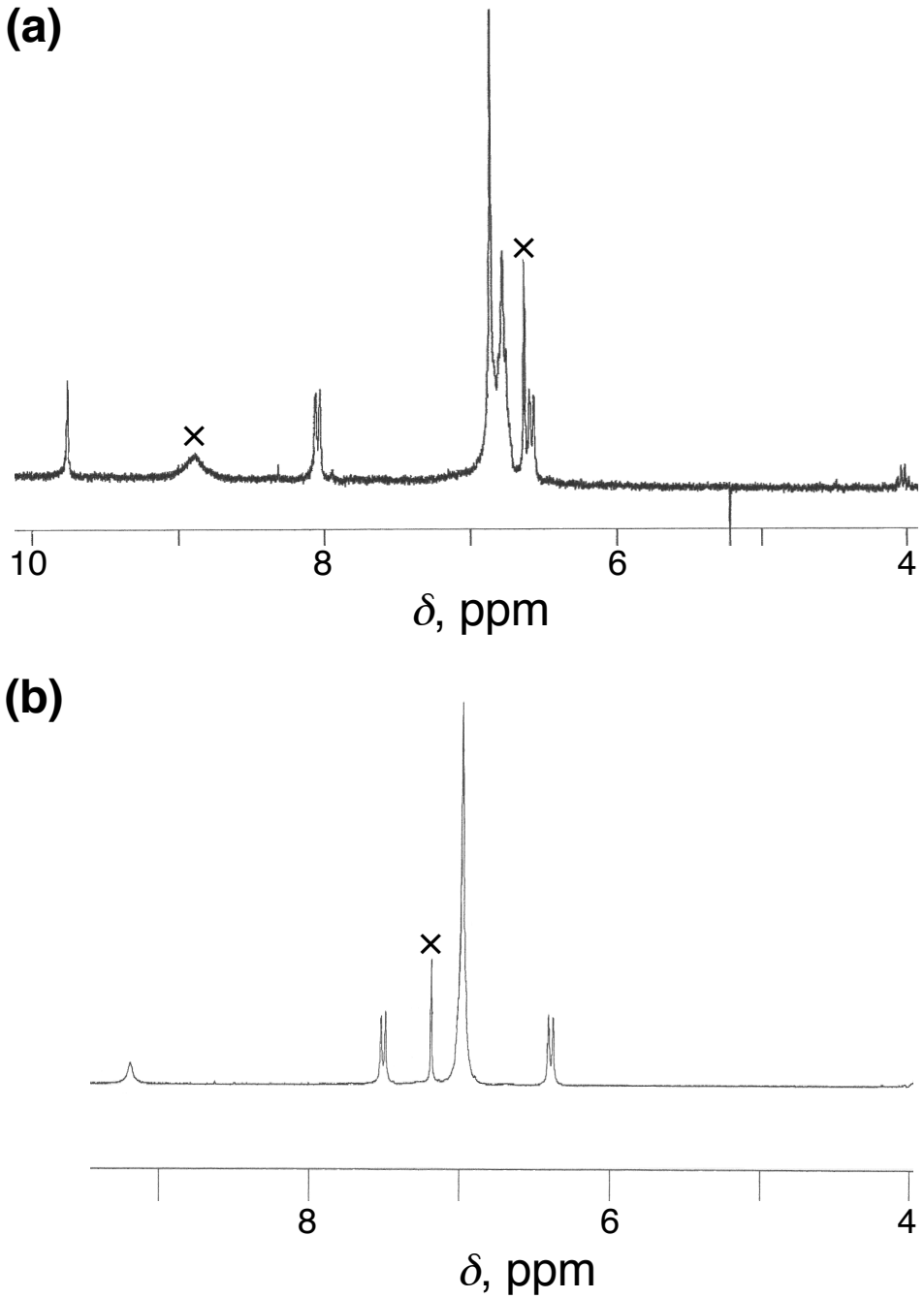

Fig. S1 ^{1}H NMR spectra of **1** (a) and **2** (b) in DMSO-d_6 at room temperature.

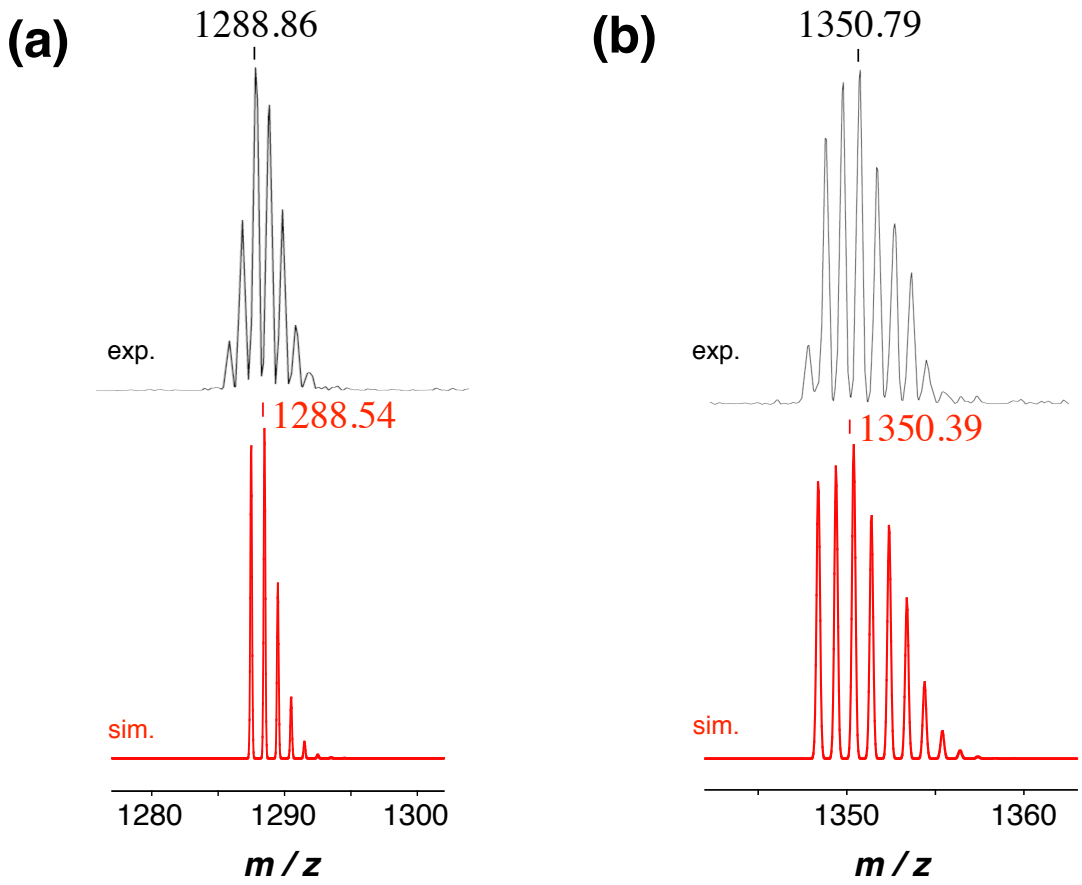

Fig. S2 MALDI-TOF-MS spectra of **1** (a) and **2** (b) using dithranol as a matrix: above: experimental results, below: simulated spectra. The slight differences between the experimental and simulated isotope distribution patterns are probably caused by overlapping of the signals attributable to the species having different protonated numbers in the experimental results.

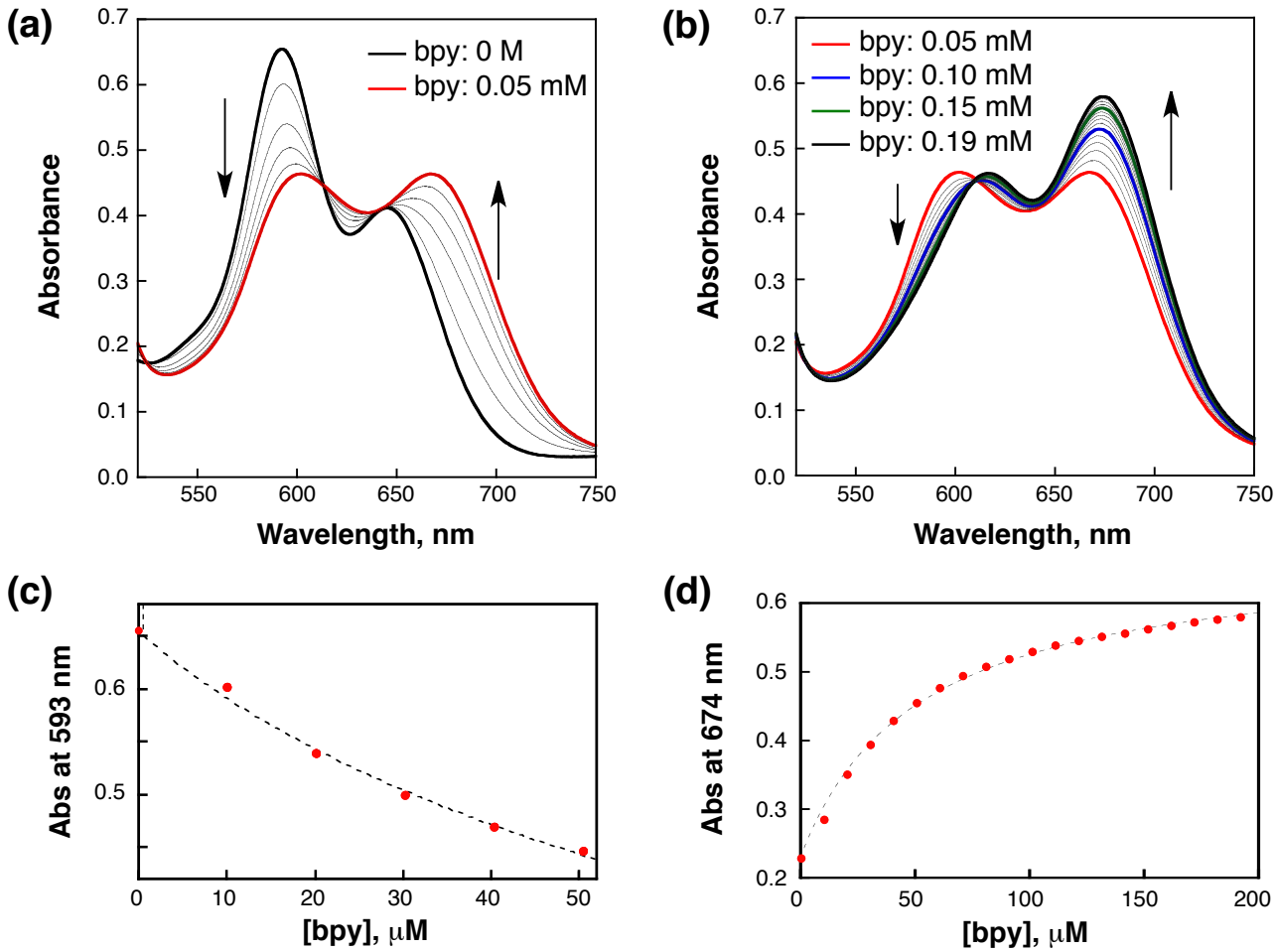

Fig. S3 Spectral Changes of **3** in CH_2Cl_2 at room temperature upon addition of bpy: 0–1 eq (a) and 1–4 eq (b). Plots of the absorbance changes against the concentration of bpy: at 593 nm in the course of 0–1 eq bpy (c) and 674 nm in the course of 0–4 eq bpy (d).

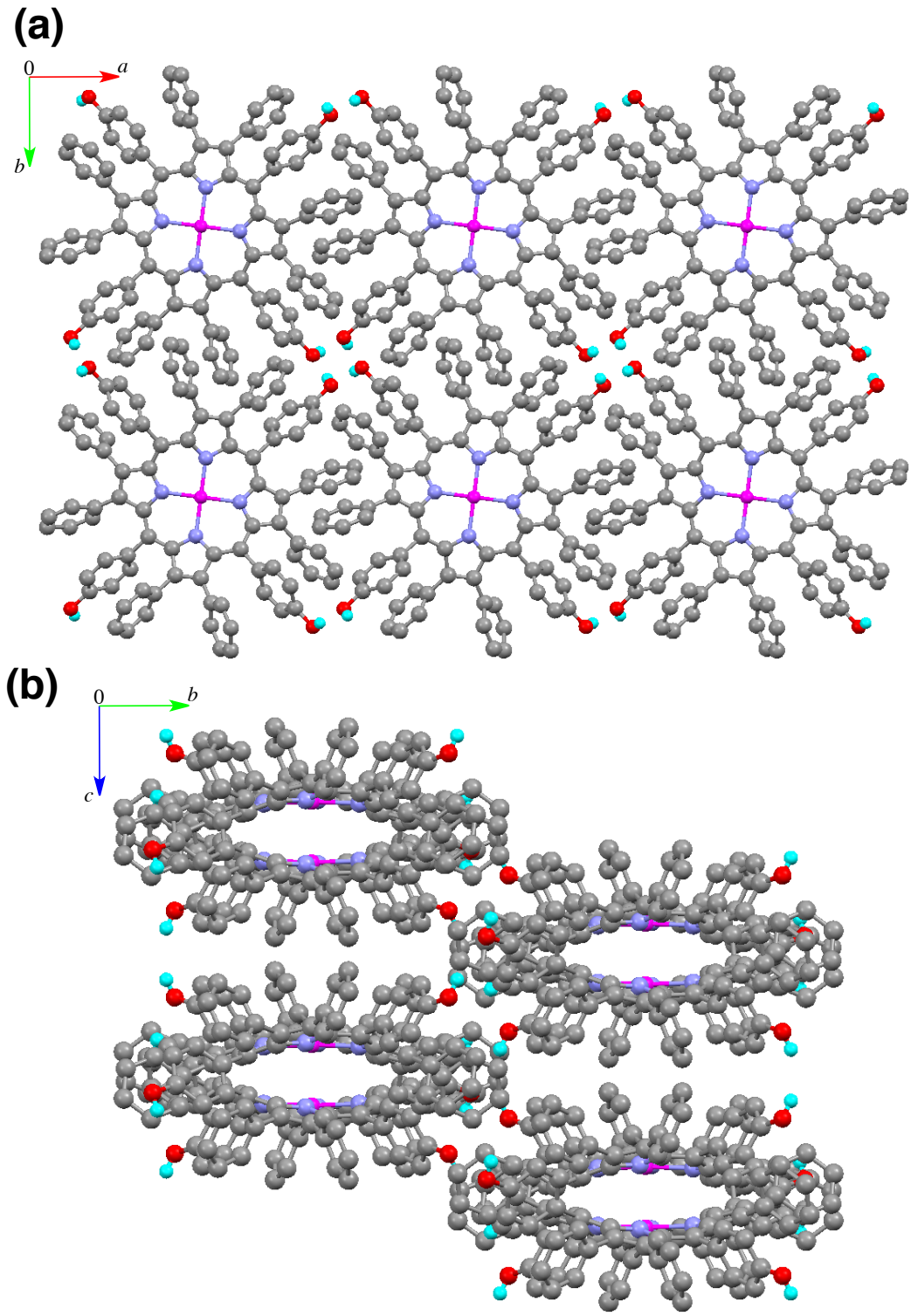

Fig. S4 Crystal packing diagrams of **2** from *c*- (a) and *a*-axis (b). Hydrogen bonds are expressed with dotted lines. Hydrogen atoms except O-Hs are omitted for clarity.

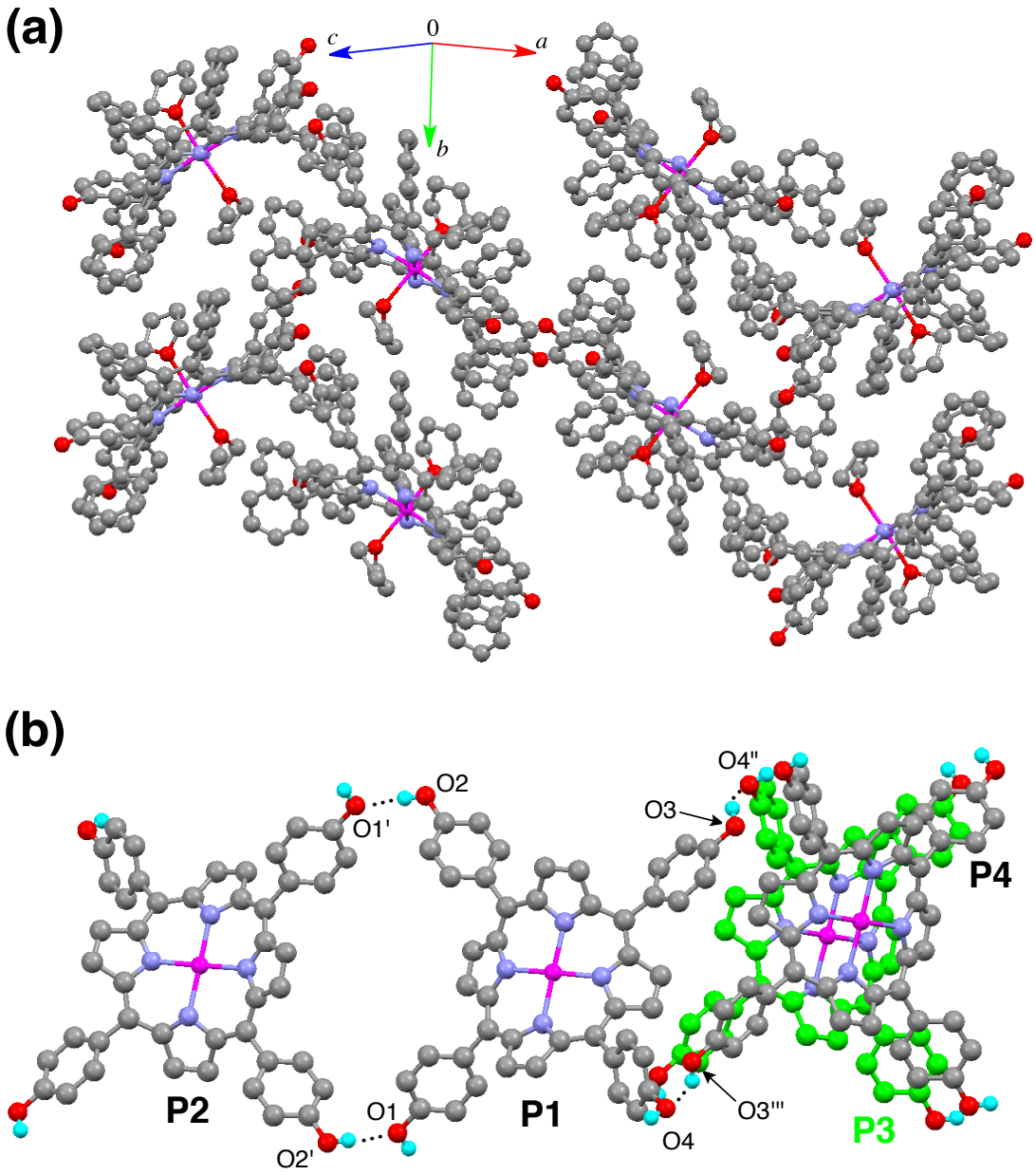

Fig. S5 Crystal packing diagram of **2**-THF_2 (a) and the hydrogen-bonding manner (b). Hydrogen atoms are omitted for clarity in (a) and also omitted except O-Hs in (b). The *β*–phenyl groups and the axial THF ligands are also omitted and the carbon atoms of the P3-porphyrin are depicted in green color for clarity in (b). Hydrogen bonds are presented with dotted lines.

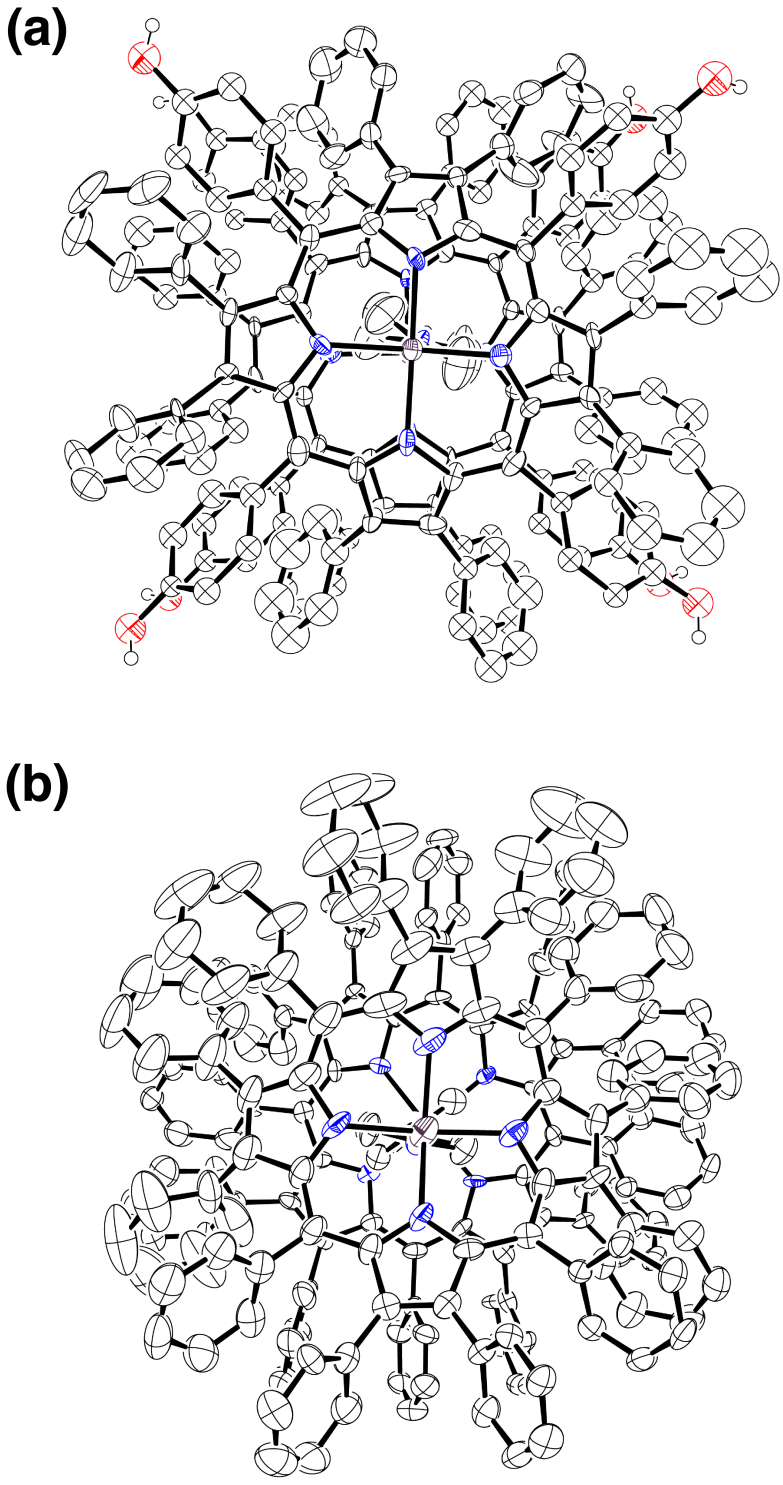

Fig. S6 ORTEP drawings for top views of **2**-bpy-**2** (a) and **3**-bpy-**3** (b) with thermal ellipsoids of 50% probability. Hydrogen atoms except OHs of **2**-bpy-**2** are omitted for clarity.

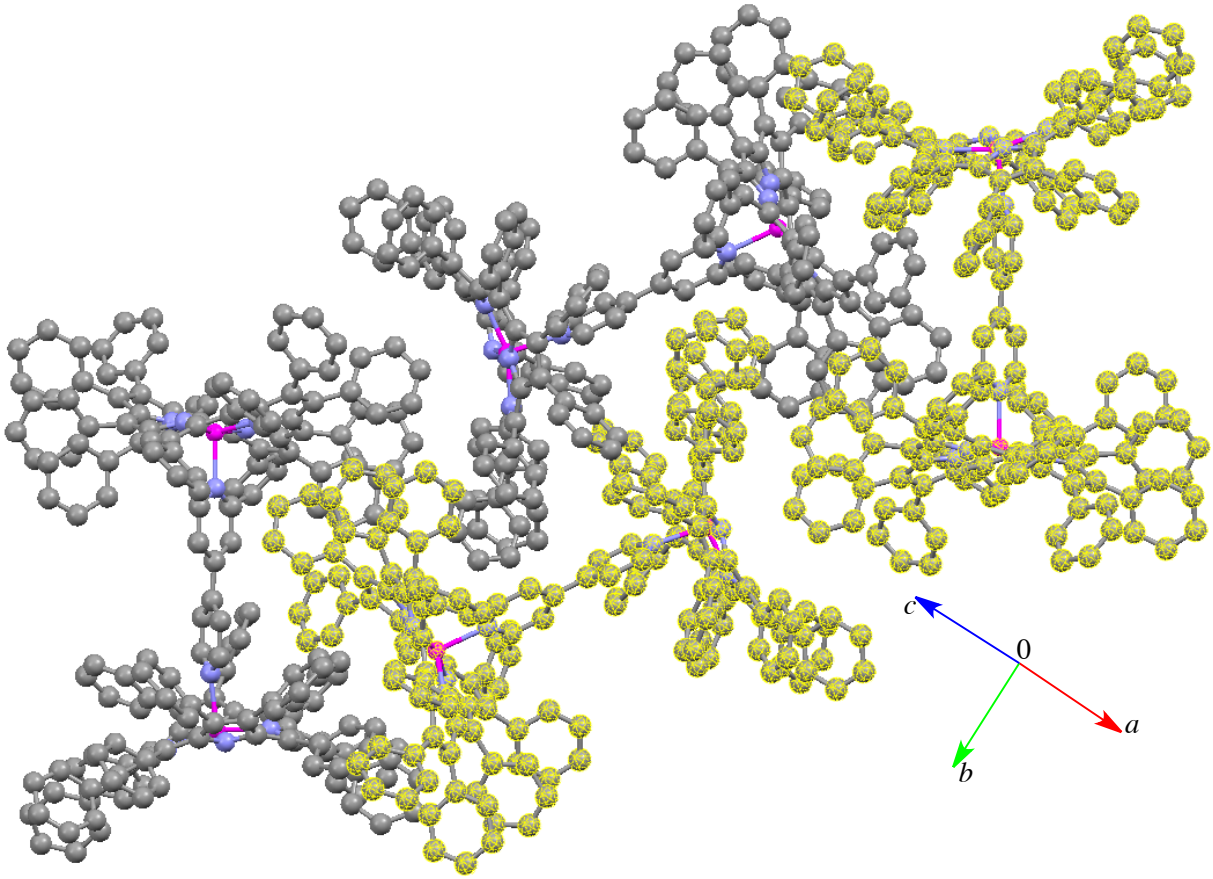

Fig. S7 A top view of **3**-bpy-**3** with ORTEP drawing (a) and the crystal packing diagram of (b). Hydrogen atoms except O-Hs are omitted for clarity.

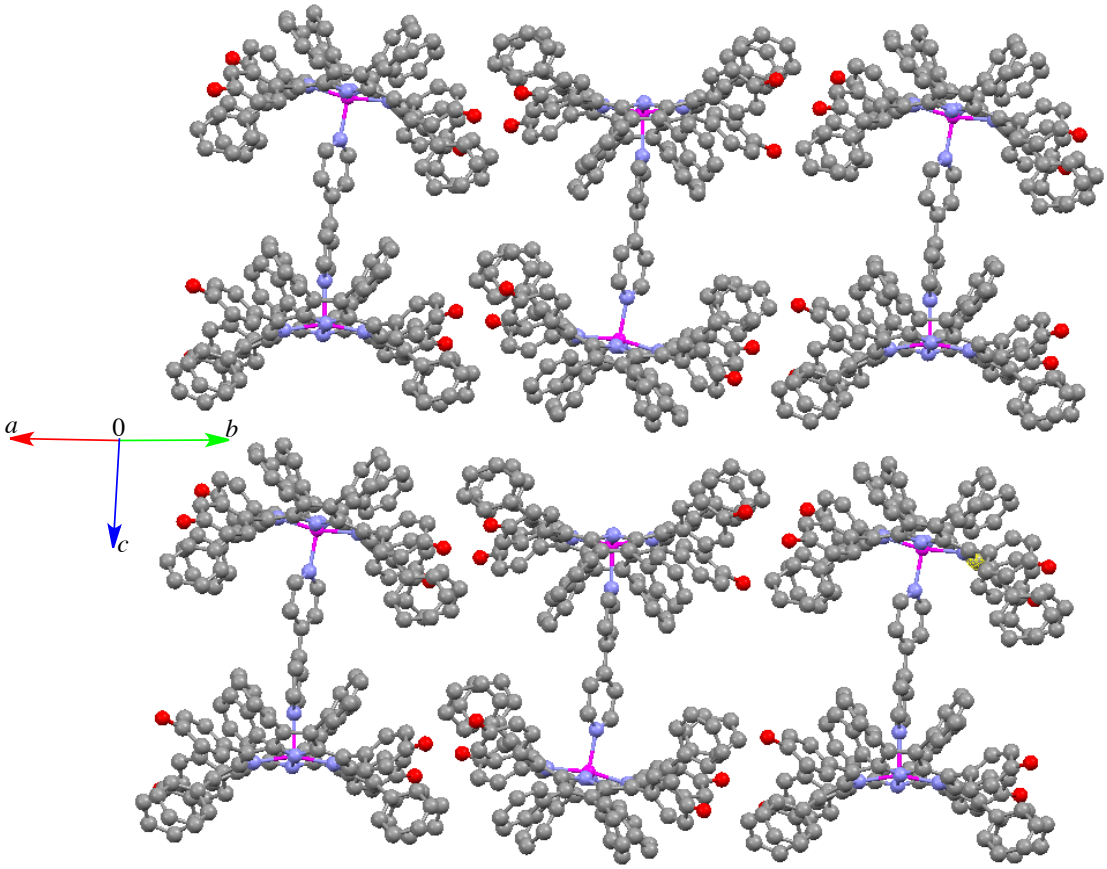

Fig. S8 The crystal-packing diagram of **2**-bpy-**2**. Hydrogen atoms except O-Hs are omitted for clarity.

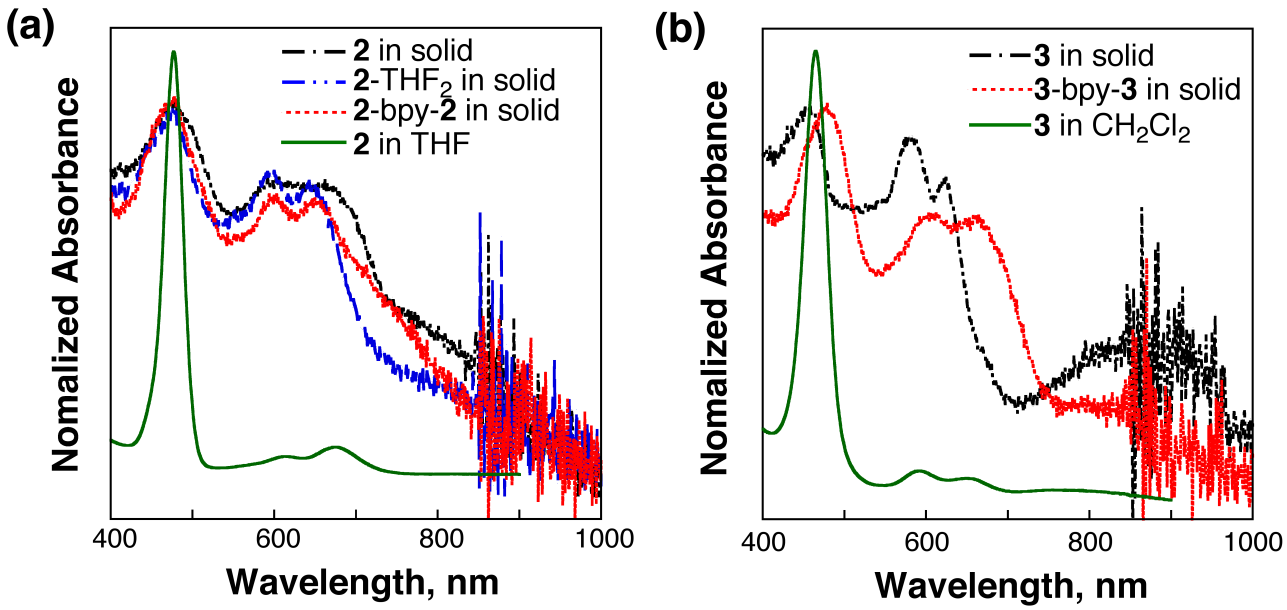

Fig. S9 Absorption spectra of **2** (a) and **3** in the solid state at room temperature.