The roles of the coordination modes of bridging ligands for the formation of two 3D metal-organic coordination networks

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Experimental Section

Materials and Methods. All of the chemicals were obtained from commercial sources and used without further purification, except pyridine-2,3,5,6-tetracarboxylic acid (H_4pdtc) was synthesized according to the reported method.[1] The determinations of the unit cells and data collections for the crystals of compounds **1** and **2** were performed on a CrysAlisPro, Oxford Diffraction Ltd. The data were collected using graphite−monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved by direct methods, and refined by full-matrix least-square methods with the **SHELX-97** program package.[2] The uncoordinated carboxylate group of Hpdtc[3-] (O3, O3', O4 and O4') in **1** is protonated and disordered. Thus, we attempted to solve the crystal structure by refining the carboxylate group as occupying two disordered positions. Initially, the occupancies were refined using free variables, but in the final cycles of refinement, these occupancies were held as fixed values near the refined values of 50% for O3, O3', O4 and O4' atoms, respectively. H atoms on C atoms were generated geometrically. The H atoms of the disordered carboxylate group and the half occupied lattice water molecule were not located out. The H atoms of the other water molecules were clearly visible in difference maps, and these were placed in the difference-map positions, then their positions were idealized and constrained to ride on their parent O atoms. The IR spectra were recorded from KBr pellets on a FTS-40 spectrophotometer. Powder X-ray diffraction data (PXRD) were recorded on a RIGAKU D/MAX 2550/PC for Cu-Kα ($\lambda = 1.5406$ Å). Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 4 ^{o}C/min.

References:

1. N. J. Babu, A. Nangia, *Cryst. Growth Des.*, 2006, **6**, 1753.

2. G. M. Sheldrick, *Program for Structure Refinement*: University of Göttingen, Germany, **1997**.

Tables:

Table S1. Crystal data and structure refinements for **1** and **2**.

Compound	1	2
Formula	$C_{38}H_{34}Cu_3N_6O_{23}$	$C_{28}H_{32}N_4O_{27}Zn_4$
Formula weight	1133.33	1118.06
Crystal size (mm^3)	$0.21 \times 0.15 \times 0.06$	$0.34 \times 0.24 \times 0.16$
Crystal color	Blue	Colorless
Crystal system, Space group	Monoclinic, $P2/n$	Monoclinic, $P2_1/c$
a (Å)	12.2892(15)	14.4711(3)
b (Å)	11.0889(14)	14.6161(3)
c (Å)	16.490(2)	17.8745(5)
β (^{o})	110.129(14)	90.238(2)
Volume ($Å^3$)	2109.8(5)	3780.62(15)
Z	2	4
Calculated density (g·cm^{-3})	1.784	1.964
F(000)	1150	2256
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Absorption coefficient (mm^{-1})	1.599	2.617
θ for data collection (^{o})	3.13 to 25.04	3.32 to 26.00
Limiting indices	$-14 \leq h \leq 14$, $-13 \leq k \leq 10$, $-18 \leq l \leq 19$	$-17 \leq h \leq 17$, $-17 \leq k \leq 18$, $-22 \leq l \leq 22$
Reflections collected	8929 [R(int) = 0.0721]	42908 [R(int) = 0.0510]
Unique reflections / parameters	3681 / 322	7408 / 568
Observed reflections ($I > 2\sigma(I)$)	1746	4985
Goodness-of-fit on F^2	0.912	0.941
R1 (wR2) [$I > 2\sigma(I)$]	0.0507 (0.0788)	0.0307 (0.0677)
R1 (wR2) (all data)	0.1190 (0.0851)	0.0555 (0.0708)
Largest diff. peak and hole (e·$Å^3$)	0.615 and -0.563	0.927 and -0.706

R1 = $\sum(|F_o| - |F_c|) / \sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths	(Å)	Bond angles	(°)	Bond angles	(°)
Cu(1)-N(1)#1	1.923(5)	N(1)#1-Cu(1)-N(4)	177.9(2)	N(3)#2-Cu(2)-N(2)	180.0(1)
Cu(1)-N(4)	1.957(6)	N(1)#1-Cu(1)-O(8)#1	80.6(2)	N(3)#2-Cu(2)-O(6)#3	89.46(13)
Cu(1)-O(8)#1	2.010(4)	N(4)-Cu(1)-O(8)#1	97.3(2)	O(6)-Cu(2)-O(9)	95.00(14)
Cu(1)-O(1)#1	2.064(5)	N(1)#1-Cu(1)-O(1)#1	79.8(2)	N(3)#2-Cu(2)-O(9)#3	90.99(14)
Cu(1)-O(10)	2.360(4)	N(4)-Cu(1)-O(1)#1	102.3(2)	N(2)-Cu(2)-O(9)#3	89.01(14)
Cu(1)-O(5)	2.384(4)	O(8)#1-Cu(1)-O(1)#1	160.3(2)	O(6)#3-Cu(2)-O(9)#3	95.00(14)
Cu(2)-N(3)#2	2.017(7)	N(1)#1-Cu(1)-O(10)	91.79(18)	O(6)-Cu(2)-O(9)#3	85.02(14)
Cu(2)-N(2)	2.022(7)	N(4)-Cu(1)-O(10)	88.57(19)	O(9)-Cu(2)-O(9)#3	178.0(3)
Cu(2)-O(6)#3	2.037(4)	O(8)#1-Cu(1)-O(10)	96.18(19)	N(2)-Cu(2)-O(6)#3	90.54(13)
Cu(2)-O(6)	2.037(4)	O(1)#1-Cu(1)-O(10)	86.2(2)	N(3)#2-Cu(2)-O(6)	89.46(13)
Cu(2)-O(9)	2.329(4)	N(1)#1-Cu(1)-O(5)	94.29(16)	N(2)-Cu(2)-O(6)	90.54(13)
Cu(2)-O(9)#3	2.329(4)	N(4)-Cu(1)-O(5)	85.88(17)	O(6)#3-Cu(2)-O(6)	178.9(3)
		O(8)#1-Cu(1)-O(5)	99.04(15)	N(3)#2-Cu(2)-O(9)	90.99(14)
		O(1)#1-Cu(1)-O(5)	80.74(16)	N(2)-Cu(2)-O(9)	89.01(14)
		O(10)-Cu(1)-O(5)	164.4(2)	O(6)#3-Cu(2)-O(9)	85.02(14)

Symmetry transformations used to generate equivalent atoms: #1: -x, -y-2, -z; #2: x, y+1, z; #3: -x+1/2, y, -z-1/2.

Table S3. Selected bond lengths (Å) and angles (°) for **2**.

Bond lengths	(Å)	Bond angles	(°)	Bond angles	(°)
Zn(1)-O(14)	1.947(2)	O(14)-Zn(1)-O(3)#1	104.47(9)	O(6)#5-Zn(3)-O(12)	94.03(9)
Zn(1)-O(3)#1	1.978(2)	O(14)-Zn(1)-N(1)#2	132.8(1)	O(6)#5-Zn(3)-N(2)#6	140.0(1)
Zn(1)-N(1)#2	2.046(2)	O(3)#1-Zn(1)-N(1)#2	116.70(9)	O(12)-Zn(3)-N(2)#6	125.12(9)
Zn(1)-O(2)#2	2.103(2)	O(14)-Zn(1)-O(2)#2	105.45(8)	O(6)#5-Zn(3)-O(9)#6	101.39(8)
Zn(1)-O(8)#2	2.249(2)	O(3)#1-Zn(1)-O(2)#2	115.19(8)	O(12)-Zn(3)-O(9)#6	106.17(8)
Zn(2)-O(18)	2.043(2)	N(1)#2-Zn(1)-O(2)#2	77.74(8)	N(2)#6-Zn(3)-O(9)#6	77.40(8)
Zn(2)-O(19)	2.113(2)	O(14)-Zn(1)-O(8)#2	88.85(8)	O(6)#5-Zn(3)-O(15)#6	98.50(8)
Zn(2)-O(11)	2.149(2)	O(3)#1-Zn(1)-O(8)#2	84.46(8)	O(12)-Zn(3)-O(15)#6	89.34(8)
Zn(2)-N(4)#3	2.156(2)	N(1)#2-Zn(1)-O(8)#2	73.98(8)	N(2)#6-Zn(3)-O(15)#6	76.28(8)
Zn(2)-O(17)	2.159(2)	O(2)#2-Zn(1)-O(8)#2	150.80(7)	O(9)#6-Zn(3)-O(15)#6	153.68(7)
Zn(2)-O(7)#4	2.194(2)	O(18)-Zn(2)-O(19)	88.55(9)	O(16)-Zn(4)-O(21)	88.90(9)
Zn(3)-O(6)#5	1.925(2)	O(18)-Zn(2)-O(11)	87.75(9)	O(16)-Zn(4)-O(20)	91.11(9)
Zn(3)-O(12)	1.961(2)	O(19)-Zn(2)-O(11)	83.70(8)	O(21)-Zn(4)-O(20)	95.73(9)
Zn(3)-N(2)#6	2.012(2)	O(18)-Zn(2)-N(4)#3	91.39(9)	O(16)-Zn(4)-N(3)	89.53(8)
Zn(3)-O(9)#6	2.129(2)	O(19)-Zn(2)-N(4)#3	176.91(9)	O(21)-Zn(4)-N(3)	174.71(10)
Zn(3)-O(15)#6	2.215(2)	O(11)-Zn(2)-N(4)#3	99.39(9)	O(20)-Zn(4)-N(3)	89.35(9)
Zn(4)-O(16)	2.088(2)	O(18)-Zn(2)-O(17)	178.59(8)	O(16)-Zn(4)-O(22)	89.42(8)
Zn(4)-O(21)	2.099(2)	O(19)-Zn(2)-O(17)	92.56(9)	O(21)-Zn(4)-O(22)	87.79(9)
Zn(4)-O(20)	2.099(2)	O(11)-Zn(2)-O(17)	93.23(8)	O(20)-Zn(4)-O(22)	176.45(8)
Zn(4)-N(3)	2.137(2)	N(4)#3-Zn(2)-O(17)	87.45(9)	N(3)-Zn(4)-O(22)	87.14(9)
Zn(4)-O(22)	2.155(2)	O(18)-Zn(2)-O(7)#4	94.39(9)	O(16)-Zn(4)-O(4)	175.22(8)
Zn(4)-O(4)	2.173(2)	O(19)-Zn(2)-O(7)#4	86.85(7)	O(21)-Zn(4)-O(4)	86.43(9)
		O(11)-Zn(2)-O(7)#4	170.26(7)	O(20)-Zn(4)-O(4)	88.37(8)
		N(4)#3-Zn(2)-O(7)#4	90.07(8)	N(3)-Zn(4)-O(4)	95.22(9)
		O(17)-Zn(2)-O(7)#4	84.81(8)	O(22)-Zn(4)-O(4)	91.40(8)

Symmetry transformations used to generate equivalent atoms: #1: x, -y+5/2, z+1/2; #2: -x+2, y+1/2, -z-1/2; #3: -x+1, -y+3, -z; #4: x-1, y, z+1; #5: x-1, -y+5/2, z+1/2; #6: -x+1, -y+2, -z.

Table S4. Hydrogen bond lengths (Å) and bond angles (°) in **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(9)-H(9A)...O(1)#1	0.81	2.05	2.857(6)	169.5
O(9)-H(9B)...O(5)	0.82	2.00	2.714(6)	145.4
O(10)-H(10G)...O(101)#2	0.83	2.16	2.739(8)	127.0
O(10)-H(10G)...N(4)	0.83	2.45	3.028(6)	127.4

Symmetry transformations used to generate equivalent atoms: #6: x+1, y, z; #7: x+1/2, -y-1, z+1/2

Table S5.   Hydrogen bond lengths (Å) and bond angles (°) in **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(17)-H(17A)...O(12)	0.82	1.96	2.729(3)	154.5
O(17)-H(17A)...O(15)#6	0.82	2.61	3.122(3)	122.1
O(17)-H(17B)...O(104)#6	0.82	1.93	2.711(3)	160.1
O(18)-H(18A)...O(9)#7	0.82	1.91	2.725(3)	174.2
O(18)-H(18B)...O(103)#1	0.82	1.89	2.699(4)	168.9
O(19)-H(19B)...O(8)#4	0.83	1.89	2.707(3)	167.3
O(19)-H(19C)...O(105)	0.82	2.10	2.826(4)	146.9
O(20)-H(20B)...O(5)#1	0.83	2.06	2.886(3)	175.3
O(20)-H(20C)...O(2)#2	0.81	1.98	2.787(3)	171.2
O(21)-H(21A)...O(102)	0.82	1.99	2.683(4)	142.2
O(21)-H(21B)...O(4)	0.82	2.43	2.925(3)	120.0
O(22)-H(22B)...O(3)	0.82	1.87	2.667(3)	166.4
O(22)-H(22C)...O(17)#6	0.82	1.97	2.787(3)	175.7
O(101)-H(10I)...O(103)	0.83	2.10	2.821(4)	145.8
O(101)-H(10J)...O(6)#5	0.82	2.36	3.173(4)	169.5
O(102)-H(10C)...O(5)#1	0.82	2.61	3.211(4)	131.1
O(102)-H(10D)...O(13)#8	0.82	2.00	2.807(4)	166.7
O(103)-H(10G)...O(101)#3	0.82	2.09	2.897(4)	165.5
O(103)-H(10H)...O(14)	0.82	2.01	2.820(4)	170.7
O(104)-H(10A)...O(1)	0.82	2.25	2.796(3)	124.5
O(105)-H(10E)...O(10)	0.82	2.19	2.797(4)	130.7
O(105)-H(10F)...O(22)#6	0.82	2.07	2.864(3)	161.3

Symmetry transformations used to generate equivalent atoms: #1: x, -y+5/2, z+1/2; #2: -x+2, y+1/2, -z-1/2; #3: -x+1, -y+3, -z; #4: x-1, y, z+1; #5: x-1, -y+5/2, z+1/2; #6: -x+1, -y+2, -z; #7: -x+1, y+1/2, -z+1/2; #8: -x+2, -y+2, -z.

Figures:
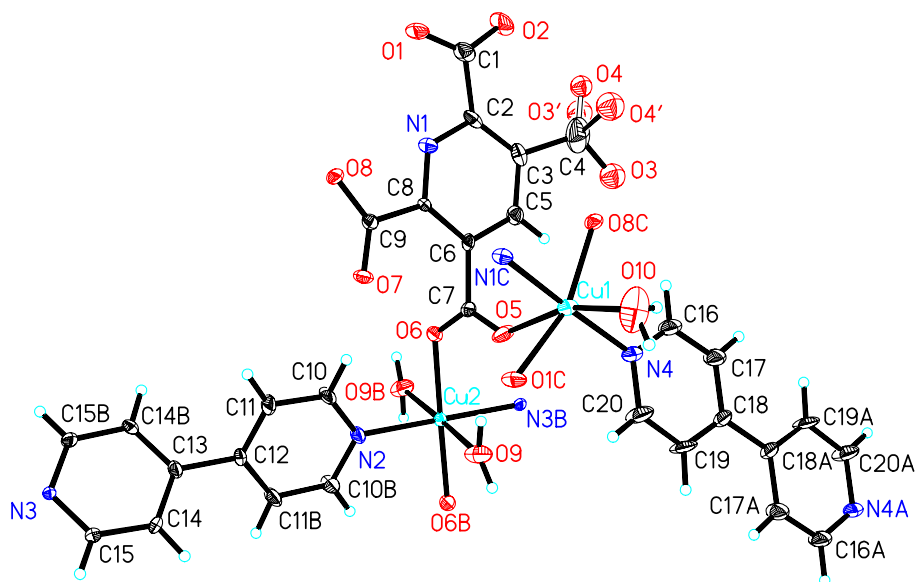
Fig. S1. ORTEP representation of the symmetry expanded local structure for **1** (25% probability ellipsoids).
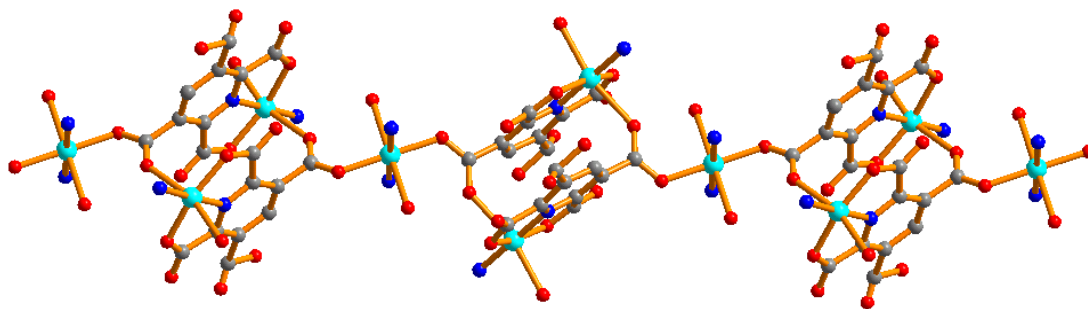
Fig. S2. A view of the bicopper units and the coordination mode of Hpdtc^{3-} in the 1D chain of **1**.
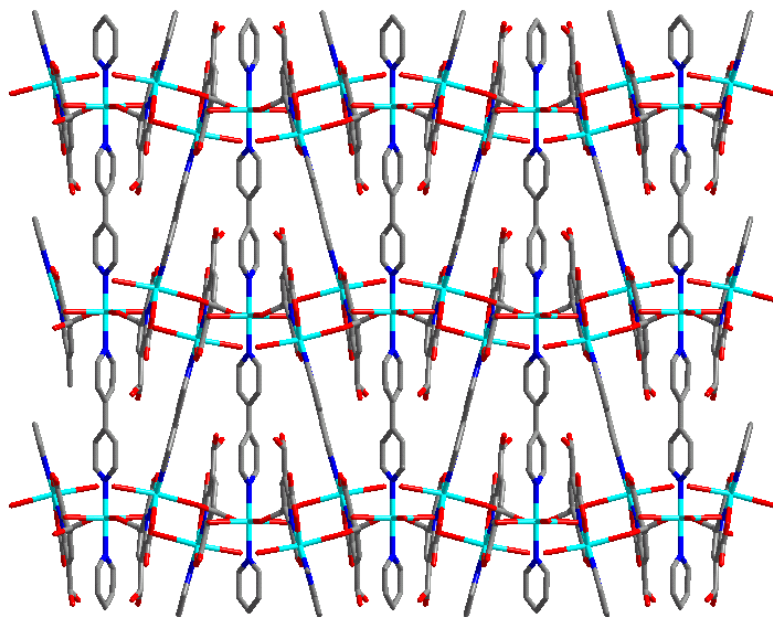
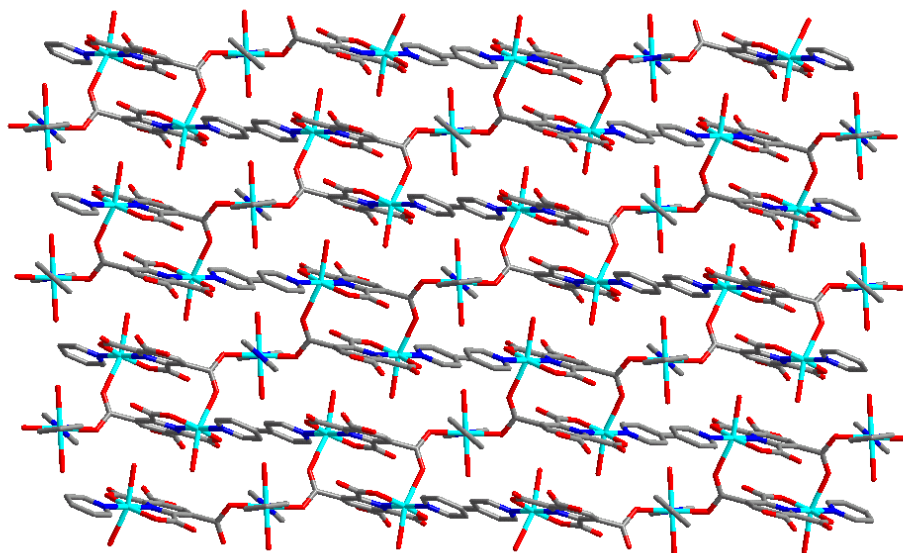**Fig. S3**. A view of the 3D framework of **1** down the *a* axis.

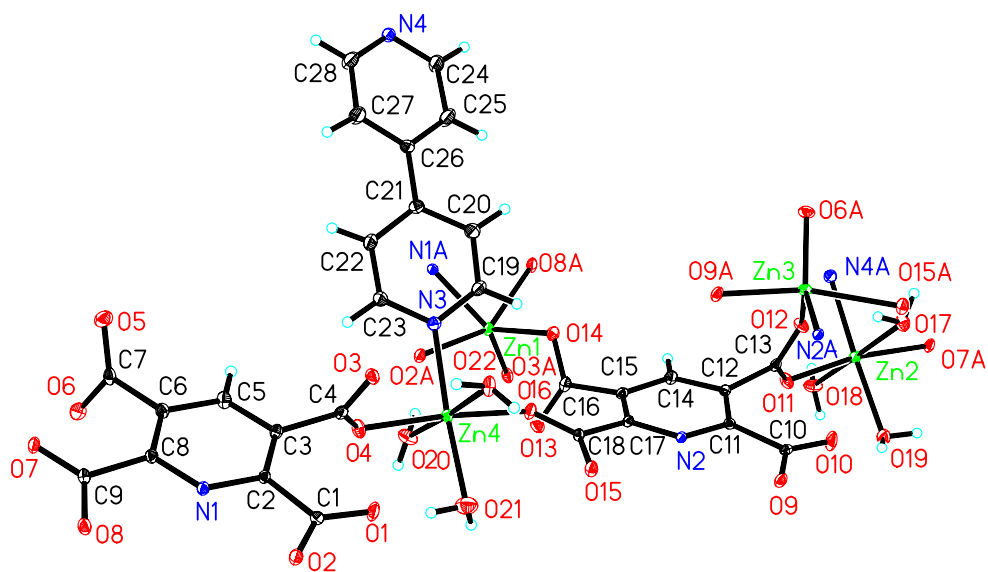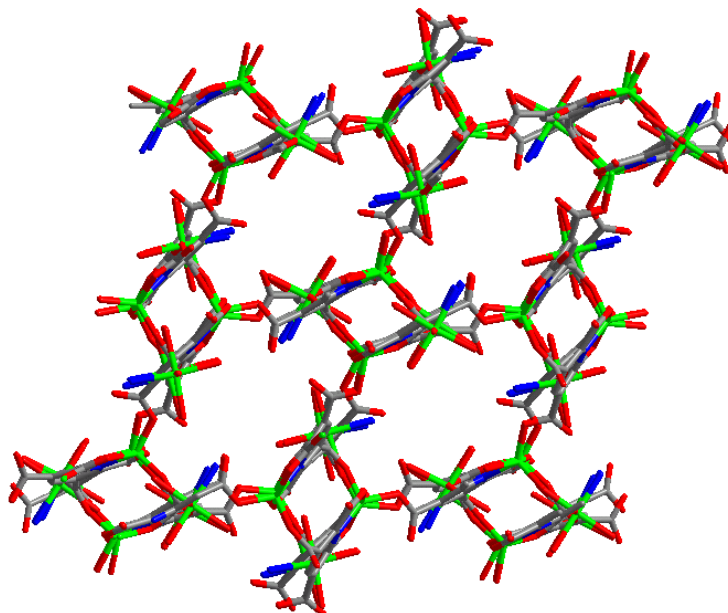**Fig. S4**. A view of the 3D framework of **1** down the *b* axis.

Fig. S5. ORTEP representation of the symmetry expanded local structure for **2** (25% probability ellipsoids).
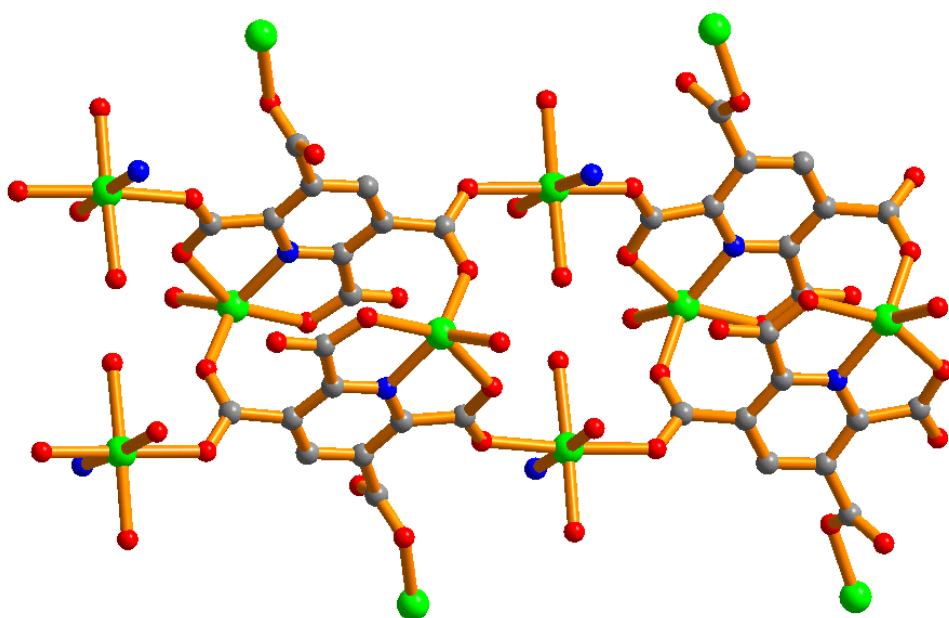
Fig. S6. A view of the bizinc units and the coordination mode of pdtc[4-] in **2**.

Fig. S7. A view of the 3D framework structure of pdtc^{4-} linking up zinc cations in **2**.
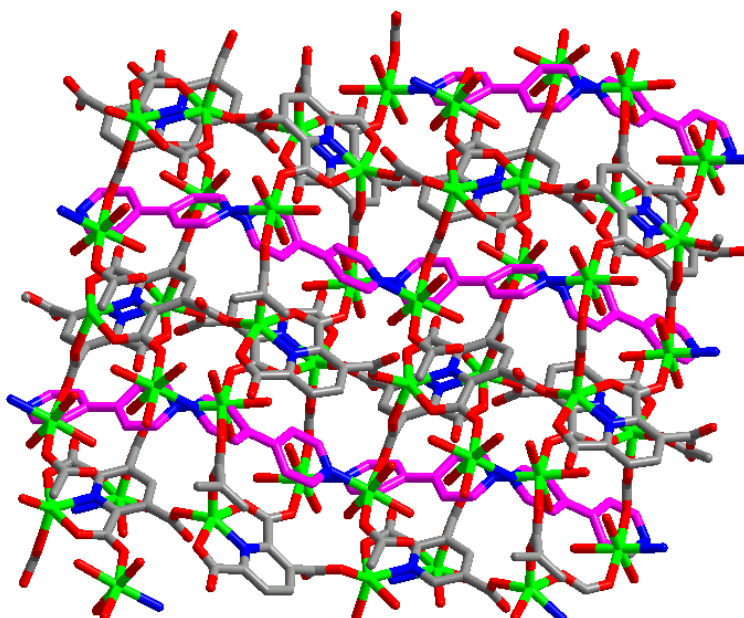
Fig. S8. Packing diagram of **2** viewed down the *a* axis.
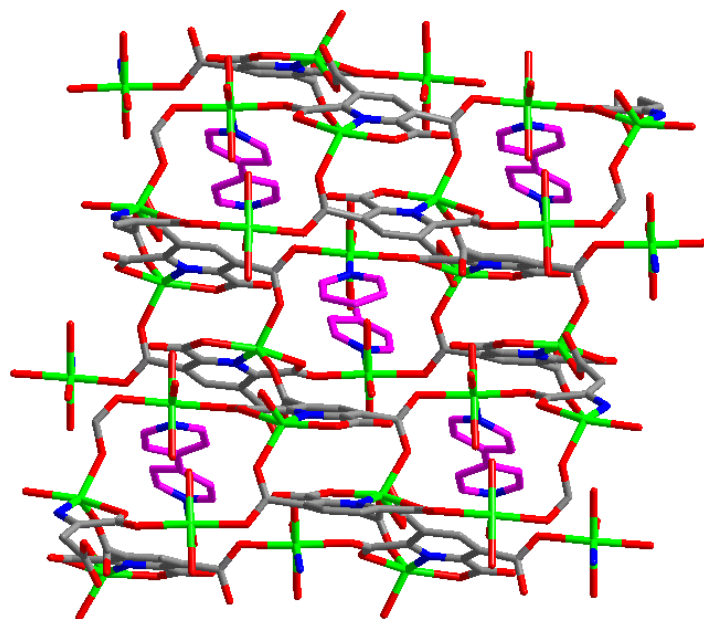
Fig. S9. Packing diagram of **2** viewed down the *b* axis.
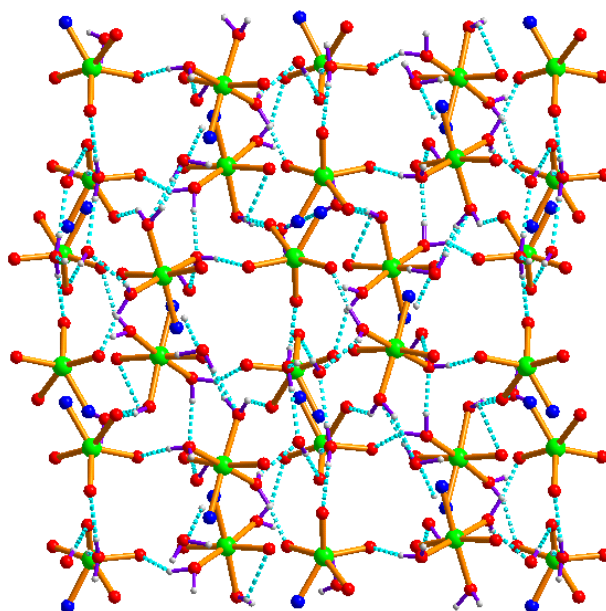
Fig. S10. The 3D supramolecular framework of water molecules linking up zinc polyhedra in **2** viewed down the *a* axis.
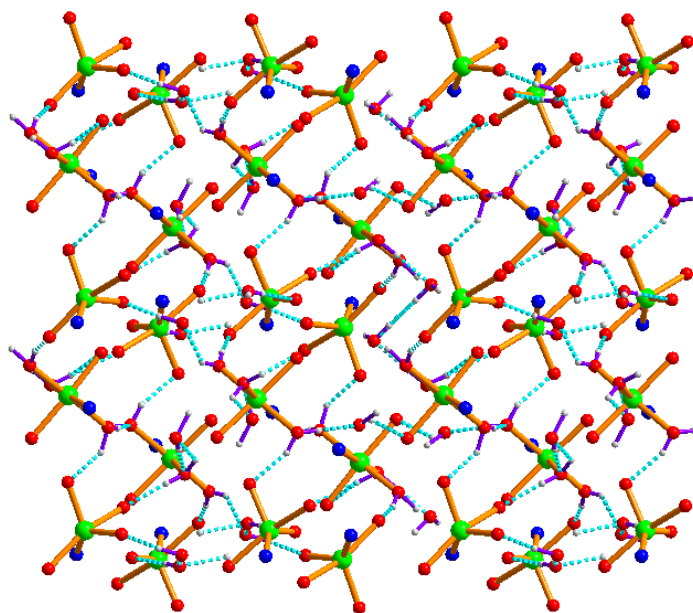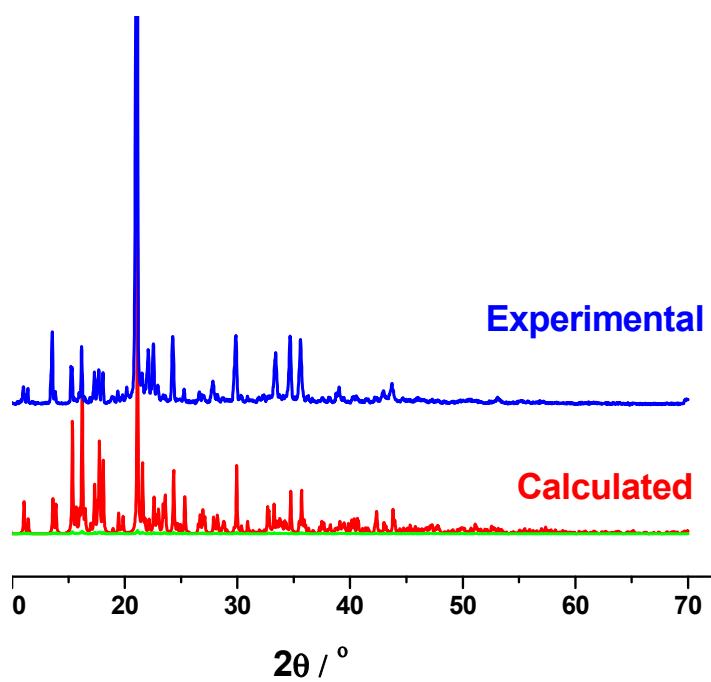
Fig. S11. The 3D supramolecular framework of water molecules linking up zinc polyhedra in **2** viewed down the *b* axis.
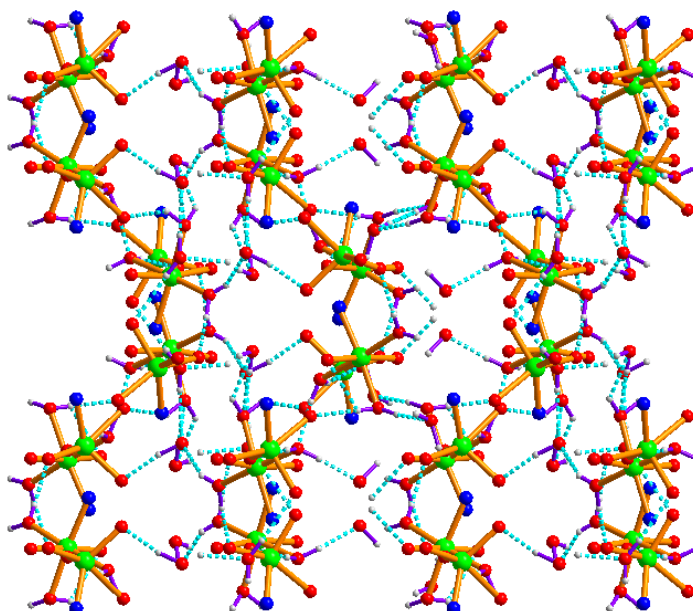
Fig. S12. The 3D supramolecular framework of water molecules linking up zinc polyhedra in **2** viewed down the *c* axis.

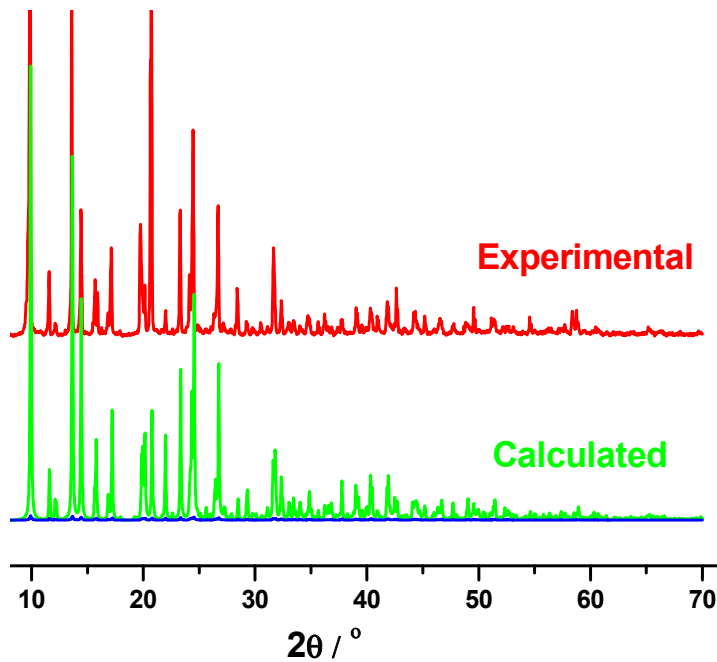**Fig. S13**. Powder X-ray diffraction patterns for compound **1**.
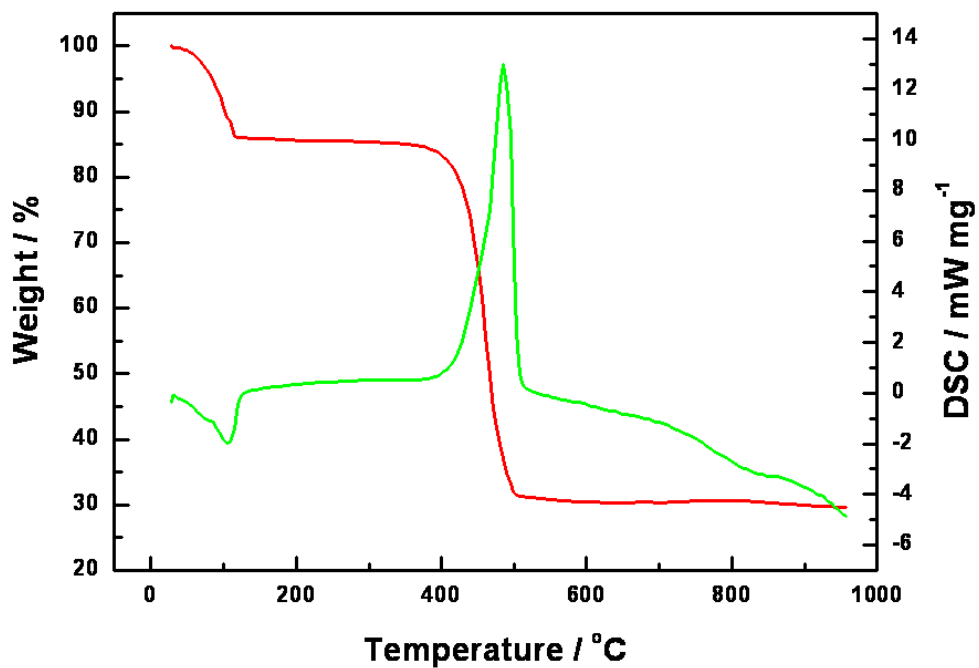

Fig. S14. Powder X-ray diffraction patterns for compound **2**.

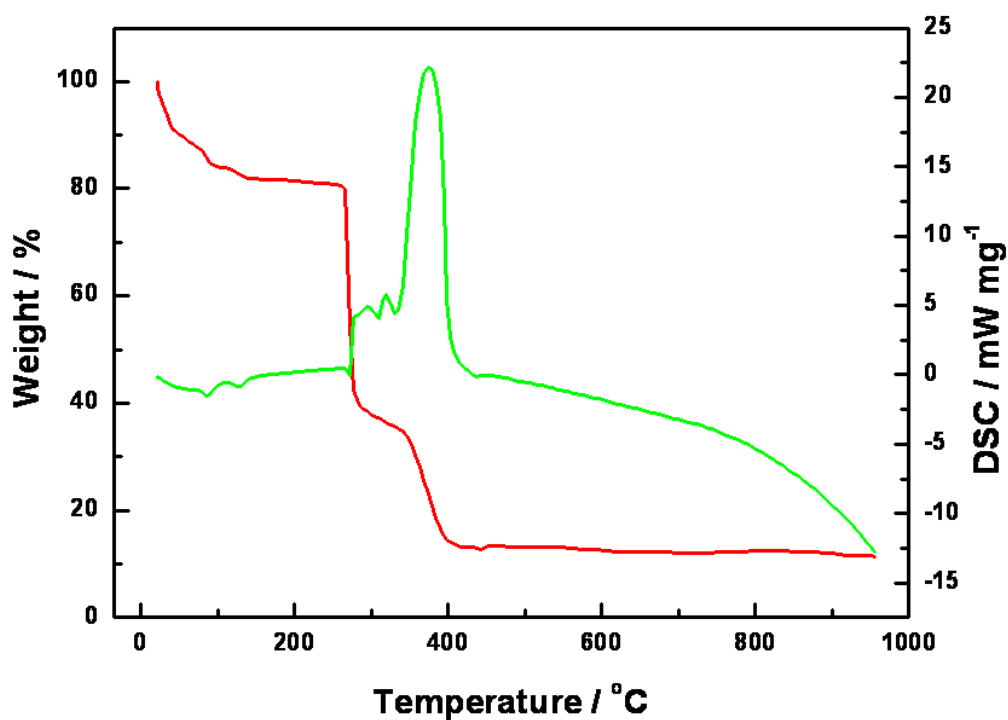**Fig. S15**. Thermogravimetric analysis result of **1**.

Fig. S16. Thermogravimetric analysis result of **2**.