Supplementary Material (ESI) for *CrystEngComm*

2D and 3D coordination polymers constructed by a novel hexakis(1,2,4-triazol-ylmethy1)benzene ligand and different carboxylate anions: syntheses, structures, and luminescent properties

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Synthesis of Htrb. The hexakis(bromomethyl)benzene was prepared according to the procedures reported previously.[1] Bromine (17.5 mL) was added slowly over 2 h to a boiling solution of hexamethylbenzene (6.5 g, 0.04 mol) in 1,2-dibromoethane (150 mL) and refluxed continuously for 30 h. Then, the hexakis(bromomethyl)benzene was cooled down and collected by filtration (22.4 g, yield: 88%).

Hexakis(bromomethyl)benzene (5.00 g, 7.86 mmol) was added to a stirred solution of 1,2,4-triazole (3.21 g, 47.16 mmol) and NaOH (1.89 g, 47.25 mmol) in 100 mL DMF. Then, the mixture was heated at 80 ℃ for 3 h, cooled and solvent removed. Washed with MeOH for three times and dried so as to get pure Htrb with a yield of 78.5%.

1 A. D. U. Hardy, D. D. MacNicol and D. R. Wilson, *J. Chem. Soc*., *Perkin Trans*. 1979, 1011.

Table S1. Selected bond distances (Å) and angles (°) for **1**

Zn(1)-O(4)#1	1.898(3)	Zn(1)-N(1)	1.978(3)
Zn(1)-O(5)	1.982(3)	Zn(1)-N(7)#2	2.038(3)
Zn(2)-O(1)	1.895(2)	Zn(2)-O(6)	1.948(2)
Zn(2)-N(4)	1.985(3)	Zn(2)-O(8)#3	1.986(2)
O(4)#1-Zn(1)-N(1)	125.69(12)	O(4)#1-Zn(1)-O(5)	101.47(12)
N(1)-Zn(1)-O(5)	111.67(12)	O(4)#1-Zn(1)-N(7)#2	105.14(13)
N(1)-Zn(1)-N(7)#2	106.44(11)	O(5)-Zn(1)-N(7)#2	104.57(11)
O(1)-Zn(2)-O(6)	113.38(11)	O(1)-Zn(2)-N(4)	116.08(11)
O(6)-Zn(2)-N(4)	110.62(11)	O(1)-Zn(2)-O(8)#3	94.65(10)
O(6)-Zn(2)-O(8)#3	106.24(12)	N(4)-Zn(2)-O(8)#3	114.64(11)

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

Table S2. Selected bond distances (Å) and angles (°) for **2**

Zn(1)-O(1)	1.975(4)	Zn(1)-N(1)	2.001(4)
Zn(1)-N(7)#1	2.002(4)	Zn(1)-O(5)	2.060(3)
Zn(1)-O(6)	2.356(3)	Zn(1)-C(13)	2.555(4)
Zn(2)-N(4)#2	2.046(3)	Zn(2)-N(4)	2.046(3)
Zn(2)-O(2)#2	2.115(3)	Zn(2)-O(2)	2.115(3)
Zn(2)-O(5)	2.243(3)	Zn(2)-O(5)#2	2.243(3)
O(1)-Zn(1)-N(1)	106.85(17)	O(1)-Zn(1)-N(7)#1	93.21(14)
N(1)-Zn(1)-N(7)#1	123.37(16)	O(1)-Zn(1)-O(5)	103.67(14)
N(1)-Zn(1)-O(5)	107.88(14)	N(7)#1-Zn(1)-O(5)	118.00(14)
O(1)-Zn(1)-O(6)	158.61(15)	N(1)-Zn(1)-O(6)	91.41(14)
N(7)#1-Zn(1)-O(6)	85.61(13)	O(5)-Zn(1)-O(6)	59.01(12)
O(1)-Zn(1)-C(13)	132.26(16)	N(1)-Zn(1)-C(13)	102.23(15)
N(7)#1-Zn(1)-C(13)	101.44(14)	O(5)-Zn(1)-C(13)	30.19(13)
O(6)-Zn(1)-C(13)	28.88(12)	N(4)#2-Zn(2)-N(4)	180.0(2)
N(4)#2-Zn(2)-O(2)#2	86.02(13)	N(4)-Zn(2)-O(2)#2	93.98(13)
N(4)#2-Zn(2)-O(2)	93.98(13)	N(4)-Zn(2)-O(2)	86.02(13)
O(2)#2-Zn(2)-O(2)	180.00(18)	N(4)#2-Zn(2)-O(5)	88.84(13)
N(4)-Zn(2)-O(5)	91.16(13)	O(2)#2-Zn(2)-O(5)	92.45(11)
O(2)-Zn(2)-O(5)	87.55(11)	N(4)#2-Zn(2)-O(5)#2	91.16(13)
N(4)-Zn(2)-O(5)#2	88.84(13)	O(2)#2-Zn(2)-O(5)#2	87.55(11)
O(2)-Zn(2)-O(5)#2	92.45(11)	O(5)-Zn(2)-O(5)#2	180.0(2)

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

Table S3. Selected bond distances (Å) and angles (°) for **3**

Zn(1)-N(17)#1	2.055(6)	Zn(1)-N(1)	2.057(5)
Zn(1)-O(1W)	2.084(4)	Zn(1)-O(11)	2.105(4)
Zn(1)-O(5)	2.173(4)	Zn(1)-O(1)	2.277(4)
Zn(2)-N(14)	2.061(5)	Zn(2)-N(11)#2	2.094(5)

Zn(2)-O(7)	2.100(4)	Zn(2)-O(2W)	2.110(4)
Zn(2)-O(12)	2.216(4)	Zn(2)-O(9)	2.238(4)
Zn(3)-N(4A)#3	2.082(5)	Zn(3)-N(4)#3	2.082(5)
Zn(3)-O(2)	2.098(4)	Zn(3)-O(3W)	2.099(4)
Zn(3)-N(7)#4	2.099(5)	Zn(3)-O(6)#5	2.153(4)
Zn(3)-O(3)#4	2.183(4)		
N(17)#1-Zn(1)-N(1)	168.3(2)	N(17)#1-Zn(1)-O(1W)	92.3(2)
N(1)-Zn(1)-O(1W)	99.3(2)	N(17)#1-Zn(1)-O(11)	93.7(2)
N(1)-Zn(1)-O(11)	87.57(19)	O(1W)-Zn(1)-O(11)	90.51(16)
N(17)#1-Zn(1)-O(5)	88.2(2)	N(1)-Zn(1)-O(5)	90.7(2)
O(1W)-Zn(1)-O(5)	88.82(16)	O(11)-Zn(1)-O(5)	178.0(2)
N(17)#1-Zn(1)-O(1)	81.3(2)	N(1)-Zn(1)-O(1)	87.11(19)
O(1W)-Zn(1)-O(1)	172.90(19)	O(11)-Zn(1)-O(1)	92.79(15)
O(5)-Zn(1)-O(1)	88.07(15)	N(14)-Zn(2)-N(11)#2	170.2(2)
N(14)-Zn(2)-O(7)	94.3(2)	N(11)#2-Zn(2)-O(7)	92.8(2)
N(14)-Zn(2)-O(2W)	95.0(2)	N(11)#2-Zn(2)-O(2W)	91.3(2)
O(7)-Zn(2)-O(2W)	93.09(16)	N(14)-Zn(2)-O(12)	88.75(19)
N(11)#2-Zn(2)-O(12)	84.20(19)	O(7)-Zn(2)-O(12)	92.56(16)
O(2W)-Zn(2)-O(12)	172.97(17)	N(14)-Zn(2)-O(9)	87.85(19)
N(11)#2-Zn(2)-O(9)	85.22(18)	O(7)-Zn(2)-O(9)	177.51(19)
O(2W)-Zn(2)-O(9)	85.39(15)	O(12)-Zn(2)-O(9)	88.82(15)
N(4A)#3-Zn(3)-N(4)#3	0.0(5)	N(4A)#3-Zn(3)-O(2)	96.1(2)
N(4)#3-Zn(3)-O(2)	96.1(2)	N(4A)#3-Zn(3)-O(3W)	88.3(3)
N(4)#3-Zn(3)-O(3W)	88.3(3)	O(2)-Zn(3)-O(3W)	89.16(17)
N(4A)#3-Zn(3)-N(7)#4	170.9(2)	N(4)#3-Zn(3)-N(7)#4	170.9(2)
O(2)-Zn(3)-N(7)#4	88.04(18)	O(3W)-Zn(3)-N(7)#4	99.9(2)
N(4A)#3-Zn(3)-O(6)#5	83.6(2)	N(4)#3-Zn(3)-O(6)#5	83.6(2)
O(2)-Zn(3)-O(6)#5	93.52(17)	O(3W)-Zn(3)-O(6)#5	171.8(2)
N(7)#4-Zn(3)-O(6)#5	88.0(2)	N(4A)#3-Zn(3)-O(3)#4	89.6(2)
N(4)#3-Zn(3)-O(3)#4	89.6(2)	O(2)-Zn(3)-O(3)#4	172.14(17)

O(3W)-Zn(3)-O(3)#4	85.55(16)	N(7)#4-Zn(3)-O(3)#4	87.15(17)
O(6)#5-Zn(3)-O(3)#4	92.53(17)		

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

Table S4. Selected bond distances (Å) and angles (°) for **4**

Zn(1)-O(4)#1	1.983(3)	Zn(1)-O(1)	1.995(3)
Zn(1)-N(1)	2.014(3)	Zn(1)-N(4)#2	2.025(4)
O(4)#1-Zn(1)-O(1)	95.98(12)	O(4)#1-Zn(1)-N(1)	104.52(12)
O(1)-Zn(1)-N(1)	111.53(13)	O(4)#1-Zn(1)-N(4)#2	115.28(13)
O(1)-Zn(1)-N(4)#2	116.01(13)	N(1)-Zn(1)-N(4)#2	112.03(14)

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

Table S5a. Selected bond distances (Å) and angles (°) for **5**

Cd(1)-N(4)#1	2.3022(17)	Cd(1)-O(1)	2.3132(16)
Cd(1)-O(1W)	2.3212(16)	Cd(1)-N(1)	2.3402(19)
Cd(1)-O(4)#2	2.3439(15)	Cd(1)-O(2)	2.5752(17)
Cd(1)-O(3)#2	2.5924(16)	C(1)-C(3)#3	1.396(3)
C(1)-C(2)	1.404(3)	C(1)-C(4)	1.523(3)
C(2)-C(3)	1.405(3)	C(2)-C(7)	1.511(3)
C(3)-C(1)#3	1.396(3)	C(3)-C(10)	1.520(3)
N(4)#1-Cd(1)-O(1)	135.01(6)	N(4)#1-Cd(1)-O(1W)	93.73(6)
O(1)-Cd(1)-O(1W)	89.93(6)	N(4)#1-Cd(1)-N(1)	98.05(7)
O(1)-Cd(1)-N(1)	85.20(6)	O(1W)-Cd(1)-N(1)	167.26(6)
N(4)#1-Cd(1)-O(4)#2	137.12(6)	O(1)-Cd(1)-O(4)#2	87.79(5)
O(1W)-Cd(1)-O(4)#2	81.79(6)	N(1)-Cd(1)-O(4)#2	86.26(6)
N(4)#1-Cd(1)-O(2)	83.09(6)	O(1)-Cd(1)-O(2)	52.86(5)

O(1W)-Cd(1)-O(2)	83.10(6)	N(1)-Cd(1)-O(2)	103.08(7)
O(4)#2-Cd(1)-O(2)	137.66(5)	N(4)#1-Cd(1)-O(3)#2	85.31(6)
O(1)-Cd(1)-O(3)#2	139.43(5)	O(1W)-Cd(1)-O(3)#2	91.74(6)
N(1)-Cd(1)-O(3)#2	84.41(6)	O(4)#2-Cd(1)-O(3)#2	52.48(5)
O(2)-Cd(1)-O(3)#2	166.96(5)		

Table S5b. Hydrogen bonds for **5** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1A)···O(2)#4	0.84	1.85	2.679(2)	167.1
O(1W)-H(1B)···O(2W)#4	0.85	1.89	2.730(3)	172.3
O(2W)-H(2A)···O(3W)	0.85	2.03	2.852(4)	162.9
O(2W)-H(2B)···O(3)	0.85	1.93	2.771(3)	170.2
O(3W)-H(3B)···N(7)#5	0.87	2.50	2.961(4)	113.8
O(4W)-H(4)···O(3W)	0.85	2.33	3.180(11)	175.1

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

Table S6a. Selected bond distances (Å) and angles (°) for **6**

Co(1)-O(1)	2.069(3)	Co(1)-O(1W)	2.092(3)
Co(1)-N(1)	2.131(3)	Co(1)-N(4)#1	2.157(3)
Co(1)-O(4)#2	2.194(2)	Co(1)-O(3)#2	2.363(3)
O(1)-Co(1)-O(1W)	89.40(10)	O(1)-Co(1)-N(1)	87.28(10)
O(1W)-Co(1)-N(1)	171.48(10)	O(1)-Co(1)-N(4)#1	125.64(11)
O(1W)-Co(1)-N(4)#1	92.01(10)	N(1)-Co(1)-N(4)#1	96.30(11)
O(1)-Co(1)-O(4)#2	91.50(10)	O(1W)-Co(1)-O(4)#2	84.10(10)
N(1)-Co(1)-O(4)#2	88.14(10)	N(4)#1-Co(1)-O(4)#2	142.69(10)
O(1)-Co(1)-O(3)#2	148.19(10)	O(1W)-Co(1)-O(3)#2	90.87(10)
N(1)-Co(1)-O(3)#2	87.83(10)	N(4)#1-Co(1)-O(3)#2	86.14(10)

O(4)#2-Co(1)-O(3)#2 56.93(8)

Table S6b. Hydrogen bonds for **6** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1A)...O(4W)#4	0.85	1.91	2.740(4)	167.7
O(1W)-H(1B)...O(2)	0.85	3.21	3.272(4)	86.8

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

Table S7. Selected bond distances (Å) and angles (°) for **7**

Cu(1)-N(1)	1.970(4)	Cu(1)-N(4)#1	1.992(4)
Cu(1)-O(5)	1.999(4)	Cu(1)-O(1)	2.031(5)
Cu(1)-O(6)#1	2.063(4)	Cu(1)-O(2B)	2.085(19)
Cu(2)-O(4)#3	1.838(3)	Cu(2)-O(8)	1.900(5)
Cu(2)-N(7)#2	2.036(5)	Cu(2)-O(1W)	2.117(17)
Cu(2)-O(7)	2.147(5)	Cu(2)-O(1W')	2.354(17)
Cu(2)-C(28)	2.362(6)		
N(1)-Cu(1)-N(4)#1	179.17(15)	N(1)-Cu(1)-O(5)	91.46(17)
N(4)#1-Cu(1)-O(5)	88.92(18)	N(1)-Cu(1)-O(1)	91.49(19)
N(4)#1-Cu(1)-O(1)	88.81(19)	O(5)-Cu(1)-O(1)	132.1(2)
N(1)-Cu(1)-O(6)#1	91.66(16)	N(4)#1-Cu(1)-O(6)#1	87.55(17)
O(5)-Cu(1)-O(6)#1	136.4(2)	O(1)-Cu(1)-O(6)#1	91.2(2)
N(1)-Cu(1)-O(2B)	95.9(5)	N(4)#1-Cu(1)-O(2B)	84.9(5)
O(5)-Cu(1)-O(2B)	90.0(8)	O(1)-Cu(1)-O(2B)	42.2(7)
O(6)#1-Cu(1)-O(2B)	132.8(8)	O(4)#3-Cu(2)-O(8)	155.00(18)
O(4)#3-Cu(2)-N(7)#2	98.51(17)	O(8)-Cu(2)-N(7)#2	97.07(19)
O(4)#3-Cu(2)-O(1W)	96.6(5)	O(8)-Cu(2)-O(1W)	97.5(6)
N(7)#2-Cu(2)-O(1W)	106.8(4)	O(4)#3-Cu(2)-O(7)	95.66(18)

O(8)-Cu(2)-O(7)	62.12(18)	N(7)#2-Cu(2)-O(7)	150.4(2)
O(1W)-Cu(2)-O(7)	97.2(5)	O(4)#3-Cu(2)-O(1WA)	89.3(5)
O(8)-Cu(2)-O(1WA)	99.6(5)	N(7)#2-Cu(2)-O(1WA)	120.3(5)
O(1W)-Cu(2)-O(1WA)	14.4(6)	O(7)-Cu(2)-O(1WA)	85.7(5)
O(4)#3-Cu(2)-C(28)	124.76(19)	O(8)-Cu(2)-C(28)	31.75(19)
N(7)#2-Cu(2)-C(28)	125.0(2)	O(1W)-Cu(2)-C(28)	100.6(6)
O(7)-Cu(2)-C(28)	30.50(18)	O(1W')-Cu(2)-C(28)	94.9(5)

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

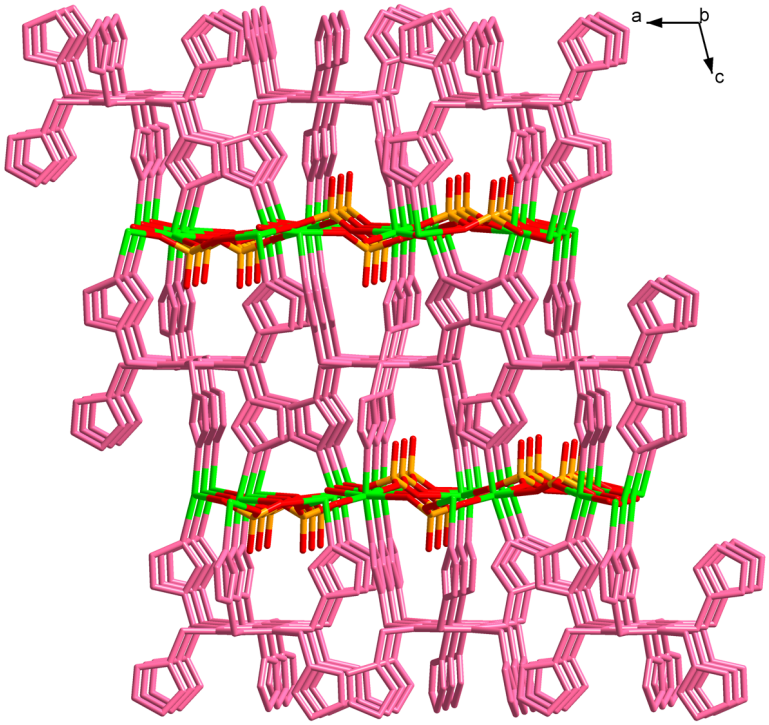


Fig. S1 View of the 3D framework of **3**.

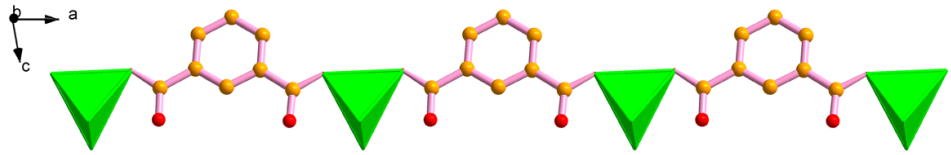
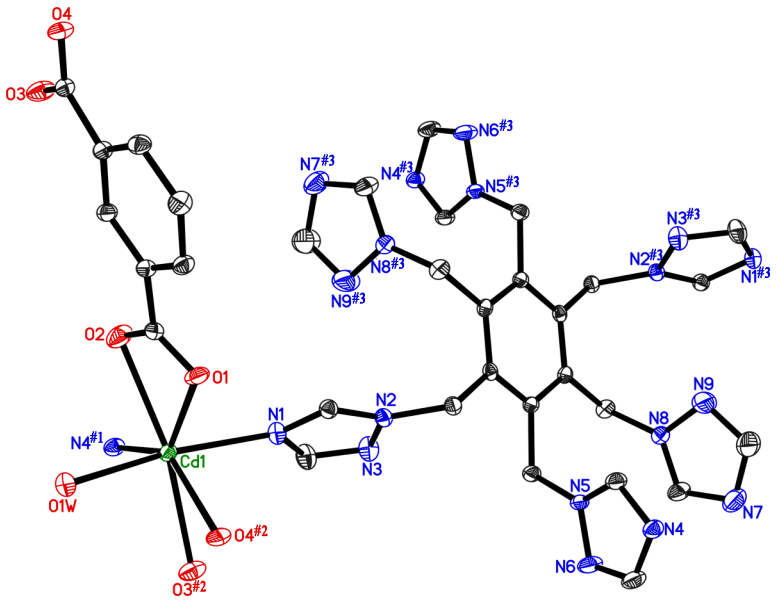
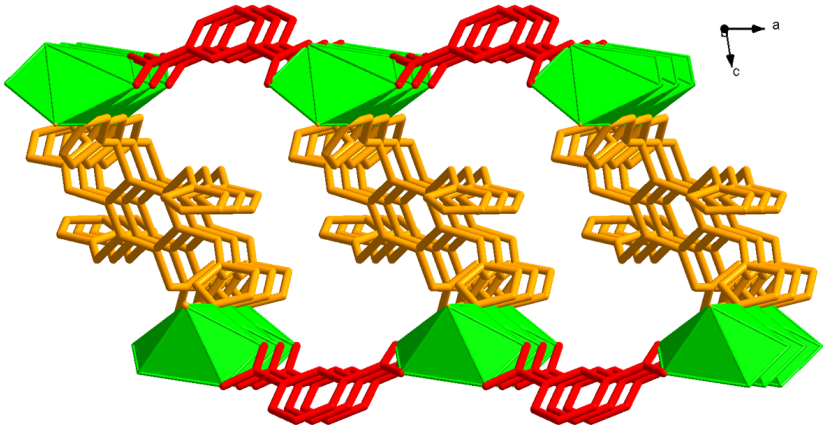
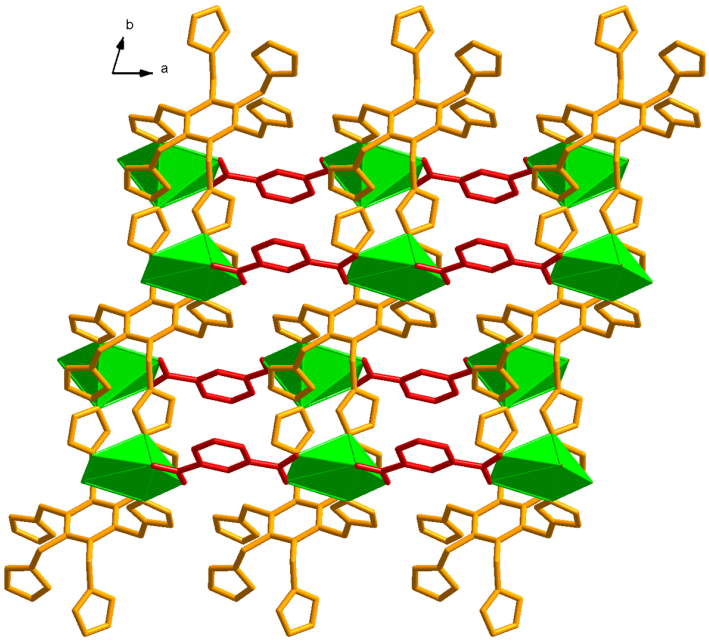


Fig. S2 1D chain constructed by L1 anions and Zn(II) ions in **4**.

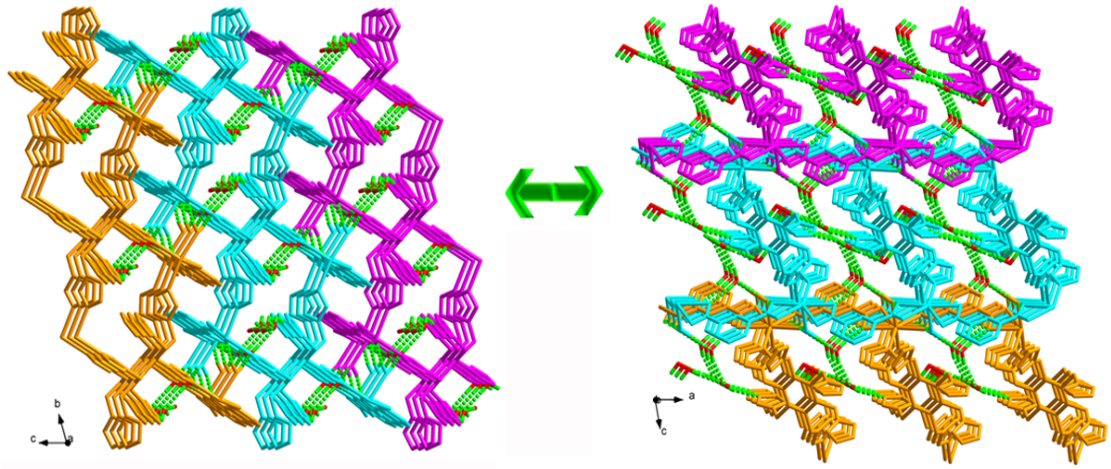


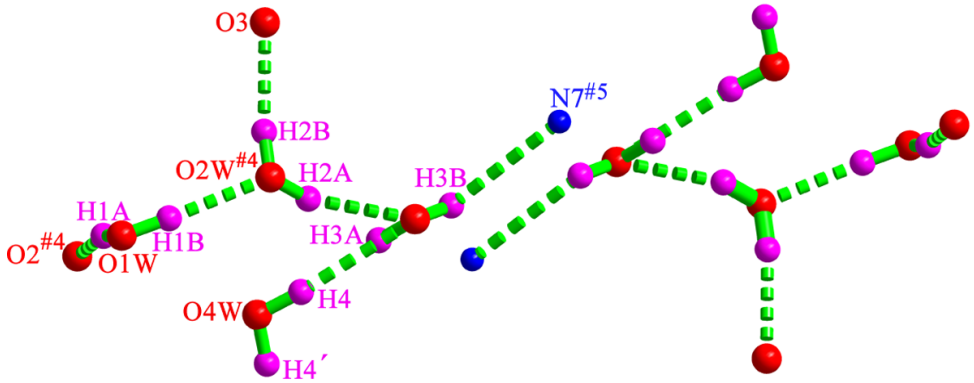
(a)





(b)

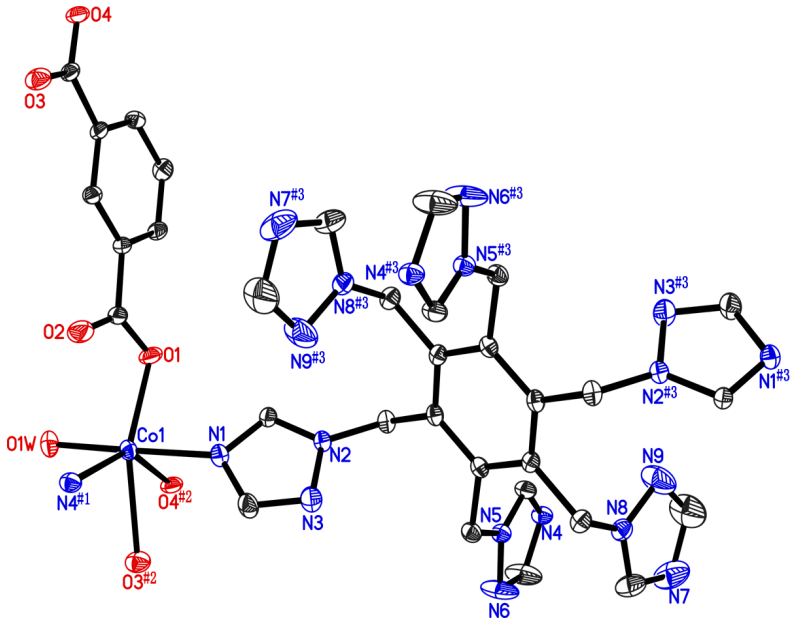




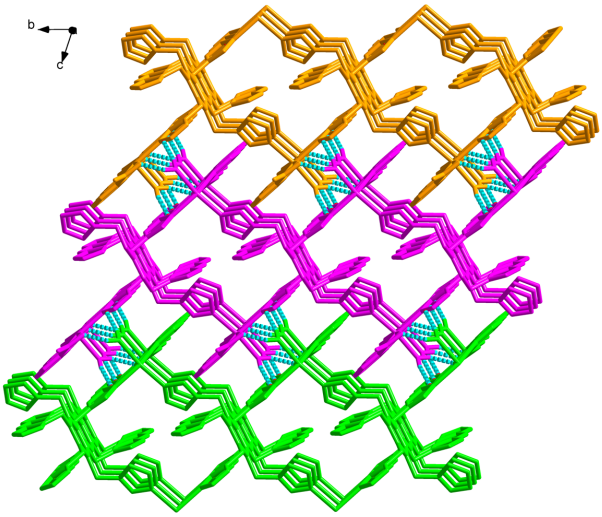
(c)

Fig. S3 (a) Coordination environment of the Cd(II) ion in **5** (30% probability displacement ellipsoids). Symmetry codes: #1 x, y-1, z; #2 x+1, y, z; #3 -x, -y+1, -z; #4 -x,

-y-1, -z+1; #5 x-1, y-1, z. (b) Front view and side view of the 2D sheet constructed by Htrb ligands, L1 anions and Cd(II) ions. (c) View of the 3D supramolecular structure connected by hydrogen-bonding interactions among the water molecules and carboxylate anions.



(a)



(b)

Fig. S4 (a) Coordination environment of the Zn(II) ion in **6** with solvent water molecules omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: #1 x, y+1, z; #2 x-1, y, z; #3 -x, -y-1, -z+1. (b) View of the 3D supramolecular structure connected by hydrogen-bonding interactions.

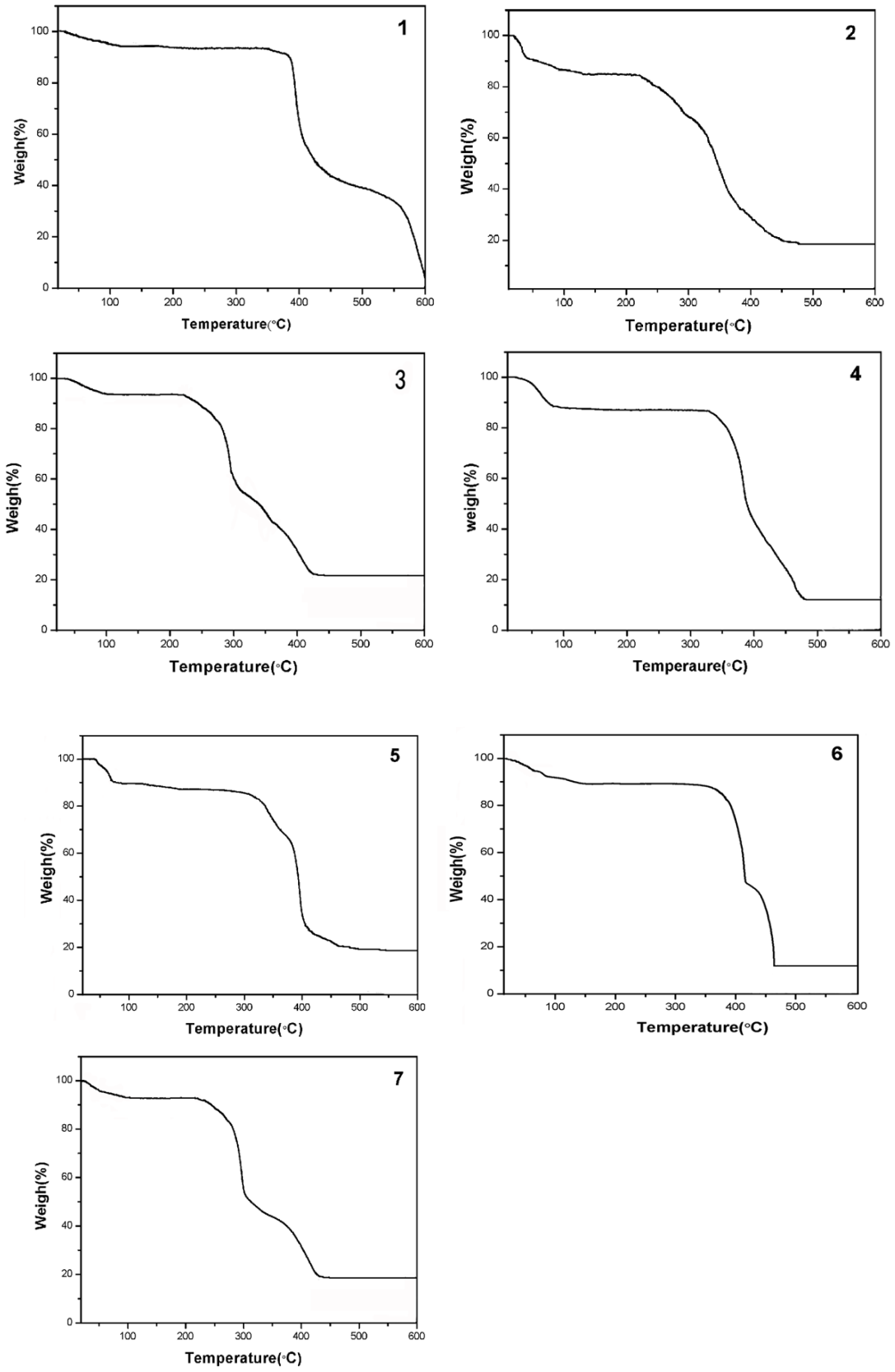
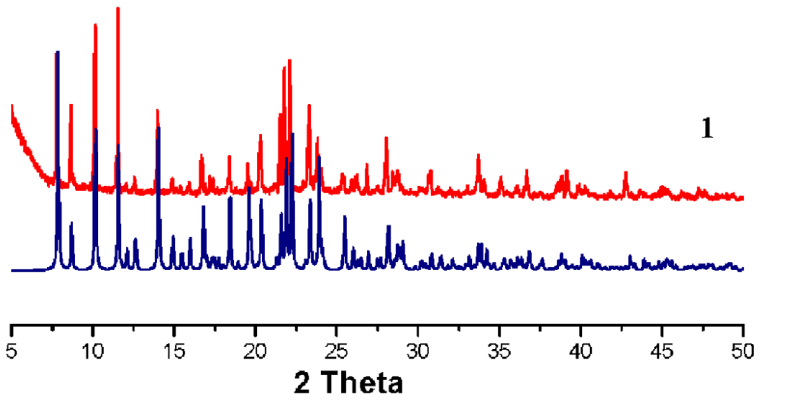
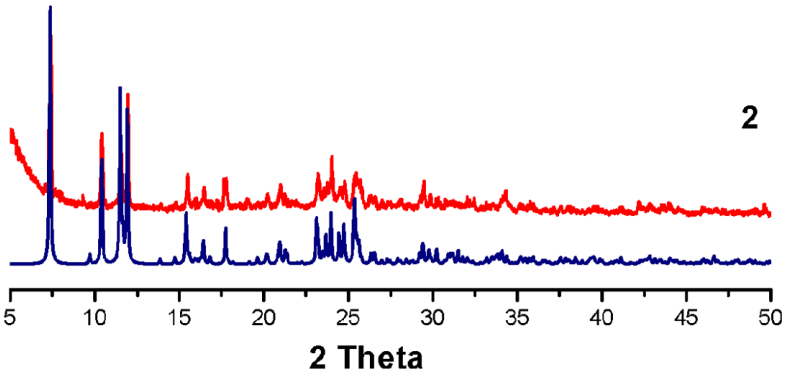
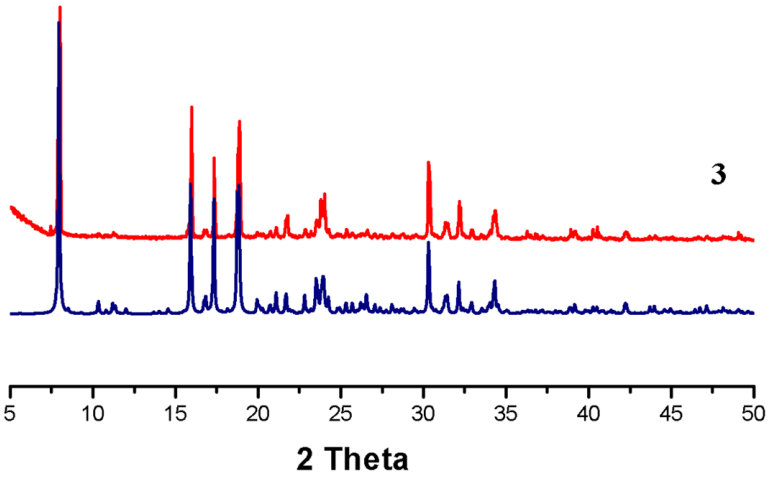
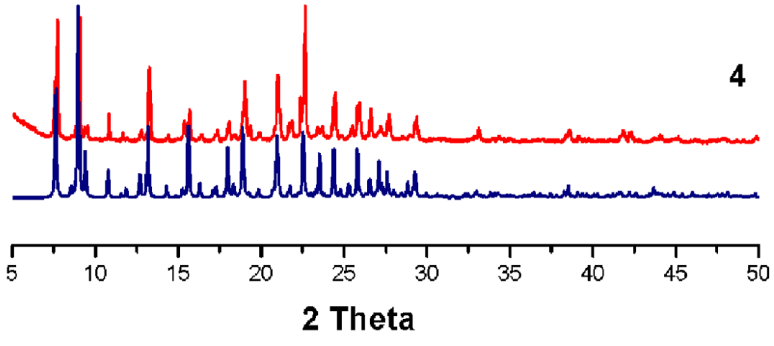


Fig. S5 The TGA curves of compounds **1-7**.









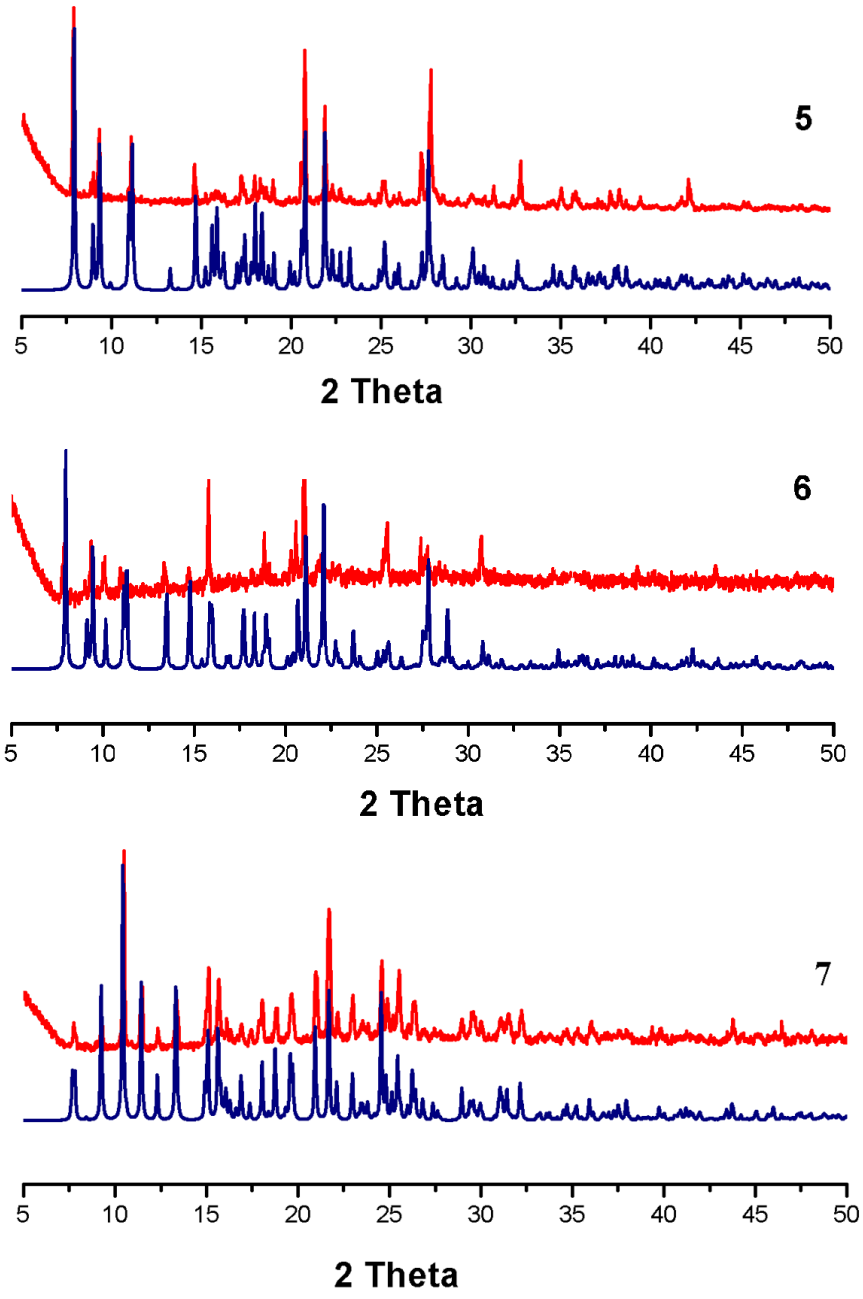


Fig. S6 The simulated (red) and experimental (blue) XRD patterns for **1**-**7**.