Electronic Supplementary Information (ESI)

A series of mixed-ligand 2D and 3D coordination polymers assembled from a novel multifunctional pyridine-tricarboxylate building block: hydrothermal syntheses, structural and topological diversity, and magnetic and luminescent properties

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Table S1 Selected bond lengths [Å] and angles [°] for the compounds **1-6**[a].

1					
Cd(1)-O(1)	2.458(3)	Cd(1)-O(2)	2.345(3)	Cd(1)-O(6)#1	2.245(3)
Cd(1)-O(7)	2.195(2)	Cd(1)-N(2)	2.418(4)	Cd(1)-N(3)	2.351(3)
Cd(2)-O(3)#3	2.279(3)	Cd(2)-O(5)#1	2.336(3)	Cd(2)-O(7)	2.280(2)
Cd(2)-O(7)#2	2.275(2)	Cd(2)-N(4)	2.433(3)	Cd(2)-N(5)	2.338(3)
O(7)-Cd(1)-O(6)#1	107.28(10)	O(7)-Cd(1)-O(2)	96.51(9)	O(6)#1-Cd(1)-O(2)	103.81(11)
O(7)-Cd(1)-N(3)	108.00(10)	O(6)#1-Cd(1)-N(3)	88.26(12)	O(2)-Cd(1)-N(3)	148.19(11)
O(7)-Cd(1)-N(2)	98.57(10)	O(6)#1-Cd(1)-N(2)	150.48(11)	O(2)-Cd(1)-N(2)	86.82(12)
N(3)-Cd(1)-N(2)	70.04(12)	O(7)-Cd(1)-O(1)	150.51(9)	O(6)#1-Cd(1)-O(1)	87.01(10)
O(2)-Cd(1)-O(1)	54.46(9)	N(3)-Cd(1)-O(1)	97.87(10)	N(2)-Cd(1)-O(1)	76.84(11)
O(7)#2-Cd(2)-O(3)#3	90.46(9)	O(7)#2-Cd(2)-O(7)	81.84(9)	O(3)#3-Cd(2)-O(7)	97.52(9)
O(7)#2-Cd(2)-O(5)#1	167.74(10)	O(3)#3-Cd(2)-O(5)#1	80.68(10)	O(7)-Cd(2)-O(5)#1	90.88(9)
O(7)#2-Cd(2)-N(5)	105.88(10)	O(3)#3-Cd(2)-N(5)	155.19(11)	O(7)-Cd(2)-N(5)	103.12(10)
O(5)#1-Cd(2)-N(5)	85.33(11)	O(7)#2-Cd(2)-N(4)	105.27(11)	O(3)#3-Cd(2)-N(4)	87.39(11)
O(7)-Cd(2)-N(4)	171.40(11)	O(5)#1-Cd(2)-N(4)	82.91(11)	N(5)-Cd(2)-N(4)	70.54(12)
Cd(1)-O(7)-Cd(2)	111.62(9)	Cd(1)-O(7)-Cd(2)#2	127.32(12)	Cd(2)#2-O(7)-Cd(2)	98.16(9)
2					
Mn(1)-O(1)	2.191(4)	Mn(1)-O(8)	2.194(4)	Mn(1)-O(12)#1	2.139(4)
Mn(1)-O(13)	2.198(5)	Mn(1)-N(3)	2.270(5)	Mn(1)-N(4)	2.354(5)
Mn(2)-O(2)	2.135(5)	Mn(2)-O(7)	2.156(5)	Mn(2)-O(9)#3	2.185(4)
Mn(2)-O(10)#3	2.304(4)	Mn(2)-O(11)#2	2.115(4)	Mn(3)-O(3)	2.053(6)
Mn(3)-O(4)#4	2.114(5)	Mn(3)-O(5)#5	2.464(8)	Mn(3)-O(6)#5	2.217(6)
Mn(3)-N(5)	2.280(6)	Mn(3)-N(6)	2.259(6)		
O(12)#1-Mn(1)-O(1)	84.74(16)	O(12)#1-Mn(1)-O(8)	94.53(16)	O(1)-Mn(1)-O(8)	82.92(18)
O(12)#1-Mn(1)-O(13)	85.94(17)	O(1)-Mn(1)-O(13)	168.66(17)	O(8)-Mn(1)-O(13)	91.4(2)
O(12)#1-Mn(1)-N(3)	177.54(19)	O(1)-Mn(1)-N(3)	97.63(17)	O(8)-Mn(1)-N(3)	85.15(17)
O(13)-Mn(1)-N(3)	91.63(19)	O(12)#1-Mn(1)-N(4)	108.83(18)	O(1)-Mn(1)-N(4)	86.64(18)
O(8)-Mn(1)-N(4)	153.39(17)	O(13)-Mn(1)-N(4)	102.52(19)	N(3)-Mn(1)-N(4)	72.04(19)
O(11)#2-Mn(2)-O(2)	93.11(18)	O(11)#2-Mn(2)-O(7)	101.31(18)	O(2)-Mn(2)-O(7)	94.0(2)
O(11)#2-Mn(2)-O(9)#3	99.80(16)	O(2)-Mn(2)-O(9)#3	109.72(18)	O(7)-Mn(2)-O(9)#3	147.11(18)
O(11)#2-Mn(2)-O(10)#3	85.65(17)	O(2)-Mn(2)-O(10)#3	167.51(19)	O(7)-Mn(2)-O(10)#3	98.41(18)
O(9)#3-Mn(2)-O(10)#3	58.44(17)	O(3)-Mn(3)-O(4)#4	107.0(3)	O(3)-Mn(3)-O(6)#5	135.2(2)
O(4)#4-Mn(3)-O(6)#5	82.3(2)	O(3)-Mn(3)-N(6)	108.1(2)	O(4)#4-Mn(3)-N(6)	138.3(2)
O(6)#5-Mn(3)-N(6)	88.5(2)	O(3)-Mn(3)-N(5)	88.8(2)	O(4)#4-Mn(3)-N(5)	86.3(2)
O(6)#5-Mn(3)-N(5)	135.9(2)	N(6)-Mn(3)-N(5)	72.6(2)	O(3)-Mn(3)-O(5)#5	84.0(2)
O(4)#4-Mn(3)-O(5)#5	116.3(2)	O(6)#5-Mn(3)-O(5)#5	54.1(2)	N(6)-Mn(3)-O(5)#5	89.4(2)
N(5)-Mn(3)-O(5)#5	157.5(3)				
3					
Cd(1)-O(4)	2.394(5)	Cd(1)-N(1)	2.308(5)	Cd(1)-N(2)	2.317(6)
Cd(1)-N(3)	2.303(6)	Cd(1)-N(6)	2.485(6)	Cd(1)-N(7)	2.291(6)
Cd(2)-O(1)#2	2.528(6)	Cd(2)-O(2)#2	2.287(5)	Cd(2)-O(5)#1	2.212(5)
Cd(2)-N(5)	2.344(6)	Cd(2)-N(10)	2.357(6)	Cd(2)-N(11)	2.411(8)
N(7)-Cd(1)-N(3)	106.5(2)	N(7)-Cd(1)-N(1)	152.3(2)	N(3)-Cd(1)-N(1)	95.98(19)

N(7)-Cd(1)-N(2)	94.1(2)	N(3)-Cd(1)-N(2)	73.77(19)	N(1)-Cd(1)-N(2)	107.8(2)
N(7)-Cd(1)-O(4)	84.7(2)	N(3)-Cd(1)-O(4)	168.62(19)	N(1)-Cd(1)-O(4)	72.73(19)
N(2)-Cd(1)-O(4)	107.75(19)	N(7)-Cd(1)-N(6)	72.5(2)	N(3)-Cd(1)-N(6)	89.72(19)
N(1)-Cd(1)-N(6)	92.03(19)	N(2)-Cd(1)-N(6)	155.1(2)	O(4)-Cd(1)-N(6)	92.14(18)
O(5)#1-Cd(2)-O(2)#2	154.7(2)	O(5)#1-Cd(2)-N(5)	93.51(19)	O(2)#2-Cd(2)-N(5)	93.86(18)
O(5)#1-Cd(2)-N(10)	90.7(2)	O(2)#2-Cd(2)-N(10)	113.3(2)	N(5)-Cd(2)-N(10)	91.3(2)
O(5)#1-Cd(2)-N(11)	89.8(2)	O(2)#2-Cd(2)-N(11)	90.5(2)	N(5)-Cd(2)-N(11)	162.3(3)
N(10)-Cd(2)-N(11)	71.3(3)	O(5)#1-Cd(2)-O(1)#2	101.5(2)	O(2)#2-Cd(2)-O(1)#2	53.6(2)
N(5)-Cd(2)-O(1)#2	115.3(2)	N(10)-Cd(2)-O(1)#2	149.6(3)	N(11)-Cd(2)-O(1)#2	80.9(3)
4					
Pb(1)-O(1)	2.570(5)	Pb(1)-O(2)	2.665(6)	Pb(1)-O(6)#1	2.624(7)
Pb(1)-O(7)#2	2.596(5)	Pb(1)-O(7)	2.620(6)	Pb(1)-N(2)	2.799(7)
Pb(1)-N(3)	2.720(8)	Pb(2)-O(3)	2.647(6)	Pb(2)-O(4)	2.350(6)
Pb(2)-O(5)#3	2.441(6)	Pb(2)-N(4)	2.615(7)	Pb(2)-N(5)	2.556(7)
O(1)-Pb(1)-O(2)	49.7(2)	O(1)-Pb(1)-O(6)#1	75.02(19)	O(1)-Pb(1)-O(7)#2	135.53(19)
O(1)-Pb(1)-O(7)	127.89(19)	O(1)-Pb(1)-N(2)	138.9(2)	O(1)-Pb(1)-N(3)	82.2(2)
O(2)-Pb(1)-N(2)	136.6(2)	O(2)-Pb(1)-N(3)	90.0(2)	O(6)#1-Pb(1)-O(2)	122.84(19)
O(6)#1-Pb(1)-N(2)	93.0(2)	O(6)#1-Pb(1)-N(3)	96.4(2)	O(7)#2-Pb(1)-O(2)	117.1(2)
O(7)-Pb(1)-O(2)	79.08(19)	O(7) -Pb(1)-O(6)#1	156.95(17)	O(7)#2-Pb(1)-O(6)#1	90.62(19)
O(7)#2-Pb(1)-O(7)	71.1(2)	O(7)#2-Pb(1)-N(2)	82.5(2)	O(7)-Pb(1)-N(2)	71.2(2)
O(7)-Pb(1)-N(3)	90.2(2)	O(7)#2-Pb(1)-N(3)	141.9(2)	N(3)-Pb(1)-N(2)	59.8(2)
O(4)-Pb(2)-O(3)	52.13(19)	O(4)-Pb(2)-O(5)#3	76.6(2)	O(4)-Pb(2)-N(4)	72.2(2)
O(4)-Pb(2)-N(5)	82.1(2)	O(5)#3-Pb(2)-O(3)	110.7(2)	O(5)#3-Pb(2)-N(4)	131.9(2)
O(5)#3-Pb(2)-N(5)	76.0(2)	N(4)-Pb(2)-O(3)	76.8(2)	N(5)-Pb(2)-O(3)	127.5(2)
N(5)-Pb(2)-N(4)	64.3(2)				
5					
Cd(1)-O(1)	2.281(4)	Cd(1)-O(4)#1	2.233(4)	Cd(1)-O(7)	2.531(5)
Cd(1)-O(8)	2.262(4)	Cd(1)-N(4)	2.344(4)	Cd(1)-N(5)	2.381(4)
Cd(2)-O(1)	2.316(4)	Cd(2)-O(2)	2.533(19)	Cd(2)-O(3)#1	2.373(4)
Cd(2)-O(5)#2	2.236(6)	Cd(2)-N(3)	2.352(6)	Cd(2)-N(2)	2.319(5)
O(4)#1-Cd(1)-O(8)	98.72(18)	O(4)#1-Cd(1)-O(1)	90.64(17)	O(8)-Cd(1)-O(1)	135.51(16)
O(4)#1-Cd(1)-N(4)	148.58(17)	O(8)-Cd(1)-N(4)	98.47(17)	O(1)-Cd(1)-N(4)	95.25(15)
O(4)#1-Cd(1)-N(5)	79.90(16)	O(8)-Cd(1)-N(5)	106.34(16)	O(1)-Cd(1)-N(5)	118.12(14)
N(4)-Cd(1)-N(5)	70.10(17)	O(4)#1-Cd(1)-O(7)	125.6(2)	O(8)-Cd(1)-O(7)	52.94(17)
O(1)-Cd(1)-O(7)	86.49(17)	N(4)-Cd(1)-O(7)	85.6(2)	N(5)-Cd(1)-O(7)	146.05(18)
O(5)#2-Cd(2)-N(2)	118.6(2)	O(5)#2-Cd(2)-O(1)	108.3(2)	N(2)-Cd(2)-O(1)	109.13(18)
O(5)#2-Cd(2)-N(3)	135.9(2)	N(2)-Cd(2)-N(3)	71.7(2)	O(1)-Cd(2)-N(3)	107.20(16)
O(5)#2-Cd(2)-O(3)#1	80.73(19)	N(2)-Cd(2)-O(3)#1	151.62(18)	O(1)-Cd(2)-O(3)#1	80.84(14)
N(3)-Cd(2)-O(3)#1	79.96(18)	O(5)#2-Cd(2)-O(2)	81.9(4)	N(2)-Cd(2)-O(2)	85.5(5)
O(1)-Cd(2)-O(2)	51.4(4)	N(3)-Cd(2)-O(2)	141.8(4)	O(3)#1-Cd(2)-O(2)	119.4(5)
Cd(1)-O(1)-Cd(2)	117.63(16)				
6					
Zn(1)-O(3)	1.995(6)	Zn(1)-O(4)#1	1.972(5)	Zn(1)-O(6)#2	1.935(5)
Zn(1)-N(1)	2.037(6)	Zn(2)-O(1)	2.063(6)	Zn(2)-O(2)	2.412(7)
Zn(2)-O(7)	2.313(10)	Zn(2)-O(8)	2.109(9)	Zn(2)-N(3)	2.054(8)
Zn(2)-N(2)	2.065(6)				
O(3)-Zn(1)-N(1)	96.1(2)	O(4)#2-Zn(1)-O(3)	93.9(2)	O(4)#2-Zn(1)-N(1)	105.2(2)
O(6)#1-Zn(1)-O(3)	109.9(2)	O(6)#1-Zn(1)-O(4)#2	140.3(2)	O(6)#1-Zn(1)-N(1)	103.3(3)
O(1)-Zn(2)-O(2)	57.9(2)	O(1)-Zn(2)-O(7)	155.9(3)	O(1)-Zn(2)-O(8)	101.7(3)
O(1)-Zn(2)-N(2)	101.8(3)	O(7)-Zn(2)-O(2)	105.5(3)	O(8)-Zn(2)-O(2)	87.8(3)

O(8)-Zn(2)-O(7)	57.7(3)	N(3)-Zn(2)-O(1)	99.1(3)	N(3)-Zn(2)-O(2)	157.0(3)
N(3)-Zn(2)-O(7)	96.5(4)	N(3)-Zn(2)-O(8)	98.6(3)	N(3)-Zn(2)-N(2)	96.3(3)
N(2)-Zn(2)-O(2)	88.7(3)	N(2)-Zn(2)-O(7)	94.5(3)	N(2)-Zn(2)-O(8)	149.7(3)

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

Table S2 Hydrogen bonds in crystal packing [Å, °] of **1**–**4**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(7)-H(1)···O(4)	0.85	2.02	2.873	179.8	-*x*, -*y*+1, -*z*
	O(8)-H(1W)···O(2)	0.85	2.07	2.924	179.6	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(2W)···O(4)	0.85	2.01	2.862	179.4	*x*+1, *y*, *z*+1
2	O(14)-H(4W)···N(2)	0.86	1.77	2.628	176.6	-*x*-1/2, -*y*+1/2, *z*+1/2
	O(13)-H(2W) ···O(14)	0.90	2.10	2.743	127.9	-*x*+1/2, -*y*+1/2, *z*-1/2
	O(13)-H(1W) ···O(10)	0.90	1.81	2.708	173.3	*x*-1/2, -*y*+1/2, *z*-1/2
3	N(13)-H(13)···O(6)	0.86	2.36	3.089	142.5	-*x*, *y*-3//2, -*z*+1/2
	N(12)-H(12)···O(6)	0.86	1.88	2.686	155.0	-*x*, *y*-3//2, -*z*+1/2
	N(9)-H(9)···O(4)	0.86	1.93	2.742	158.1	-*x*, -*y*, -*z*
	N(8)-H(8)···O(3)	0.86	1.91	2.766	170.8	-*x*, -*y*, -*z*
	N(4)-H(4)···O(2)	0.86	1.90	2.745	168.7	-*x*+1/2, -*y*+1/2, -*z*+1/2
4	O(11)-H(1W)···O(3)	0.86	2.15	3.011	178.8	-*x*+1, -*y*+1, -*z*+1

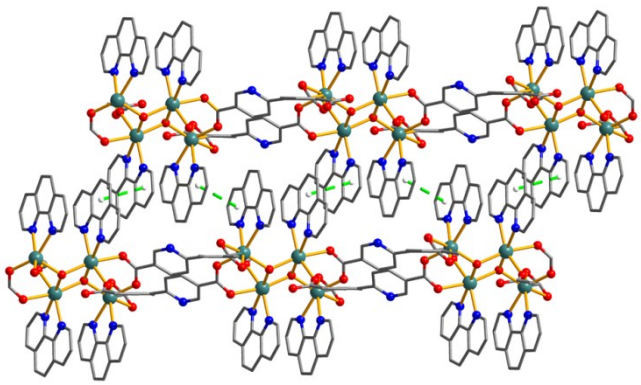

Fig. S1 The π-π stacking interactions in **1** (green dashed lines represent π-π stacking interactions).

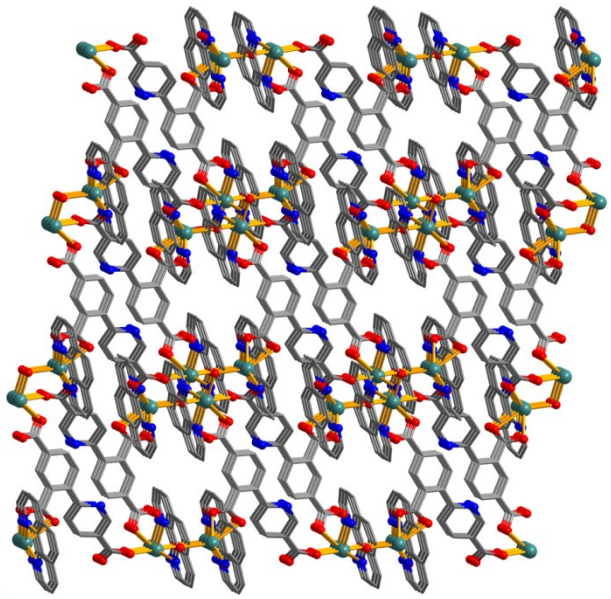

Fig. S2 A perspective of 3D supramolecular framework in **1** (view along the a*b* plane).

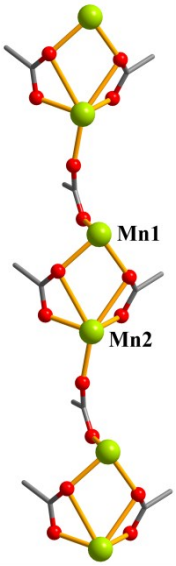

Fig. S3 Bridging of the dimeric Mn_2 units by carboxylate groups in **2**.

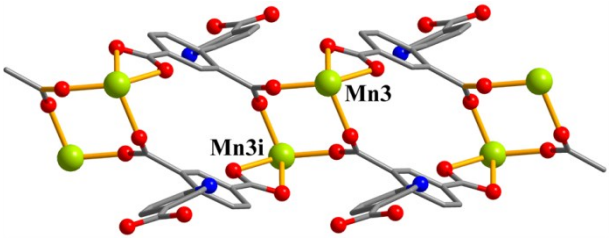

Fig. S4 Bridging of the dimeric Mn_2 units by L^{3-} ligands in **2**. Symmetry code: i = $-x + 2, -y, -z + 1$.

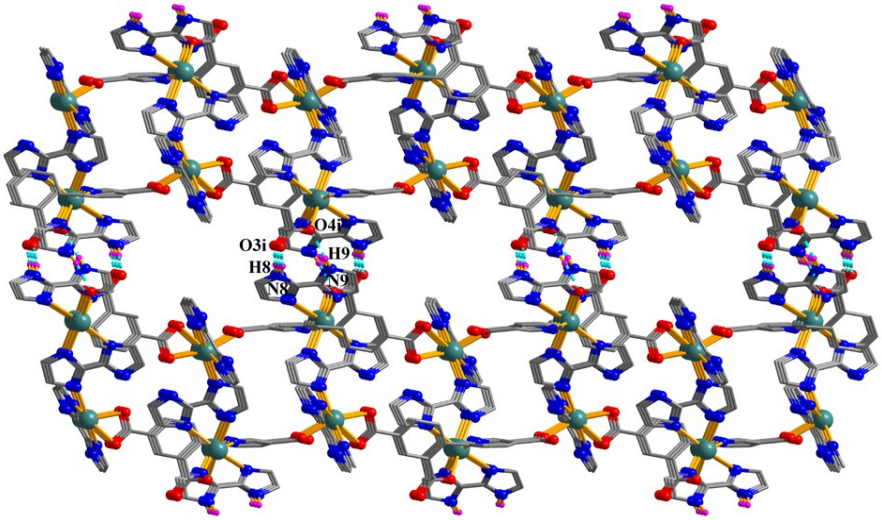

Fig. S5 A perspective of 3D supramolecular framework in **3** (view along the a*b* plane; blue dashed lines represent the hydrogen bond). Symmetry code: i = –*x*, –*y*, –*z*.

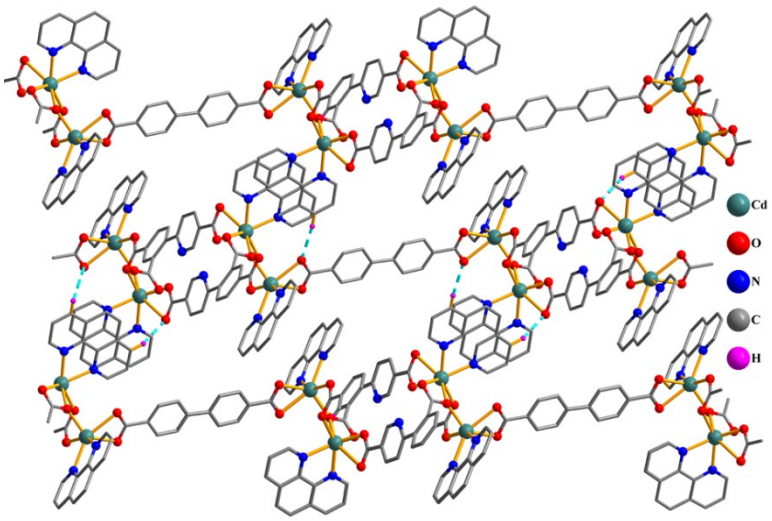

Fig. S6 3D supramolecular structure formed by hydrogen bonding interactions between the adjacent layers in **5** (blue dashed lines represent the C–H···O H-bond).

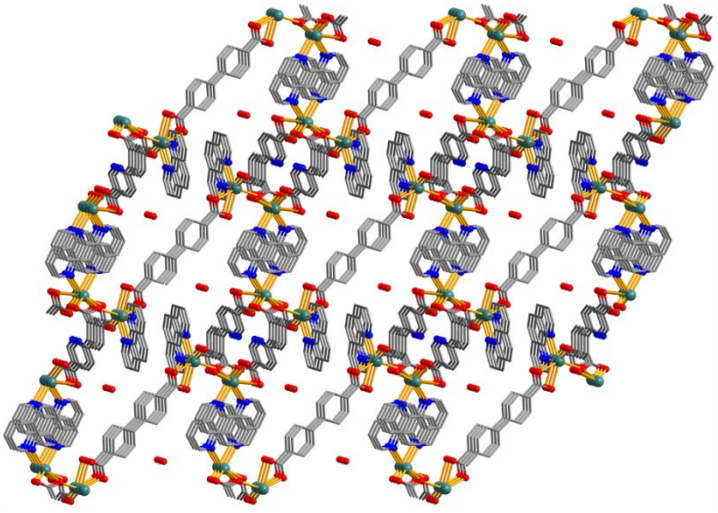

Fig. S7 A perspective of 3D supramolecular framework of **5** along the *bc* plane.

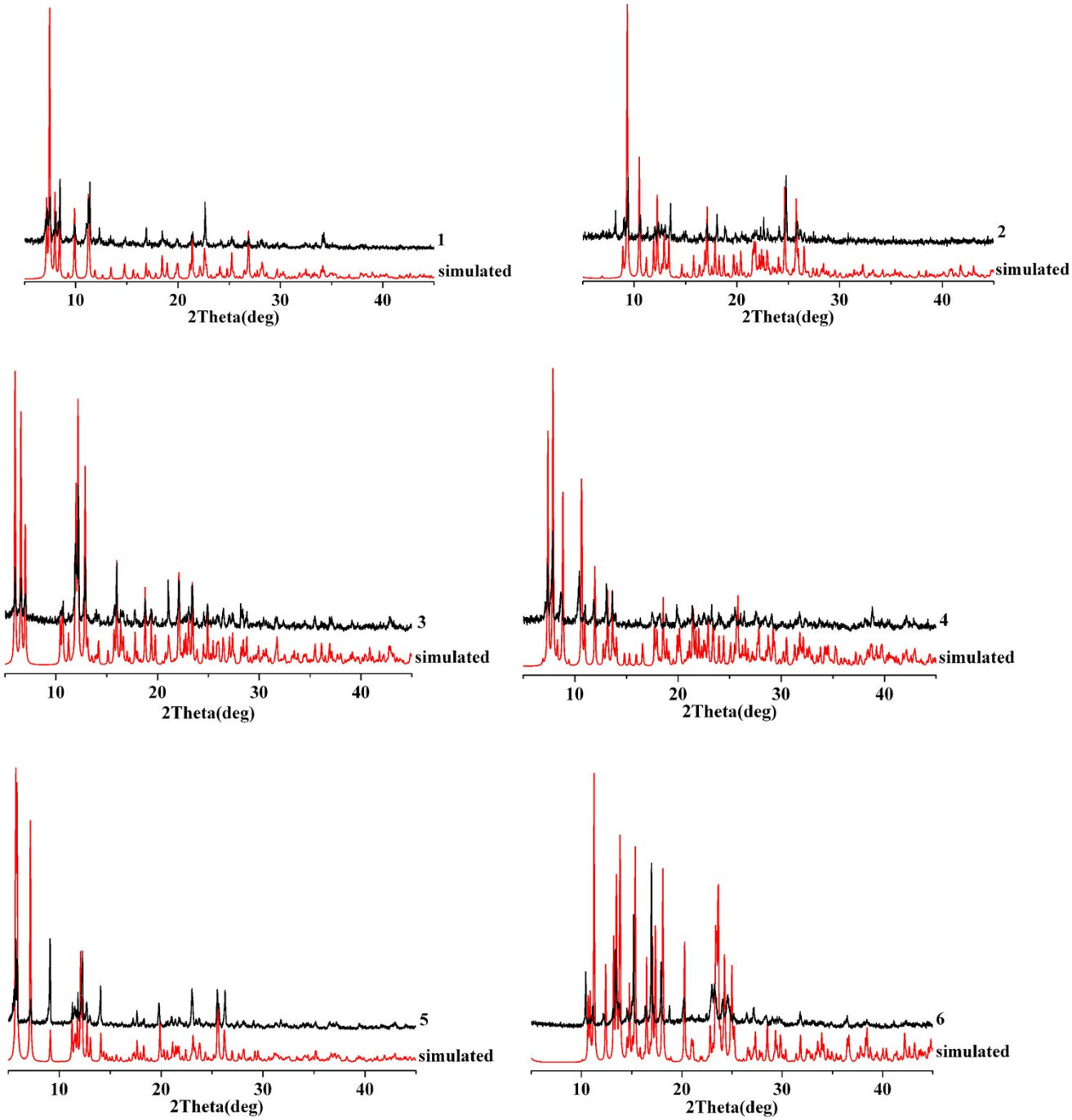

Fig. S8 The PXRD patterns of compounds **1**–**6** at room temperature.

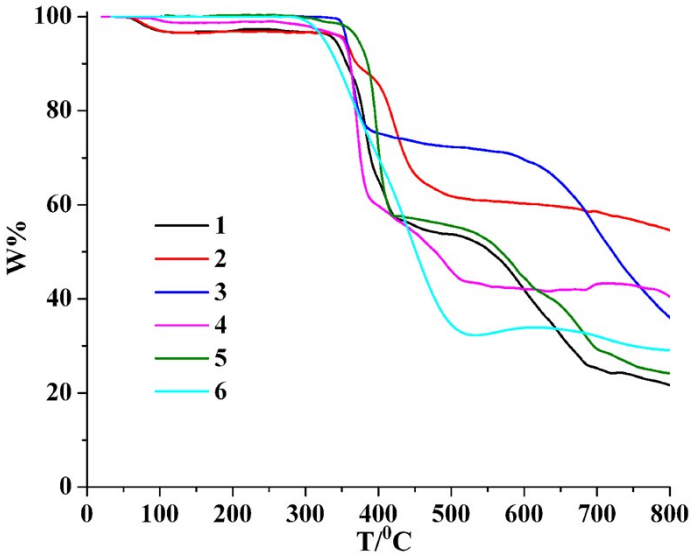

Fig. S9 Thermogravimetric analysis (TGA) curves of compounds **1**–**6**.