Supporting Information

Syntheses, Characterization and Properties of Three-Dimensional Pillared Frameworks with Entanglement

Zhi Su,[†] Jian Fan,[†] Min Chen,[†] Taka-aki Okamura,[‡] Wei-Yin Sun*,[†]

[†]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China, and* [‡]*Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Table S1 Selected Bond Lengths (Å) and Bond Angles (º) for Complexes **1 – 6**

	1		
Cd1-O1#1	2.255(4)	Cd1-O9	2.443(4)
Cd1-N7#2	2.257(5)	Cd1-O5	2.447(4)
Cd1-O6	2.398(5)	Cd1-O2#1	2.485(4)
Cd1-O10	2.434(6)	Cd2-O11	2.315(4)
Cd2-N1	2.281(4)	Cd2-O9	2.318(4)
Cd2-O7	2.311(4)	Cd2-O5	2.334(4)
Cd2-N5	2.312(5)	Cd3-O3#4	2.344(5)
Cd3-N3#3	2.297(5)	Cd3-O4#4	2.353(5)
Cd3-O7	2.323(4)	Cd3-O11	2.356(4)
Cd3-O13	2.324(5)	O1#1-Cd1-O2#1	54.79(16)
O1#1-Cd1-N7#2	102.42(19)	N7#2-Cd1-O2#1	84.44(18)
O1#1-Cd1-O6	91.99(18)	O6-Cd1-O2#1	81.86(17)
N7#2-Cd1-O6	149.1(2)	O10-Cd1-O2#1	136.03(15)
O1#1-Cd1-O10	81.34(17)	O9-Cd1-O2#1	165.93(14)
N7#2-Cd1-O10	104.3(2)	O5-Cd1-O2#1	107.70(15)
O6-Cd1-O10	104.8(2)	N7#2-Cd1-O5	106.06(18)

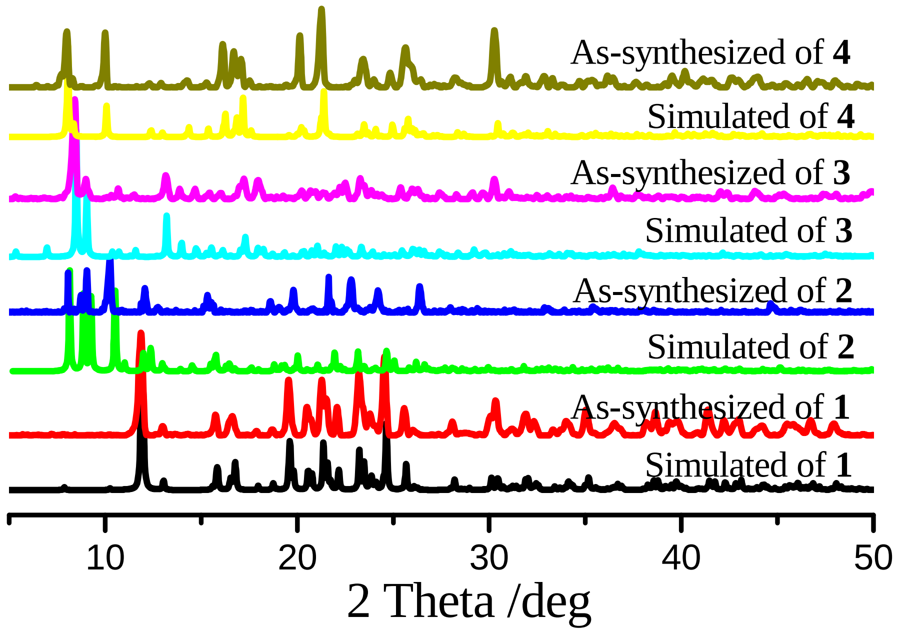
O1#1-Cd1-O9	133.46(16)	O6-Cd1-O5	53.27(14)
N7#2-Cd1-O9	82.40(17)	O10-Cd1-O5	110.74(15)
O6-Cd1-O9	107.25(16)	O9-Cd1-O5	71.44(13)
O10-Cd1-O9	53.17(14)	O7-Cd2-O9	175.64(14)
O1#1-Cd1-O5	144.71(17)	N5-Cd2-O9	88.07(16)
N1-Cd2-O7	90.21(15)	O11-Cd2-O9	103.37(14)
N1-Cd2-N5	178.15(17)	N1-Cd2-O5	84.23(15)
O7-Cd2-N5	87.94(16)	O7-Cd2-O5	106.49(14)
N1-Cd2-O11	93.38(15)	N5-Cd2-O5	96.40(16)
O7-Cd2-O11	74.58(14)	O11-Cd2-O5	177.36(13)
N5-Cd2-O11	86.03(16)	O9-Cd2-O5	75.73(14)
N1-Cd2-O9	93.77(16)	O7-Cd3-O4#4	95.3(2)
N3#3-Cd3-O7	85.70(16)	O13-Cd3-O4#4	116.7(2)
N3#3-Cd3-O13	86.05(18)	O3#4-Cd3-O4#4	54.99(19)
O7-Cd3-O13	142.43(17)	N3#3-Cd3-O11	121.54(17)
N3#3-Cd3-O3#4	82.13(19)	O7-Cd3-O11	73.59(14)
O7-Cd3-O3#4	114.87(17)	O13-Cd3-O11	79.87(17)
O13-Cd3-O3#4	100.1(2)	O3#4-Cd3-O11	156.09(17)
N3#3-Cd3-O4#4	133.11(19)	O4#4-Cd3-O11	103.33(17)
		2	
Co1-O3	2.051(4)	Co1-O13	2.082(5)
Co1-O7	2.209(4)	Co1-N12	2.119(5)
Co1-O9	2.113(4)	Co1-N132#5	2.111(5)
Co2-O4	2.028(4)	Co2-O9	2.237(4)
Co2-O5	2.211(4)	Co2-O11	2.128(4)
Co2-O7	2.132(4)	Co2-O1#6	1.999(4)
Co3-O5	2.089(4)	Co3-O2#6	2.066(4)
Co3-O11	2.241(4)	Co3-N112#6	2.078(5)
Co3-O14	2.090(5)	Co3-N32#7	2.117(5)
O3-Co1-O7	89.54(17)	O7-Co1-N132#5	173.1(2)
O3-Co1-O9	89.98(18)	O9-Co1-O13	93.92(19)
O3-Co1-O13	175.9(2)	O9-Co1-N12	171.3(2)

O3-Co1-N12	83.41(19)	O9-Co1-N132#5	95.65(19)
O3-Co1-N132#5	86.6(2)	O13-Co1-N12	92.8(2)
O7-Co1-O9	78.61(16)	O13-Co1-N132#5	91.9(2)
O7-Co1-O13	92.33(19)	N12-Co1-N132#5	89.6(2)
O7-Co1-N12	95.7(2)	O5-Co2-O11	78.82(15)
O4-Co2-O5	80.78(16)	O1#6-Co2-O9	81.50(16)
O4-Co2-O7	92.56(17)	O1#6-Co2-O11	91.00(16)
O4-Co2-O9	99.86(16)	O1#6-Co2-O5	97.87(16)
O4-Co2-O11	87.86(16)	O7-Co2-O9	77.58(16)
O1#6-Co2-O4	178.37(19)	O7-Co2-O11	179.12(18)
O5-Co2-O7	102.01(16)	O1#6-Co2-O7	88.60(17)
O5-Co2-O9	179.24(17)	O9-Co2-O11	101.59(16)
O5-Co3-O11	78.95(16)	O11-Co3-N32#7	169.80(19)
O5-Co3-O14	94.85(19)	O2#6-Co3-O14	174.95(19)
O2#6-Co3-O5	89.52(17)	O14-Co3-N112#6	93.9(2)
O5-Co3-N112#6	167.4(2)	O14-Co3-N32#7	90.1(2)
O5-Co3-N32#7	90.88(19)	O2#6-Co3-N112#6	82.19(19)
O11-Co3-O14	90.04(17)	O2#6-Co3-N32#7	87.34(19)
O2#6-Co3-O11	93.29(16)	N32#7-Co3-N112#6	98.2(2)
O11-Co3-N112#6	92.0(2)		
		3	
Cd1-N3	2.238(3)	Cd1-O1#9	2.320(3)
Cd1-O4	2.279(3)	Cd1-O3	2.445(3)
Cd1-N1#8	2.301(3)	Cd1-O2#9	2.462(3)
N3-Cd1-O4	143.19(12)	N1#8-Cd1-O3	99.70(11)
N3-Cd1-N1#8	96.98(11)	O1#9-Cd1-O3	139.28(10)
O4-Cd1-N1#8	112.11(11)	N3-Cd1-O2#9	91.21(10)
N3-Cd1-O1#9	120.58(12)	O4-Cd1-O2#9	86.05(10)
O4-Cd1-O1#9	86.95(11)	N1#8-Cd1-O2#9	131.58(11)
N1#8-Cd1-O1#9	81.17(11)	O1#9-Cd1-O2#9	54.34(9)
N3-Cd1-O3	99.86(11)	O3-Cd1-O2#9	125.78(10)
O4-Cd1-O3	54.67(9)		

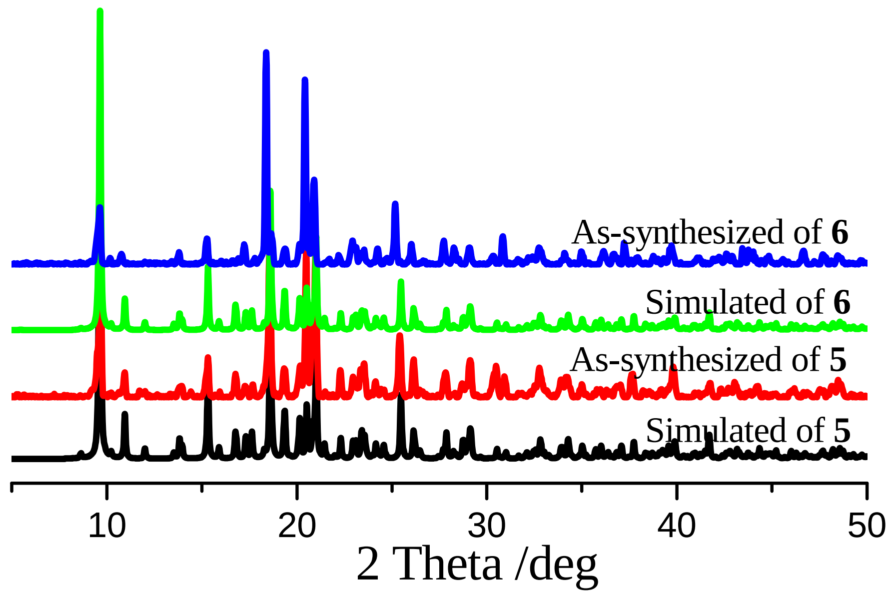
	4		
Cd1-O5	2.258(3)	Cd1-O1#11	2.376(2)
Cd1-N1	2.272(3)	Cd1-O2#11	2.508(3)
Cd1- O4#10	2.319(3)	Cd1-O4	2.601(3)
Cd1-O3	2.336(2)	O5-Cd1-O2#11	88.35(10)
O5-Cd1-N1	173.22(11)	N1-Cd1-O2#11	88.36(10)
O5-Cd1-O4#10	88.40(10)	O4#10-Cd1-O2#11	97.22(9)
N1-Cd1-O4#10	86.13(10)	O3-Cd1-O2#11	140.25(8)
O5-Cd1-O3	90.94(11)	O1#11-Cd1-O2#11	53.50(9)
N1-Cd1-O3	95.38(10)	O5-Cd1-O4	90.63(10)
O4#10-Cd1-O3	122.49(9)	N1-Cd1-O4	91.33(10)
O5-Cd1-O1#11	93.32(9)	O4#10-Cd1-O4	70.61(9)
N1-Cd1-O1#11	89.48(9)	O3-Cd1-O4	51.89(8)
O4#10-Cd1-O1#11	150.55(9)	O1#11-Cd1-O4	138.67(8)
O3-Cd1-O1#11	86.90(9)	O2#11-Cd1-O4	167.82(8)
	5		
Cd1-N3#12	2.227(3)	Cd1-N1#13	2.288(3)
Cd1-O1	2.259(2)	Cd1-O4	2.324(3)
Cd1-O2	2.518(2)	Cd1-O3	2.328(3)
N3#12-Cd1-O1	141.41(9)	O3-Cd1-O4	55.68(10)
N3#12-Cd1-N1#13	89.86(10)	N1#13-Cd1-O3	143.98(10)
O1-Cd1-N1#13	95.00(10)	N3#12-Cd1-O2	87.65(9)
N3#12-Cd1-O4	117.08(10)	O1-Cd1-O2	54.27(8)
O4-Cd1-O1	101.35(9)	N1#13-Cd1-O2	89.05(10)
O4-Cd1-N1#13	88.31(10)	O2-Cd1-O4	155.11(10)
N3#12-Cd1-O3	106.57(11)	O2-Cd1-O3	122.68(10)
O1-Cd1-O3	91.54(11)		
	6		
Cd1-N3#14	2.196(4)	Cd1-O1	2.226(3)
Cd1-N1#15	2.275(5)	Cd1-O4	2.331(4)
Cd1-O3	2.348(5)	Cd1-O2	2.530(4)
N3#14-Cd1-O1	141.71(14)	N3#14-Cd1-N1#15	89.50(16)

O1-Cd1-N1#15	95.24(16)	N3#14-Cd1-O4	111.26(19)
O1-Cd1-O4	106.88(18)	N1#15-Cd1-O4	87.78(18)
N3#14-Cd1-O3	107.49(18)	O1-Cd1-O3	91.69(18)
N1#15-Cd1-O3	142.04(17)	O4-Cd1-O3	54.61(18)
N3#14-Cd1-O2	87.21(14)	O1-Cd1-O2	54.96(12)
N1#15-Cd1-O2	89.47(15)	O4-Cd1-O2	161.29(18)
O3-Cd1-O2	124.15(17)		

Symmetry transformations used to generate equivalent atoms: #1 –x, -y, 1-z; #2 x, 1-y, 1/2+z; #3 x, -y, -1/2+z; #4 1/2-x, -1/2+y, 1/2-z; #5 3/2-x, y, -1/2+z; #6 x, 1+y, z; #7 1-x, 1-y, 1/2+z; #8 -3/2+x, 3/2-y, 1/2+z; #9 3/2-x, -1/2+y, 3/2-z; #10 2-x, 2-y, 1-z; #11 2-x, 1+y, 1/2-z; #12 1-x, -1/2+y, 1/2-z; #13 2-x, -1/2+y, 1/2-z, #14 1-x, -1/2+y, -z+1/2; #15 2-x, -1/2+y, -z+1/2.



(a)



(b)

Figure S1. Simulated and as-synthesized PXRD patterns of complexes **1 - 6**.

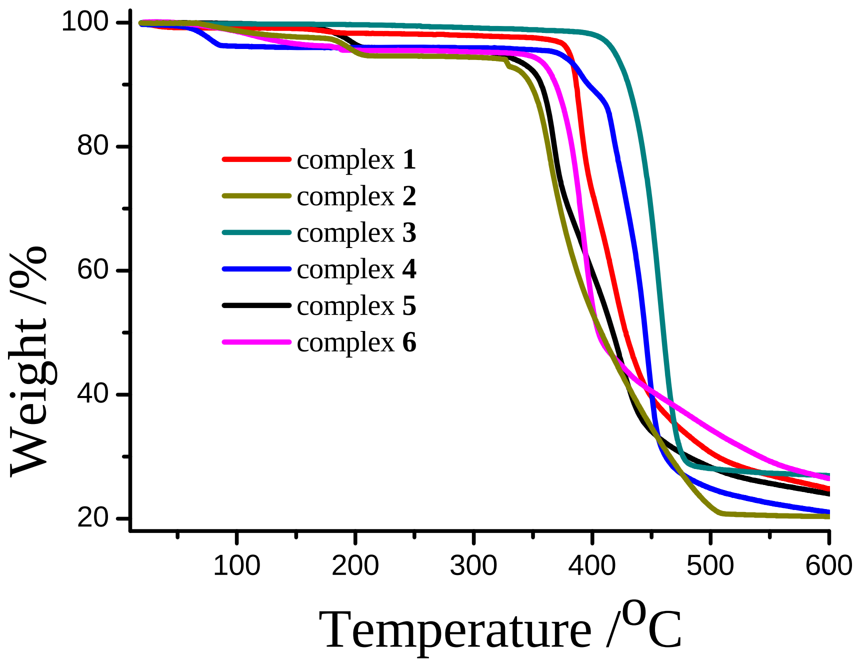


Figure S2. The TG curves of complexes **1 - 6**.

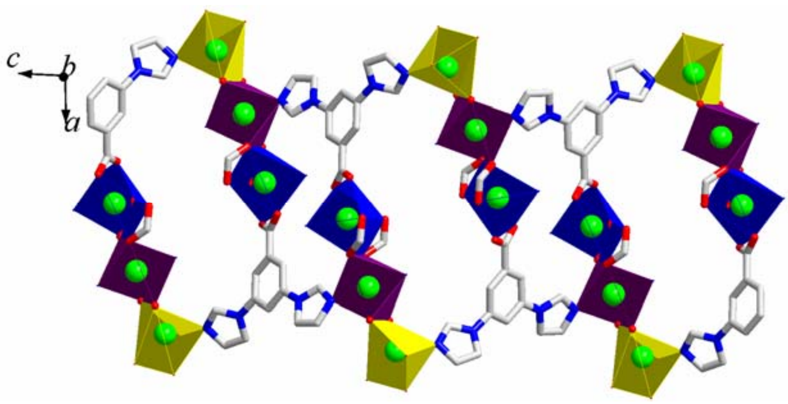


Figure S3. The 1D chain in **1**.

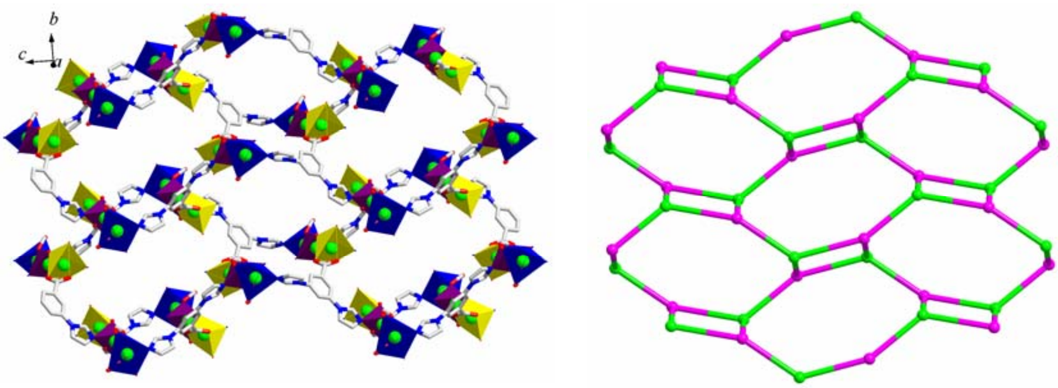


Figure S4. The 2D ($4{\cdot}8^2$) network in **1**.

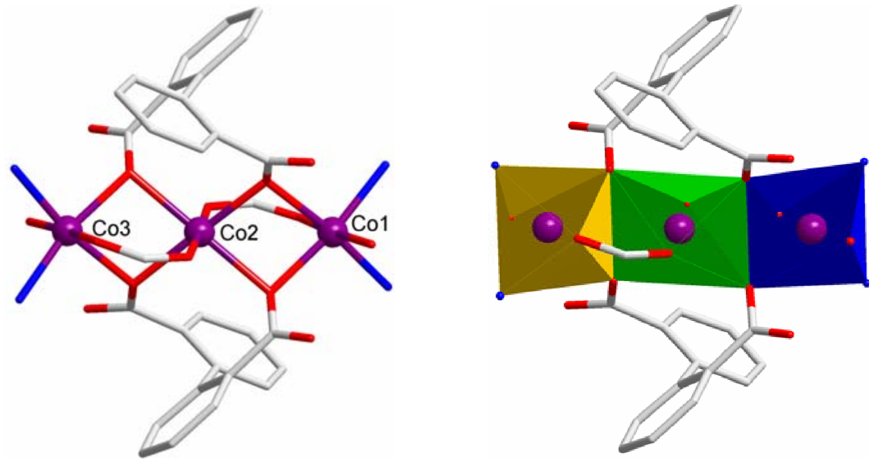


Figure S5. The trinuclear Co(II) subunit in **2**.

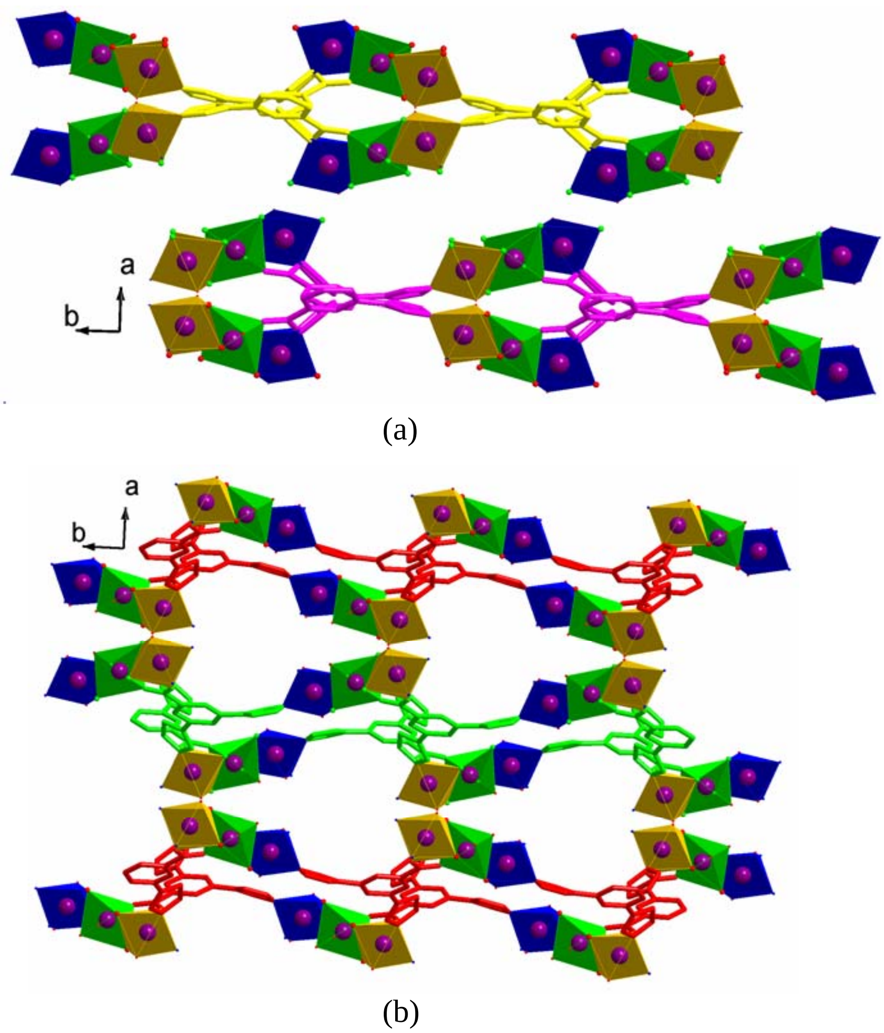


Figure 6. The –ABAB- packing diagram of 2D layers in **2**.

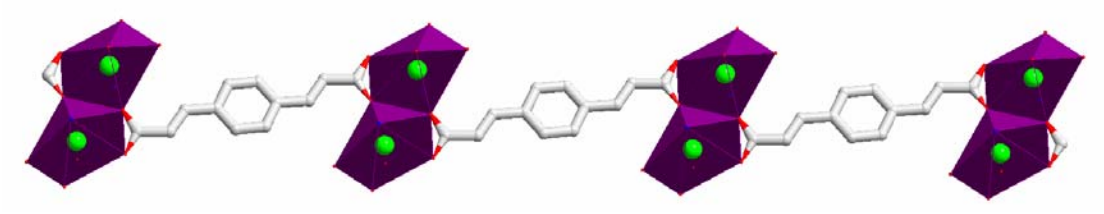


Figure S7. The 1D chain in **4**.

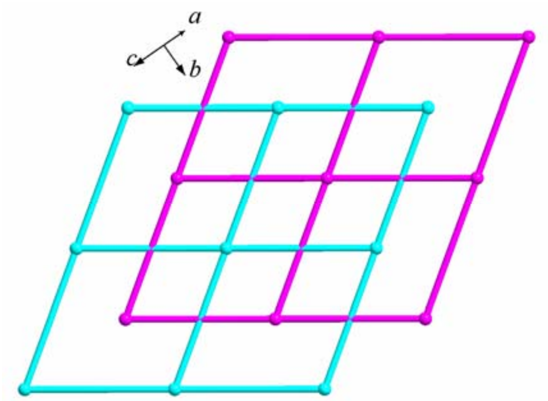


Figure S8. The interpenetrating 2D (4, 4) networks in **4**.

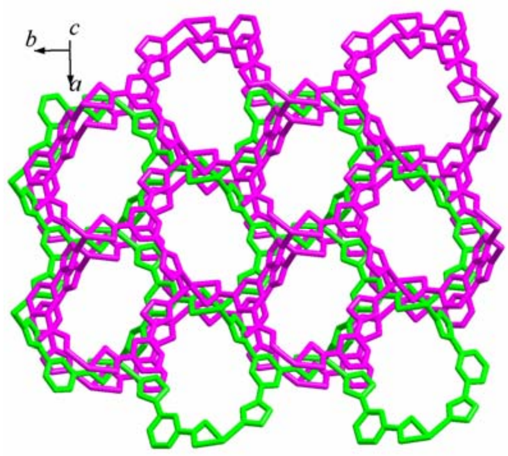


Figure S9. The -ABAB- packing diagram of 2D networks in **5**.

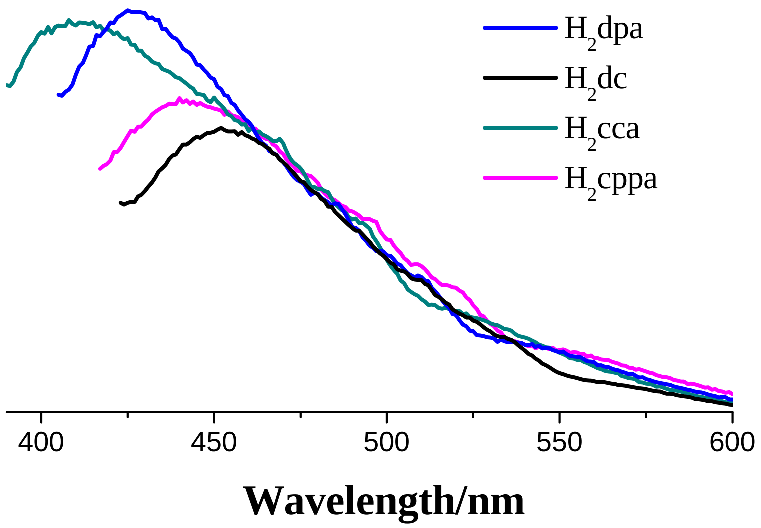


Figure S10. The emission spectra of free H_2dpa, H_2dc, H_2cca and H_2cppa ligands in the solid state at room temperature, respectively.

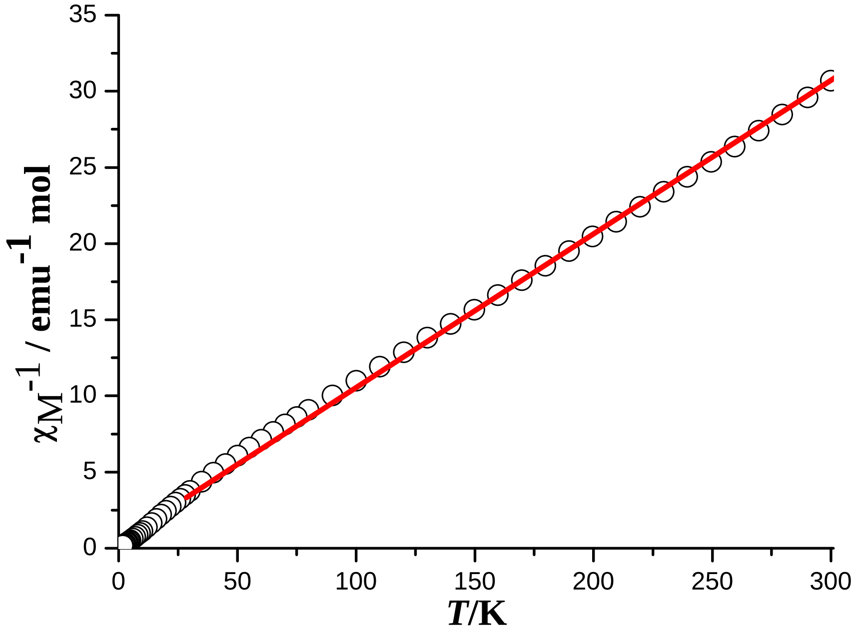


Figure S11. Plot of χ_M^{-1} *vs* T in the range of 1.8-300 K for **2**, the solid line is the linear fitting based on the Curie-Weiss law.

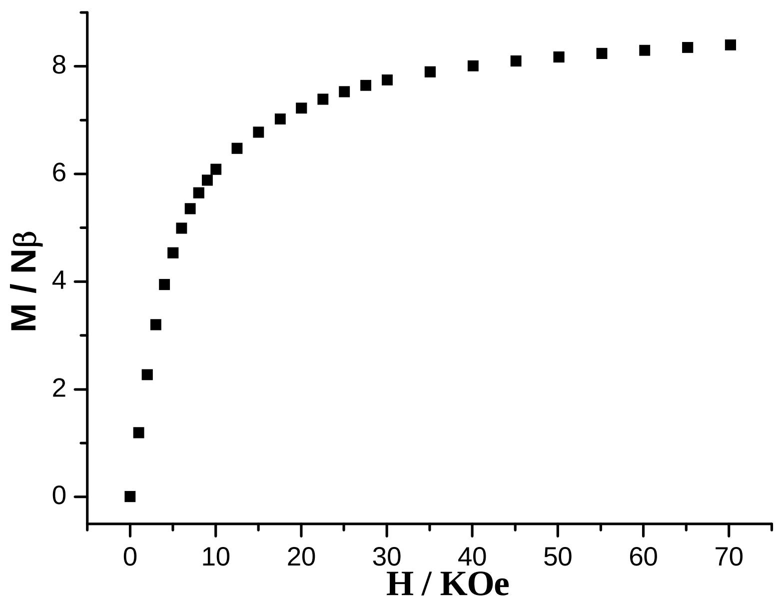


Figure S12. The plot of magnetization versus applied magnetic field of **2** at 1.8 K.

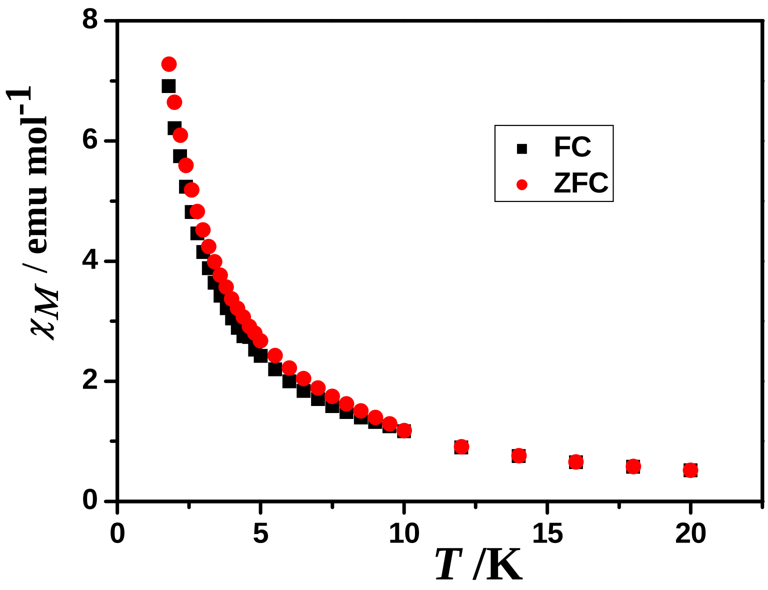


Figure S13. Zero field cooled (ZFC) and field cooled (FC) magnetization versus T measures at 10 Oe for **2**.

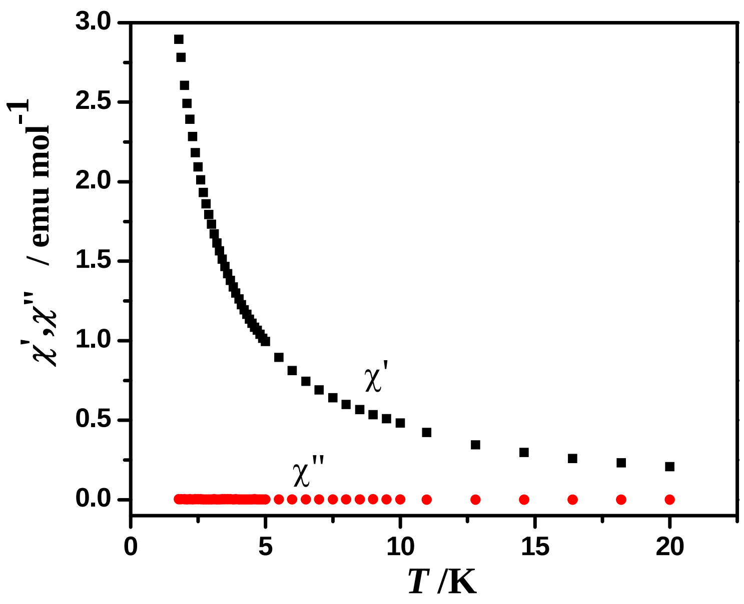


Figure S14. Temperature dependence of *ac* magnetic susceptibility for **2**.