Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

pH-dependent self-assembly of divalent metals with a new ligand containing polycarboxylate: syntheses, crystal structures, luminescent and magnetic properties

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Synthesis of 5-(4-carboxybenzyloxy)isophthalic acid (H_3L)

A mixture of diethyl 5-hydroxyisophthalate (20 mmol, 4.76 g) and NaOH (20 mmol, 0.80 g) in DMF (50 mL) was stirred at 5 ºC for 3 h, then 4-(chloromethyl)benzonitrile (20 mmol, 3.02 g) was added. The mixture was cooled to room temperature after stirring at 80 ºC for 8 h, and then poured into 200 ml of water. A white solid of diethyl 5-(4-cyanobenzyloxy)isophthalate was deposited, which was isolated by filtration in 78 % yield after drying in air.

Then a mixture of diethyl 5-(4-cyanobenzyloxy)isophthalate (15.60 mmol, 5.52 g) and sodium hydroxide (100 mmol, 4.00 g) in water (80 mL) was stirred at 100 ºC for 8 h, and was cooled to room temperature. The mixture was adjusted to approximately pH 4.5 with dilute hydrochloric acid. A white solid of H_3L formed immediately, which was isolated by filtration in 70 % yield after drying in air. Elemental analyses calcd (%) for $C_{16}H_{12}O_7$ (316.26): C, 60.76; H, 3.82. Found C, 60.79; H, 3.80. IR (KBr pellet,

cm^{-1}): 2965 (w), 1734 (s), 1690 (s), 1598 (s), 1460 (m), 1285 (s), 1206 (s), 1121 (m), 1057 (m), 889 (w), 765 (m), 664 (w), 531 (w).

Table S1 Selected bond lengths (Å) and angles (°) for complexes **1-6**[a]

		Complex **1**	
Cd(1)-O(1)	2.256(2)	Cd(1)-O(4)#1	2.305(2)
Cd(1)-O(3)#1	2.454(2)	Cd(1)-N(2)	2.333(2)
Cd(1)-N(1)#2	2.356(2)	Cd(1)-O(1W)	2.376(2)
O(1)-Cd(1)-O(4)#1	142.54(6)	O(1)-Cd(1)-N(2)	88.08(7)
O(4)#1-Cd(1)-N(2)	91.14(8)	O(1)-Cd(1)-N(1)#2	82.06(7)
O(4)#1-Cd(1)-N(1)#2	93.68(8)	N(2)-Cd(1)-N(1)#2	168.97(8)
O(1)-Cd(1)-O(1W)	88.27(7)	O(4)#1-Cd(1)-O(1W)	128.90(7)
N(2)-Cd(1)-O(1W)	84.03(8)	N(1)#2-Cd(1)-O(1W)	100.53(8)
O(1)-Cd(1)-O(3)#1	158.28(7)	O(4)#1-Cd(1)-O(3)#1	54.63(6)
N(2)-Cd(1)-O(3)#1	107.26(7)	N(1)#2-Cd(1)-O(3)#1	83.58(7)
O(1W)-Cd(1)-O(3)#1	78.42(7)		
		Complex **2**	
Cd(1)-N(1)	2.317(2)	Cd(1)-O(1)	2.358(2)
Cd(1)-O(2)	2.332(2)	Cd(2)-N(2)	2.372(2)
Cd(2)-N(3)	2.369(2)	Cd(2)-O(3)#2	2.510(2)
Cd(2)-O(4)#2	2.348(2)	Cd(2)-O(6)#3	2.396(2)
Cd(2)-O(7)#3	2.485(2)	Cd(2)-O(1W)	2.321(2)
N(1)#1-Cd(1)-O(2)	88.59(7)	N(1)-Cd(1)-N(1)#1	180.0
N(1)-Cd(1)-O(1)	90.66(7)	N(1)-Cd(1)-O(1)#1	89.34(7)
N(1)-Cd(1)-O(2)	91.41(7)	O(1)-Cd(1)-O(1)#1	180.0
O(2)#1-Cd(1)-O(1)	123.94(6)	O(2)-Cd(1)-O(1)	56.06(6)
O(2)-Cd(1)-O(2)#1	180.0		
		Complex **3**	
Co-O(1)#1	2.003(3)	Co-O(2)#2	2.006(3)
Co-O(3)	2.146(3)	Co-O(4)	2.276(3)
Co-N(1)	2.169(3)	Co-N(2)#3	2.151(3)
O(1)#1-Co-O(2)#2	120.96(2)	O(3)-Co-N(1)	87.61(1)
O(1)#1-Co-O(3)	91.41(2)	N(2)#3-Co-N(1)	178.41(3)
O(2)#2-Co-O(3)	147.60(2)	O(1)#1-Co-O(4)	150.52(1)
O(1)#1-Co-N(2)#3	87.02(2)	O(2)#2-Co-O(4)	88.51(1)
O(2)#2-Co-N(2)#3	87.79(1)	O(3)-Co-O(4)	59.15(1)
O(3)-Co-N(2)#3	92.99(1)	N(2)#3-Co-O(4)	95.45(2)
O(1)#1-Co-N(1)	91.48(1)	N(1)-Co-O(4)	86.13(1)
O(2)#2-Co-N(1)	92.50(2)		
		Complex **4**	

Co(1)-O(4)#1	2.063(3)	Co(1)-O(6)	2.150(3)
Co(1)-O(8)#2	2.082(3)	Co(1)-O(8)	2.154(3)
Co(1)-O(1)#3	2.090(3)	Co(1)-N(1)	2.156(4)
Co(2)-O(7)	1.956(4)	Co(2)-O(1W)	2.126(4)
Co(2)-O(3)#4	1.989(3)	Co(2)-O(1)#3	2.251(3)
Co(2)-O(8)	2.001(3)	Co(2)-O(2W)	2.390(9)
O(4)#1-Co(1)-O(8)#2	95.35(2)	O(1)#3-Co(1)-O(8)	81.22(2)
O(4)#1-Co(1)-O(1)#3	170.29(1)	O(6)-Co(1)-O(8)	94.01(1)
O(8)#2-Co(1)-O(1)#3	93.81(1)	O(4)#1-Co(1)-N(1)	89.92(2)
O(4)#1-Co(1)-O(6)	85.28(1)	O(8)#2-Co(1)-N(1)	98.34(2)
O(8)#2-Co(1)-O(6)	174.97(1)	O(1)#3-Co(1)-N(1)	91.91(1)
O(1)#3-Co(1)-O(6)	85.32(1)	O(6)-Co(1)-N(1)	86.64(2)
O(4)#1-Co(1)-O(8)	97.06(2)	O(8)-Co(1)-N(1)	173.01(2)
O(8)#2-Co(1)-O(8)	80.96(2)	O(7)-Co(2)-O(3)#4	148.86(2)
O(7)-Co(2)-O(8)	103.58(2)	O(8)-Co(2)-O(1)#3	80.81(1)
O(3)#4-Co(2)-O(8)	106.41(2)	O(1W)-Co(2)-O(1)#3	174.07(2)
O(7)-Co(2)-O(1W)	85.71(2)	O(7)-Co(2)-O(2W)	73.5(3)
O(3)#4-Co(2)-O(1W)	95.57(2)	O(3)#4-Co(2)-O(2W)	75.8(3)
O(8)-Co(2)-O(1W)	102.85(2)	O(8)-Co(2)-O(2W)	174.1(3)
O(7)-Co(2)-O(1)#3	88.90(2)	O(1W)-Co(2)-O(2W)	82.2(2)
O(3)#4-Co(2)-O(1)#3	87.78(1)	O(1)#3-Co(2)-O(2W)	93.9(2)
		Complex **5**	
Zn(1)-O(6)	1.931(3)	Zn(1)-O(1)#1	1.965(3)
Zn(1)-N(3)	1.997(4)	Zn(1)-N(1)	2.013(3)
O(6)-Zn(1)-O(1)#1	98.98(2)	O(6)-Zn(1)-N(1)	119.85(2)
O(6)-Zn(1)-N(3)	109.30(2)	O(1)#1-Zn(1)-N(1)	106.39(2)
O(1)#1-Zn(1)-N(3)	117.89(2)	N(3)-Zn(1)-N(1)	105.12(2)
		Complex **6**	
Zn(1)-O(8)	1.940(2)	Zn(1)-O(3)#1	1.950(2)
Zn(1)-N(8)#2	1.996(3)	Zn(1)-N(1)	1.997(2)
Zn(2)-O(6)#3	1.935(2)	Zn(2)-O(10)	1.986(2)
Zn(2)-O(2)	1.990(2)	Zn(2)-N(4)#4	2.008(3)
Zn(3)-O(14)#5	1.929(2)	Zn(3)-O(1)	1.957(2)
Zn(3)-O(11)	1.993(2)	Zn(3)-N(5)	1.998(3)
O(8)-Zn(1)-O(3)#1	108.51(1)	O(8)-Zn(1)-N(8)#2	110.63(1)
O(3)#1-Zn(1)-N(8)#2	107.11(1)	O(8)-Zn(1)-N(1)	105.79(1)
O(3)#1-Zn(1)-N(1)	115.04(1)	N(8)#2-Zn(1)-N(1)	109.77(1)
O(6)#3-Zn(2)-O(10)	118.28(1)	O(6)#3-Zn(2)-O(2)	105.54(1)
O(10)-Zn(2)-O(2)	117.98(9)	O(6)#3-Zn(2)-N(4)#4	99.96(1)
O(10)-Zn(2)-N(4)#4	111.17(1)	O(2)-Zn(2)-N(4)#4	101.17(1)

O(14)#5-Zn(3)-O(1)	121.82(1)	O(14)#5-Zn(3)-O(11)	111.43(9)
O(1)-Zn(3)-O(11)	106.60(9)	O(14)#5-Zn(3)-N(5)	104.50(1)
O(1)-Zn(3)-N(5)	109.83(1)	O(11)-Zn(3)-N(5)	100.64(1)

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

Table S2 Distances (Å) and Angles (°) of Hydrogen bonds for complexes **1** and **3**.

D-H···A	*d*(H···A)	*d*(D···A)	∠D-H···A
1			
O(6)-H(6)···O(2W)#1	1.772(1)	2.572(3)	165(1)
O(1W)-H(1A)···O(7)#2	1.891(1)	2.777(3)	173(3)
O(2W)-H(2A)···O(3)	1.882(2)	2.753(3)	166(4)
O(1W)-H(1B)···O(2)#3	1.889(1)	2.775(3)	173(3)
3			
O(1W)-H(1A)···O(4)	1.92(2)	2.798(5)	172(5)
O(1W)-H(1B)···O(3)#1	2.00(2)	2.870(5)	169(5)
O(6)-H(6)···O(1W)#2	1.90(2)	2.644(5)	144(4)

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

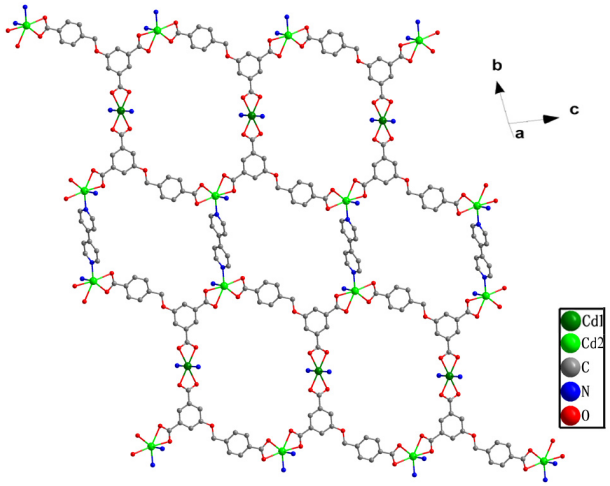

Fig. S1. View of 2D layer structure of **2**, hydrogen atoms and aqua ligands were omitted for clarity.

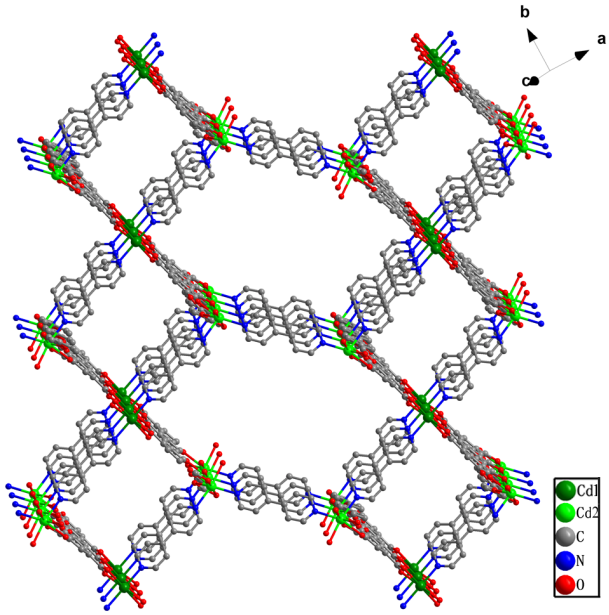

Fig. S2. View of one set of the 3D network of **2**.

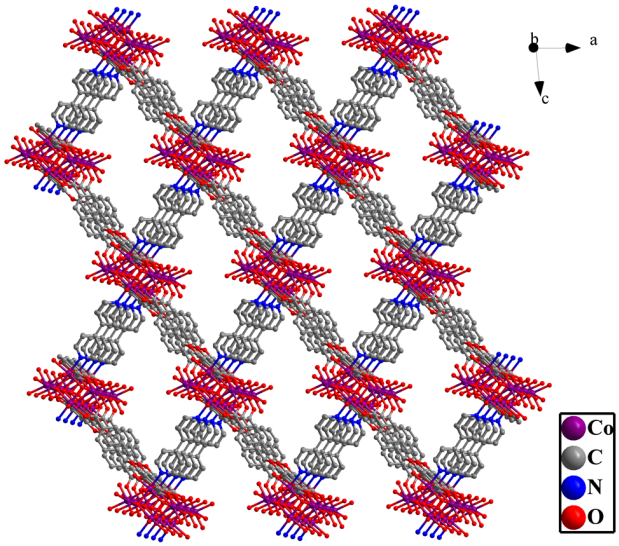

Fig. S3. View of one set of the 3D network of **4**.

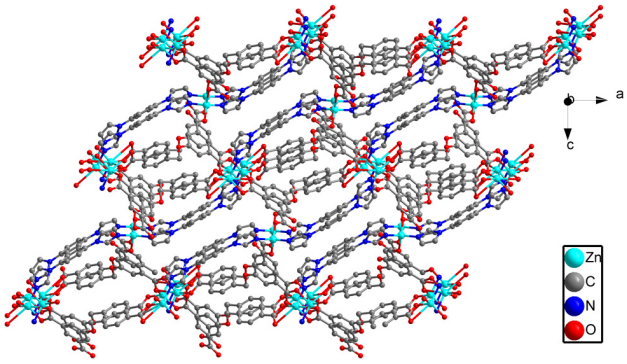

Fig. S4. View of one set of the 3D network of **6**.

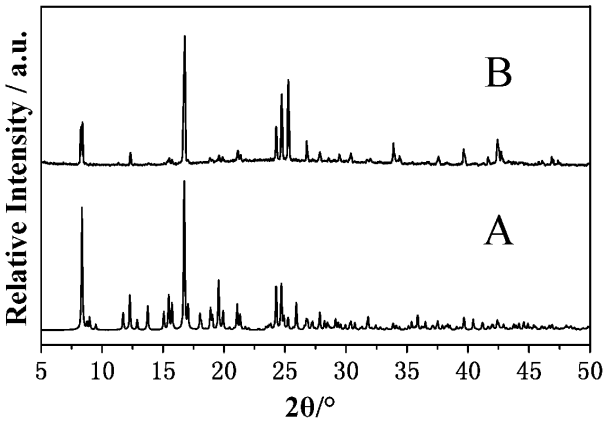

Fig. S5. Simulated and experimental PXRD spectra (A and B) of complex **1**.

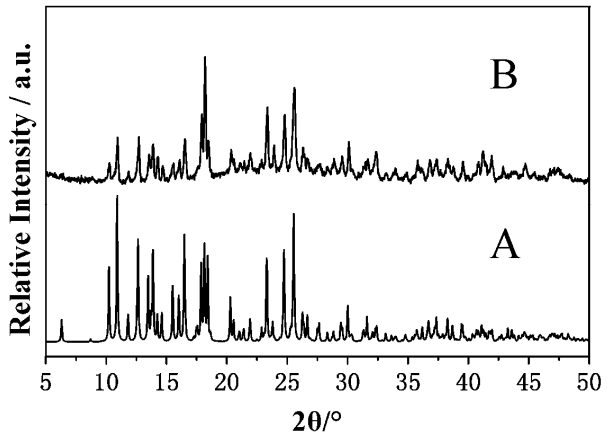

Fig. S6. Simulated and experimental PXRD spectra (A and B) of complex **2**.

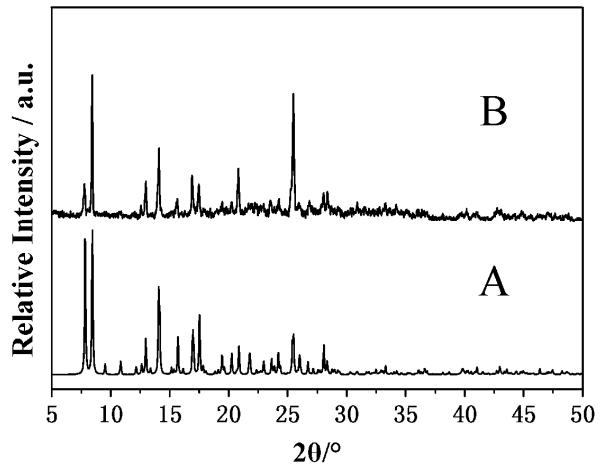

Fig. S7. Simulated and experimental PXRD spectra (A and B) of complex **3**.

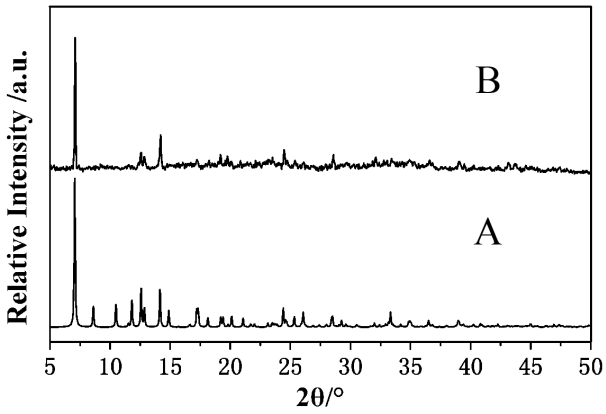

Fig. S8. Simulated and experimental PXRD spectra (A and B) of complex **4**.

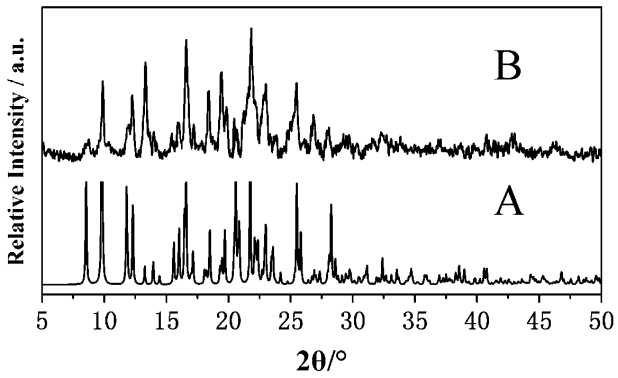

Fig. S9. Simulated and experimental PXRD spectra (A and B) of complex **5**.

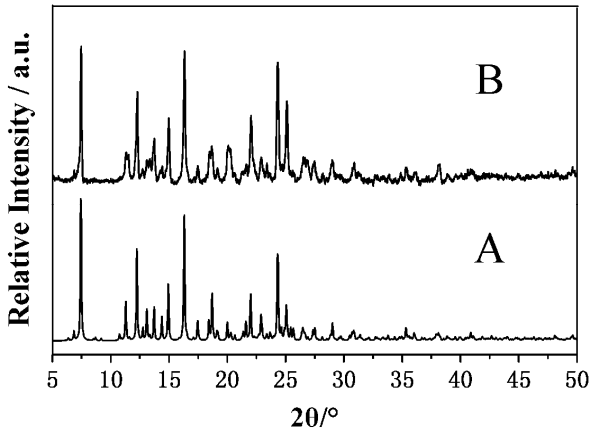

Fig. S10. Simulated and experimental PXRD spectra (A and B) of complex **6**.

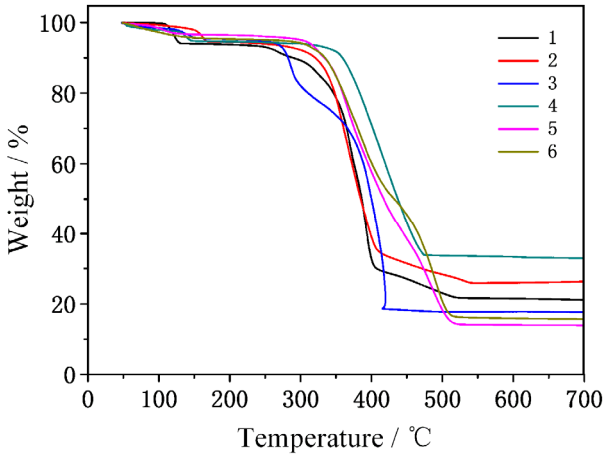

Fig. S11. TG curves of complexes **1-6**.

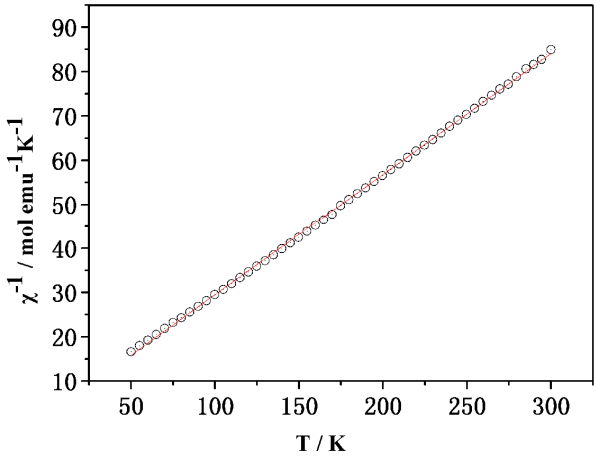

Fig. S12. Temperature dependence of the $1/\chi_m$ product for complex **3**.

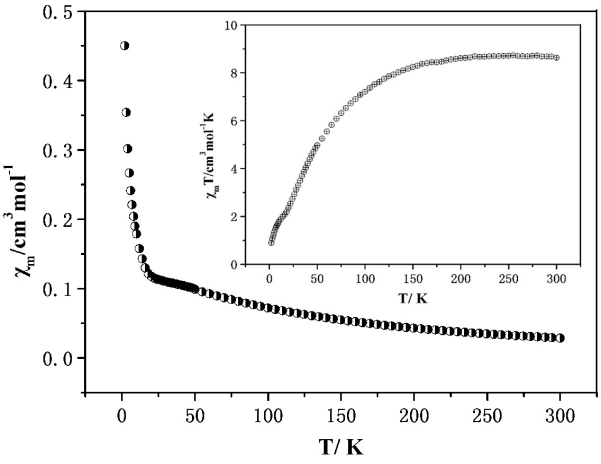

Fig. S13. Plots of χ_m and $\chi_m T$ *vs.* T for a polycrystalline sample of complex **4**.

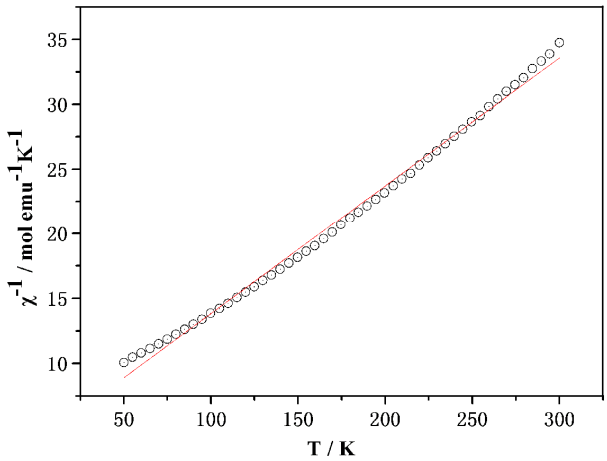

Fig. S14. Temperature dependence of the $1/\chi_m$ product for complex **4**.