Supplementary Information

Two microporous metal-organic frameworks constructed from trinuclear cobalt(II) and cadmium(II) cluster subunits†

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1. Experimental Procedures

1.1 Materials and Measurements. All the solvents and reagents for synthesis are reagent grade and purchased commercially without further purification. Elemental analyses were performed with a German Elementary Varil EL III instrument. The powder X-ray diffraction (PXRD) were recorded by a RIGAKU-DMAX2500 X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at a scanning rate of 5°/min for 2θ ranging from 5° to 50°. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449C instrument. The sample and reference (Al_2O_3) were enclosed in a platinum crucible and heated at a rate of 10 °C/min from room temperature to 1000 °C under nitrogen atmosphere. Magnetic susceptibility was measured on crystalline samples by using a Quantum Design MPMS-XL SQUID susceptometer under an applied magnetic field of 1000 Oe in the 2-300 K temperature range.

1.2 Syntheses of complex 1. A mixture of H_4TCPBDA (0.2 mmol, 133 mg) and $Co(ClO_4)_2$•$6H_2O$ (0.3 mmol, 110 mg) in *N,N'*-dimethylformamide (DMF) (8 mL) with an additional 100 μL HAc was sealed in a 25 mL Teflon-lined bomb at 100 °C for 2 days. Then the mixture was cooled to room temperatrure, yielding orange prism crystals which were collected and repeatedly washed with DMF three times. Phase purity of the crystals was confirmed by powder X-ray diffraction (PXRD). Yield: 78% (based on H_4TCPBDA). Elemental analyses calcd (%) for $C_{85}H_{99}N_7O_{37}Co_3$: C 51.37, H 5.02, N 4.93; found (%): C 51.32, H 4.98, N 4.96.

1.3 Syntheses of complex 2. A mixture of H_4TCPBDA (0.2 mmol, 133 mg) and $CdCl_2$•$2.5H_2O$ (0.3 mmol, 68 mg) in *N,N'*-dimethylformamide (DMF) (8 mL) with an additional 100 μL HAc was sealed in a 25 mL Teflon-lined bomb at 120 °C for 3 days. Then the mixture was cooled to room temperatrure, yielding colorless block crystals which were collected and repeatedly washed with DMF three times. Phase purity of the crystals was confirmed by powder X-ray diffraction (PXRD). Yield: 72% (based on H_4TCPBDA). Elemental analyses calcd (%) for $C_{88}H_{124}N_8O_{43}Cd_3$: C 45.57, H 5.39, N 4.83; found (%): C 45.62, H 5.28, N 4.78.

1.4 X-ray Crystallography. Data collections for complexes **1** and **2** were performed on Rigaku-CCD diffractometers equipped with graphite monochromated Cu-Kα radiation (λ = 1.541984 Å) by using the ω-scan mode at 100 K. All absorption corrections were applied using the *CrystalClear* program. The structure was solved by direct methods. The metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The structure was refined on F^2 by full-matrix least-squares using the *SHELXTL*-97 program package.[S1] All non-hydrogen atoms were refined anisotropically except some disordered atoms, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The free solvent molecules are highly disordered in complexes **1** and **2**, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these molecules were removed using the *SQUEEZE* routine of *PLATON*. [S2] The structures were then refined again using the data generated. The final formula of complexes **1** and **2** were determined by combining with thermogravimetric analysis (TGA) and elemental analyses. Crystal data and structure refinement of complexes **1** and **2** are summarized in Table S1.

Table S1 Crystal Data and Structure Refinement for complexes **1** and **2**.

complex reference	**1**	**2**
chemical formula	$C_{80}O_{16}H_{48}N_4Co_3$	$C_{80}O_{16}H_{48}N_4Cd_3$
formula weight	1498.01	1658.42
temperature (K)	100(2)	100(2)
crystal system	Monoclinic	Monoclinic
space group	*C2/c*	$P2_1/c$
a (Å)	40.267 (1)	26.936 (7)
b (Å)	12.903 (5)	22.123 (4)
c (Å)	25.995 (9)	26.046 (8)
α (°)	90.00	90.00
β (°)	104.20	109.74
γ (°)	90.00	90.00
V (Å^3)	14108.2 (8)	14609.5 (6)
Z	4	4
F (000)	3060	3312
R_{int}	0.034	0.051
no. of reflections measured	28579	27696
no. of independent reflections	14179	15755
goodness of fit on F^2	1.023	1.057
final *R*1 values [$I > 2\sigma(I)$]	0.0393	0.0826
final *wR* (F^2) values [$I > 2\sigma(I)$]	0.0887	0.2709

2. Additional X-ray Crystal Structures

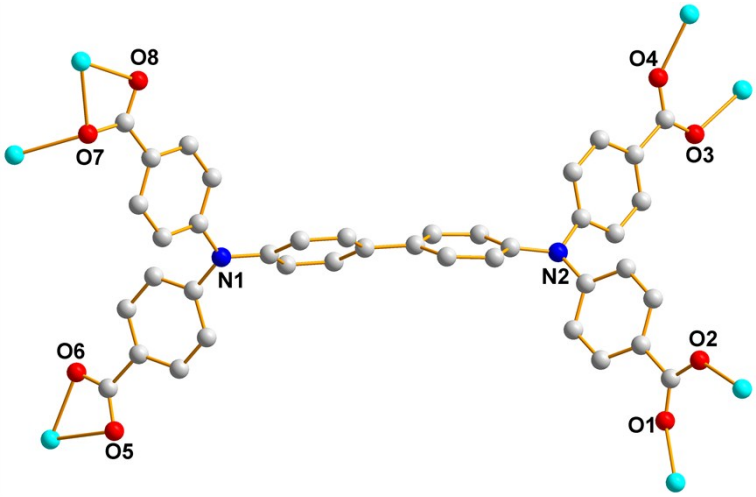

Fig. S1 Coordination environment for H_4TCPBDA in complex **1**. H atoms were omitted for clarity.

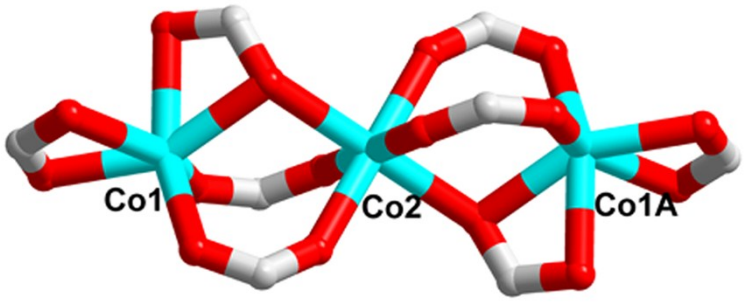

Fig. S2 The structural motif of the linear trinuclear $[Co_3(COO)_8]$ SBU in complex **1**.

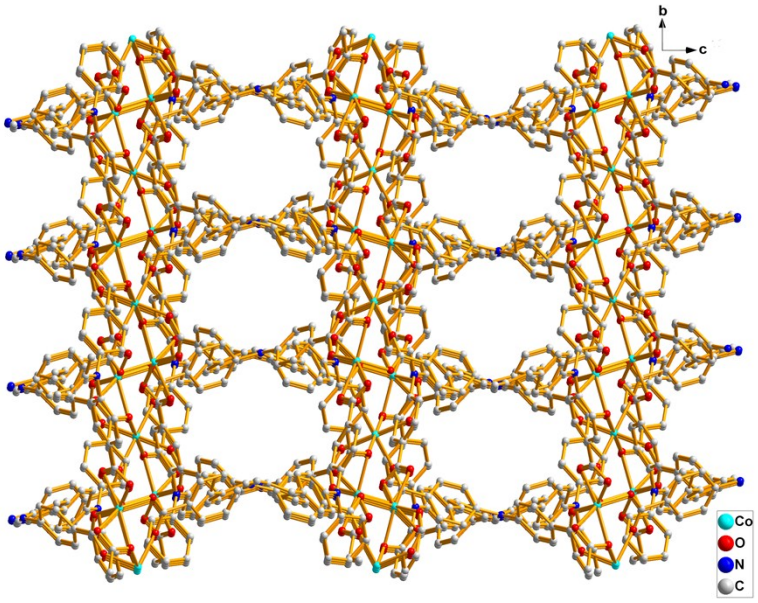

Fig. S3 The 3D framework for complex **1** viewed along the c-axis.

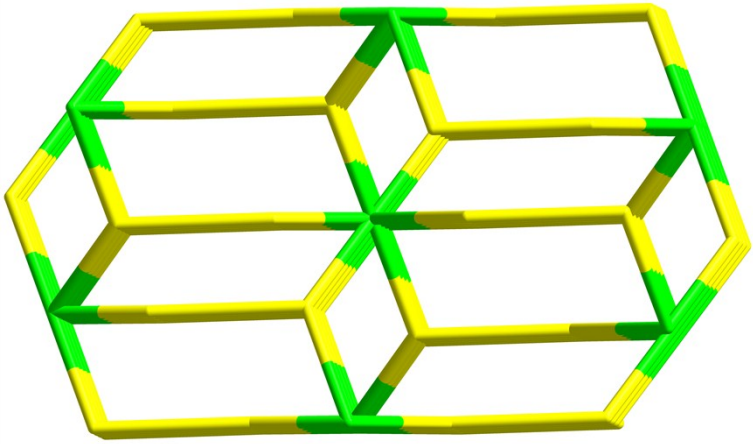

Fig. S4 The (3,3,8)-c 3-nodal topology of complex **1**.

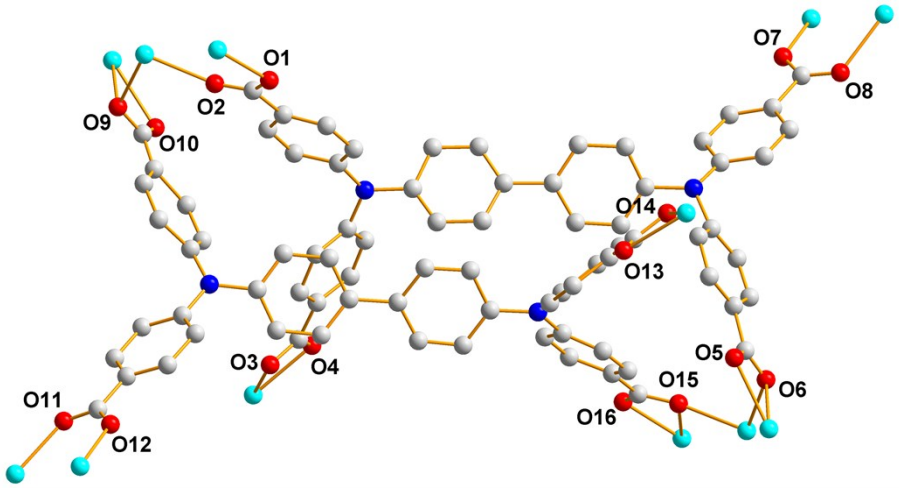

Fig. S5 Coordination environment for H_4TCPBDA in complex **2**. H atoms were omitted for clarity.

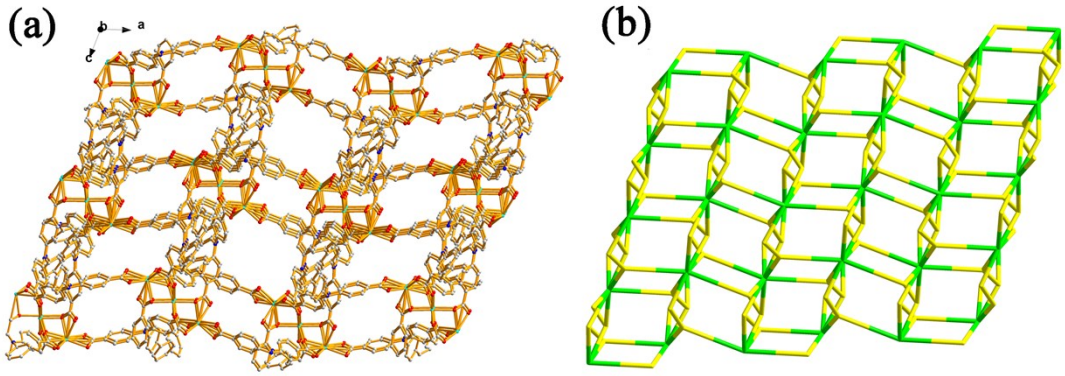

Fig. S6 The 3D framework and corresponding topology structure for complex **2** along the b-axis.

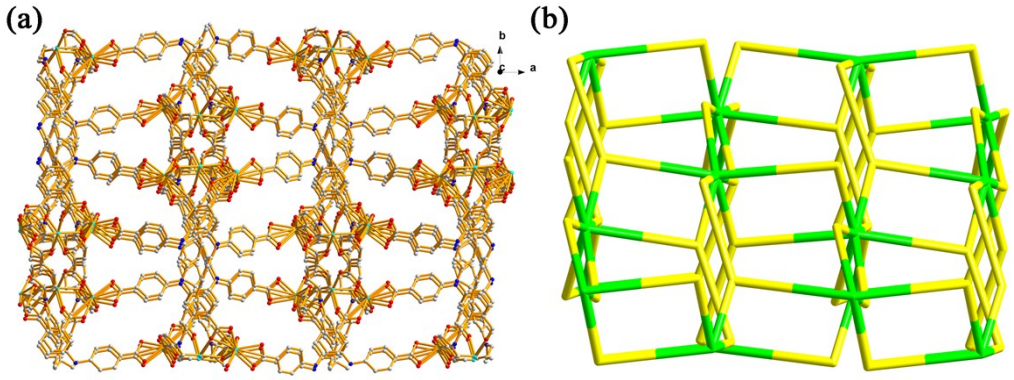

Fig. S7 The 3D framework and corresponding topology structure for complex **2** along the c-axis.

Table S2 Selected Bond Lengths (Å) and Angles (deg) for complex **1**[a].

Co(1)-O(2)	2.0745 (14)	Co(1)-O(5)vi	2.3808 (15)
Co(1)-O(3)i	2.0791 (13)	Co(1)-O(5)vi	2.3808 (15)
Co(1)-O(6)vi	2.1630 (14)	Co(2)-O(4)i	2.0909 (13)
Co(1)-O(8)v	2.2460 (13)	Co(2)-O(1)	2.0987 (14)
Co(1)-O(7)v	2.2471 (13)	Co(2)-O(7)iv	2.2870 (10)
N(1)-C(24)	1.412 (2)	N(2)-C(8)	1.405 (3)
N(1)-C(27)	1.424 (3)	N(2)-C(15)	1.421 (2)
N(1)-C(34)	1.427 (3)	N(2)-C(5)	1.424 (2)
O(2)-Co(1)-O(3)i	103.77 (6)	O(4)i-Co(2)-O(4)ii	180.000 (1)
O(2)-Co(1)-O(6)vi	92.68 (6)	O(4)i-Co(2)-O(1)	89.16 (7)
O(3)i-Co(1)-O(6)vi	101.33 (6)	O(4)ii-Co(2)-O(1)	90.84 (7)
O(2)-Co(1)-O(8)v	95.01 (6)	O(4)i-Co(2)-O(1)iii	90.84 (7)
O(3)i-Co(1)-O(8)v	151.99 (6)	O(4)ii-Co(2)-O(1)iii	89.16 (7)
O(6)vi-Co(1)-O(8)v	98.31 (5)	O(1)-Co(2)-O(1)iii	180.000 (1)
O(2)-Co(1)-O(7)v	99.99 (5)	O(4)i-Co(2)-O(7)iv	92.79 (4)
O(3)i-Co(1)-O(7)v	97.11 (5)	O(4)ii-Co(2)-O(7)iv	87.21 (4)
O(6)vi-Co(1)-O(7)v	154.44 (5)	O(1)-Co(2)-O(7)iv	87.33 (5)
O(8)v-Co(1)-O(7)v	58.76 (5)	O(1)iii-Co(2)-O(7)iv	92.67 (5)
O(2)-Co(1)-O(5)vi	148.81 (6)	O(4)i-Co(2)-O(7)v	87.21 (4)
O(3)i-Co(1)-O(5)vi	92.19 (5)	O(4)ii-Co(2)-O(7)v	92.79 (4)
O(6)vi-Co(1)-O(5)vi	57.57 (5)	O(1)-Co(2)-O(7)v	92.67 (5)
O(8)v-Co(1)-O(5)vi	81.68 (5)	O(1)iii-Co(2)-O(7)v	87.33 (5)
O(7)v-Co(1)-O(5)vi	104.47 (5)	O(7)iv-Co(2)-O(7)v	180.000 (1)
C(24)-N(1)-C(27)	121.37 (18)	C(8)-N(2)-C(15)	121.13 (17)
C(24)-N(1)-C(34)	119.77 (18)	C(8)-N(2)-C(5)	117.40 (14)
C(27)-N(1)-C(34)	118.32 (14)	C(15)-N(2)-C(5)	118.80 (18)

[a] Symmetry codes: (i) x, 1-y, -1/2+z; (ii) 3/2-x, 1/2+y, 3/2-z; (iii) 3/2-x, 3/2-y, 1-z; (iv) 1-x, 1-y, 1-z; (v) 1/2+x, 1/2+y, z; (vi) 1/2+x, -1/2+y, z.

Table S3 Selected Bond Lengths (Å) and Angles (deg) for complex **2**[b].

Cd(1)-O(1)	2.202 (5)	Cd(3)-O(11)ii	2.189 (6)
Cd(1)-O(8)i	2.215 (5)	Cd(3)-O(16)iii	2.267 (5)
Cd(1)-O(14)iv	2.296 (5)	Cd(3)-O(4)v	2.364 (7)
Cd(1)-O(13)iv	2.353 (5)	Cd(3)-O(10)	2.401 (6)
Cd(1)-O(6)iii	2.370 (5)	Cd(3)-O(3)v	2.403 (8)
Cd(1)-O(5)iii	2.372 (5)	Cd(3)-O(9)	2.424 (6)
Cd(2)-O(7)i	2.218 (5)	Cd(3)-O(15)iii	2.511 (6)
Cd(2)-O(12)ii	2.219 (5)	Cd(2)-O(2)	2.291 (5)
Cd(2)-O(9)	2.285 (5)	Cd(2)-O(6)iii	2.311 (5)
O(1)-Cd(1)-O(14)iv	94.1 (2)	O(1)-Cd(1)-O(8)i	100.0 (2)
O(8)i-Cd(1)-O(14)iv	104.0 (2)	O(14)iv-Cd(1)-O(6)iii	139.77 (18)
O(1)-Cd(1)-O(13)iv	150.1 (2)	O(13)iv-Cd(1)-O(6)iii	90.90 (19)
O(8)i-Cd(1)-O(13)iv	92.5 (2)	O(1)-Cd(1)-O(5)iii	94.1 (2)
O(14)iv-Cd(1)-O(13)iv	56.39 (19)	O(8)i-Cd(1)-O(5)iii	154.6 (2)
O(1)-Cd(1)-O(6)iii	113.2 (2)	O(14)iv-Cd(1)-O(5)iii	95.79 (19)
O(8)i-Cd(1)-O(6)iii	99.73 (19)	O(13)iv-Cd(1)-O(5)iii	85.3 (2)
O(7)i-Cd(2)-O(12)ii	91.77 (19)	O(9)-Cd(2)-O(6)iii	176.46 (17)
O(7)i-Cd(2)-O(9)	89.8 (2)	O(2)-Cd(2)-O(6)iii	87.5 (2)
O(12)ii-Cd(2)-O(9)	87.94 (18)	O(7)i-Cd(2)-O(15)iii	171.6 (2)
O(7)i-Cd(2)-O(2)	98.3 (2)	O(12)ii-Cd(2)-O(15)iii	87.3 (2)
O(12)ii-Cd(2)-O(2)	169.7 (2)	O(9)-Cd(2)-O(15)iii	81.8 (2)
O(9)-Cd(2)-O(2)	94.04 (19)	O(2)-Cd(2)-O(15)iii	83.0 (2)
O(7)i-Cd(2)-O(6)iii	86.80 (19)	O(6)iii-Cd(2)-O(15)iii	101.54 (19)
O(12)ii-Cd(2)-O(6)iii	91.08 (19)	O(16)iii-Cd(3)-O(9)	122.1 (2)
O(11)ii-Cd(3)-O(16)iii	103.5 (2)	O(4)v-Cd(3)-O(9)	82.0 (3)
O(11)ii-Cd(3)-O(4)v	92.4 (2)	O(10)-Cd(3)-O(9)	54.99 (18)
O(16)iii-Cd(3)-O(4)v	149.2 (3)	O(3)v-Cd(3)-O(9)	122.2 (2)
O(11)ii-Cd(3)-O(10)	149.1 (2)	O(11)ii-Cd(3)-O(15)iii	82.6 (2)
O(16)iii-Cd(3)-O(10)	95.0 (2)	O(16)iii-Cd(3)-O(15)iii	53.8 (2)
O(4)v-Cd(3)-O(10)	83.6 (2)	O(4)v-Cd(3)-O(15)iii	156.2 (3)
O(11)ii-Cd(3)-O(3)v	120.3 (2)	O(10)-Cd(3)-O(15)iii	88.8 (2)
O(16)iii-Cd(3)-O(3)v	95.2 (3)	O(3)v-Cd(3)-O(15)iii	146.7 (3)
O(4)v-Cd(3)-O(3)v	54.2 (3)	O(9)-Cd(3)-O(15)iii	75.15 (19)
O(10)-Cd(3)-O(3)v	81.7 (2)	O(11)ii-Cd(3)-O(9)	94.1 (2)

[b] Symmetry codes: (i) x, 1+y, z; (ii) x, 3/2-y, 1/2+z; (iii) x, 1/2-y, 1/2+z; (iv) -x, 1/2+y, 1/2-z; (v) 1-x, 1-y, 1-z.

3. Powder X-Ray Diffraction (PXRD)

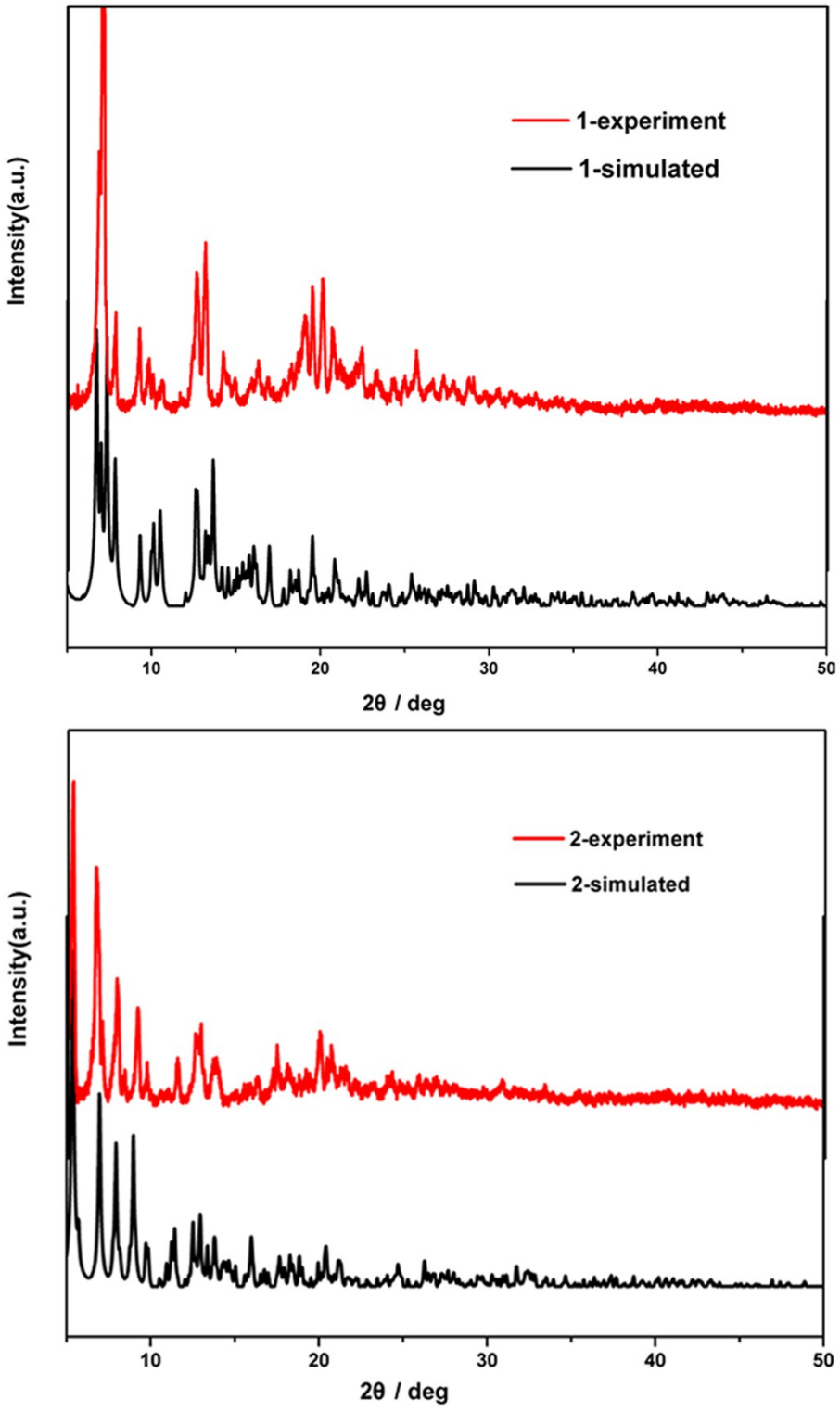

Fig. S8 PXRD patterns of complexes **1** and **2**.

4. Thermogravimetric Analysis (TGA)

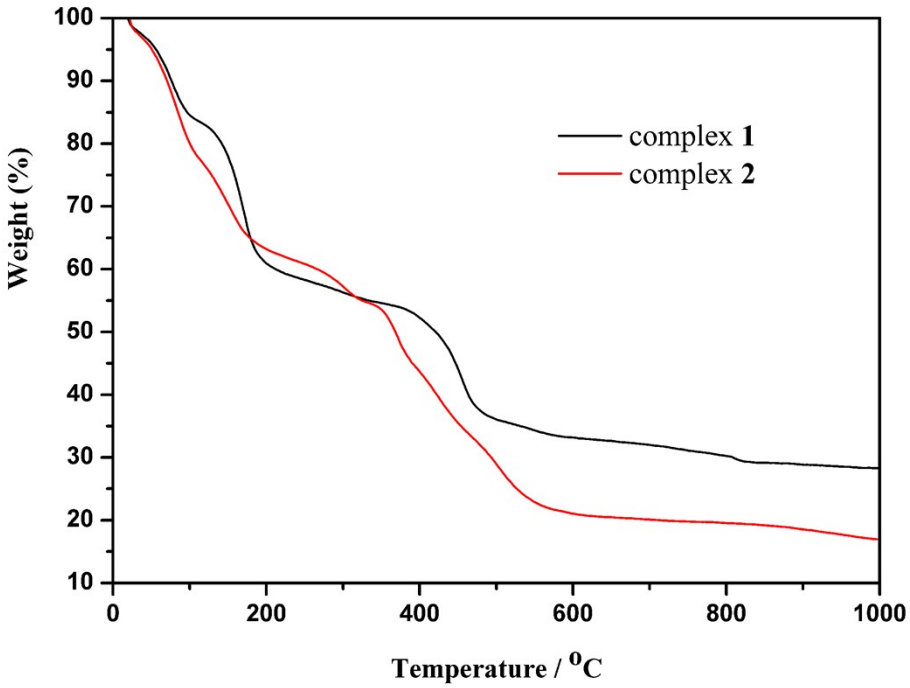

Fig. S9 The TGA Curves of complexes **1** and **2**.

The thermal stabilities of complexes **1** and **2** were investigated using thermogravimetric analysis (TGA) from 25-1000 °C under a flow of nitrogen. The TGA curve of complex **1** shows that the first weight loss of 15.4% was from 25 to 100 °C, which corresponds to the loss of the solvent H_2O molecules in complex **1** (calcd, 15.0%). The second weight loss of 3.4% was from 100 to 135 °C, which corresponds to the loss of the solvent DMF molecules in complex **1** (calcd, 3.8%). Above 135 °C, the framework decomposed. For complex **2**, the first weight loss of 19.7% occurred from 25 to 99 °C, which corresponds to the loss of the solvent H_2O molecules in complex **2** (calcd 19.4%). The second weight loss of 6.4% was from 99 to 134 °C, which corresponds to the loss of the solvent DMF molecules in complex **2** (calcd, 6.3%). Decomposition of complex **2** began at about 134 °C.

5. Magnetic properties

Magnetic susceptibilities of complex **1** were measured on crystalline samples by using a Quantum Design MPMS-XL SQUID susceptometer under an applied magnetic field of 1000 Oe in the 2-300 K temperature range.

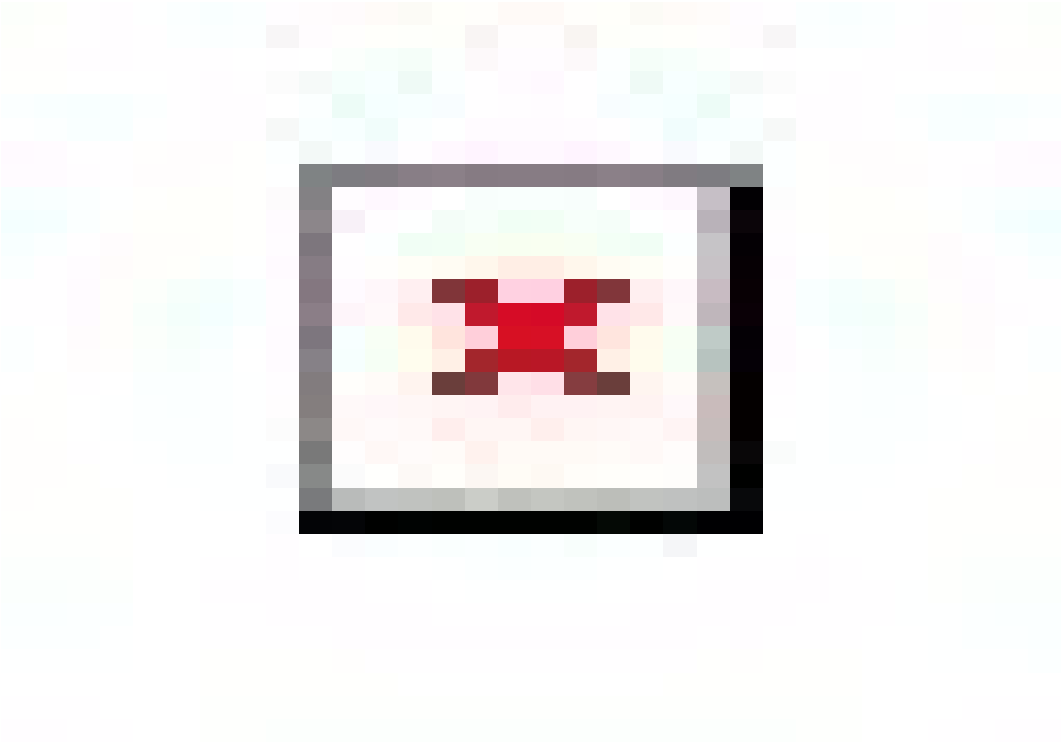

Fig. S10 The temperature dependence of χ_m and $\chi_m T$ for complex **1**.

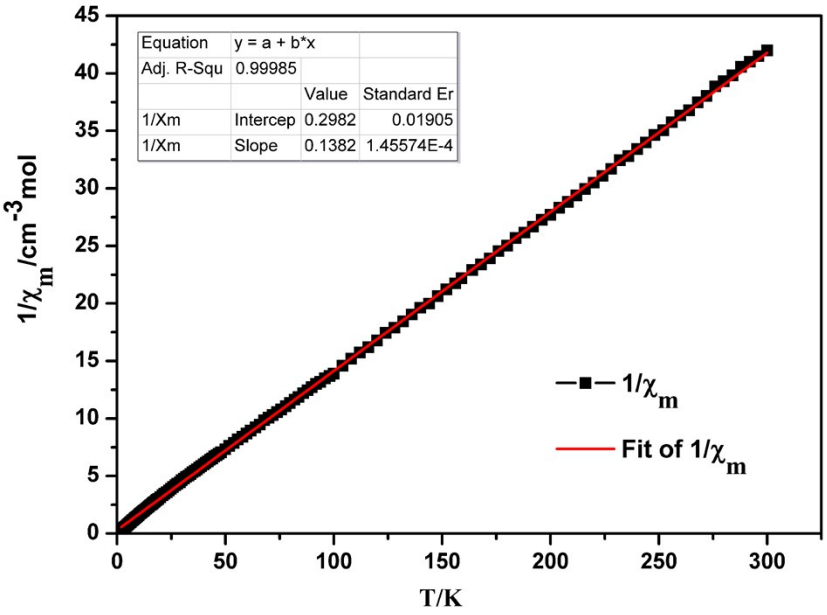

Fig. S11 The temperature dependence of $1/\chi_m$ for complex **1**.

6. References

(S1) G. M. Sheldrick, SHELXS 97, *Program for crystal Structure Solution* and *Program for crystal Structure Refiniement*, 1997, University of Göttingen.

(S2) (a) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (b) P. V. D. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.