

## Supporting Information

### General methods

Bis(4-pyridylmethyl)piperazine (bpmp) was prepared via a published procedure.<sup>1</sup> The remaining starting materials used in these synthetic reactions are purchased commercially and were used as obtained from the supplier. The power X-ray diffraction (PXRD) patterns were collected by a RIGAKU DMAX2500 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). The FT-IR spectra were obtained on a Nicolet Nexus FT-IR spectrometer in the range of 650–4000 cm<sup>-1</sup>. Elemental analysis for C, H, N was performed on a German Elementary Vario EL III instrument. Thermogravimetric analysis was recorded on a NETZSCH STA 449C unit with a heating rate of 10°C · min<sup>-1</sup> in nitrogen atmosphere. Magnetic susceptibility data were measured using a Quantum Design MPMS-XL5 SQUID magnetometer.

### Preparation of [Co<sub>4</sub>(sdb)<sub>4</sub>(bpmp)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>] $\cdot$ 2H<sub>2</sub>O (**1**)

Cobalt(II) nitrate hexahydrate (58 mg, 0.2 mmol), H<sub>2</sub>sdb (31 mg, 0.1 mmol) and bpmp (54 mg, 0.2 mmol) were placed into 8 mL of distilled H<sub>2</sub>O in a Teflon-lined 23 mL steel autoclave. The autoclave was sealed and heated at 120 °C for 72 h, and then cooled to 25 °C for 24 h. Red blocks of **1** (43% yield based on Co) were isolated after washing with distilled water and drying in air. Anal. Calcd for C<sub>52</sub>H<sub>52</sub>Co<sub>2</sub>N<sub>6</sub>O<sub>15</sub>S<sub>2</sub> **1**: C, 52.79; H, 4.43; N, 7.10. Found: C, 52.72; H, 4.39; N, 7.06%. Selected IR data: 2988 (s), 2900 (s), 1636(m), 1560 (w), 1394 (s), 879 (m), 780(w).

### Preparation of [Cd<sub>4</sub>(sdb)<sub>4</sub>(bpmp)<sub>3</sub>] (**2**)

Cadmium(II) nitrate tetrahydrate (62 mg, 0.2 mmol), H<sub>2</sub>sdb (31 mg, 0.1 mmol) and bpmp (54 mg, 0.2 mmol) were placed into 8 mL of distilled H<sub>2</sub>O in a Teflon-lined 23 mL steel autoclave. The autoclave was sealed and heated at 120 °C for 72 h, and then cooled to 25 °C for 24 h. Yellow blocks of **2** (39% yield based on Cd) were isolated after washing with distilled water and drying in air. Anal. Calcd for C<sub>52</sub>H<sub>46</sub>Cd<sub>2</sub>N<sub>6</sub>O<sub>12</sub>S<sub>2</sub> **2**: C, 50.53; H, 3.75; N, 6.80. Found: C, 50.58; H, 3.72; N, 6.75. Selected IR data: 1624 (s), 1560 (m), 1400 (s), 1323(m), 1162 (s), 779 (m).

## X-Ray crystallography

Diffraction data for **1** and **2** were collected on a Rigaku Mercury CCD and SuperNova, Dual, Mo at zero, Atlas diffractometers respectively. The structures were solved using direct methods and refined on  $F^2$  using SHELXTL<sup>2</sup>. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. Hydrogen atoms of the water molecules were found in the electron density map and refined by riding. Selected bond distances and angles of the **1-2** are listed in Table S1.

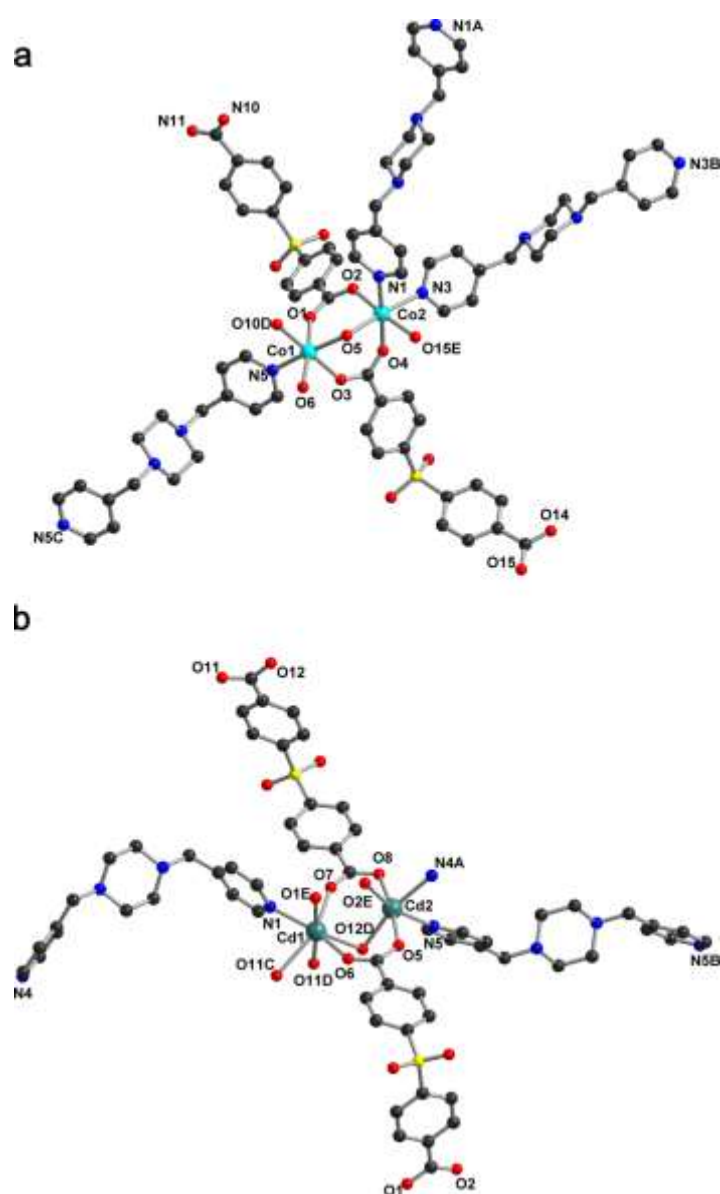


Fig. S1 Coordination environments of **1** (a) and **2** (b).

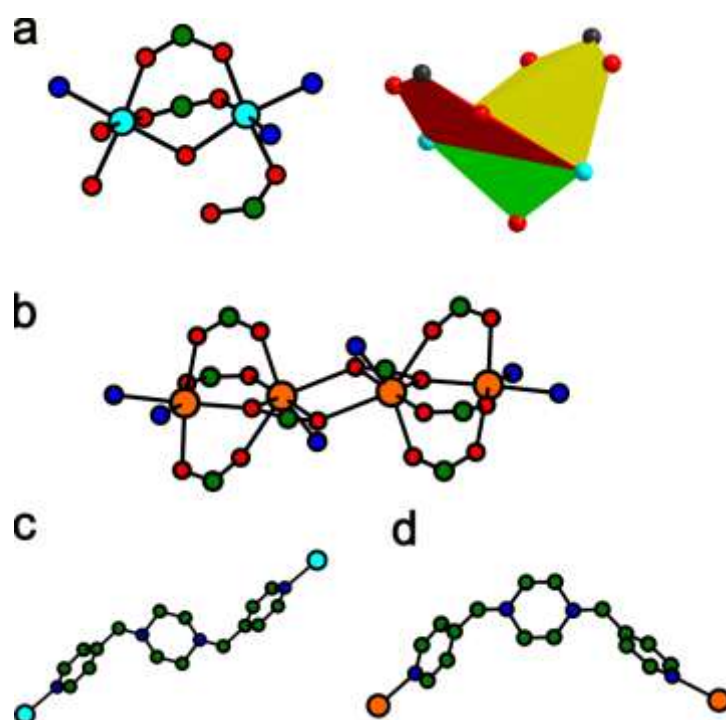


Fig.S2 a  $\{\text{Co}(\text{COO})_2\text{H}_2\text{O}\}$  three-bladed paddlewheel SBU (left) and its schematic perspective (right) in **1**; b doubled paddlewheel SBU in **2**; c trans conformation of bimp in **1**; d cis conformation of bimp in **2** (cobalt, turquoise; carbon, black; oxygen, red).

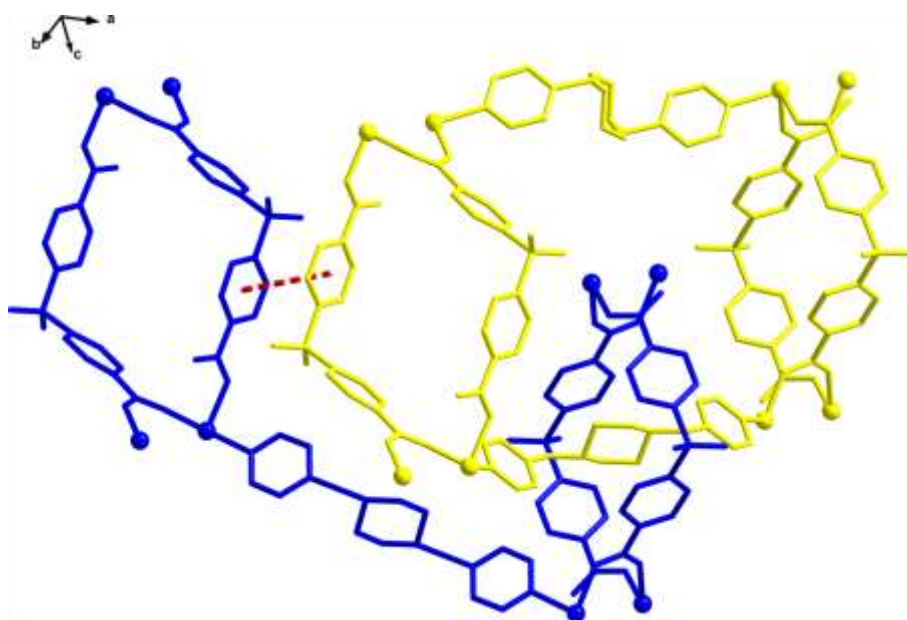


Fig. S3 The  $\pi \cdots \pi$  interactions (the red dotted lines) between the  $\text{sdb}^{2-}$  rings from different sets of frameworks in **1**.

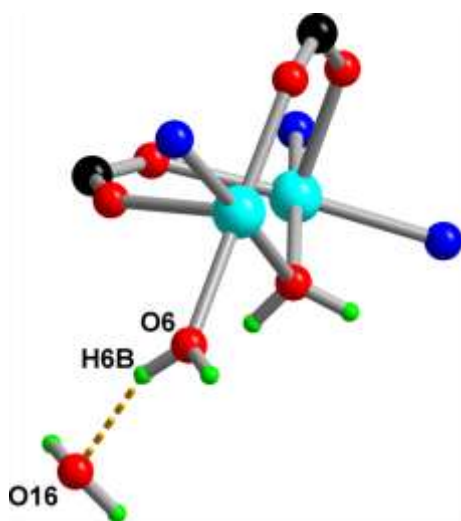


Fig. S4 H bond (the yellow dotted lines) between aqua ligand and free water molecule in **1**. ( $d(\text{O6}\dots\text{H6B}) = 0.83\text{\AA}$ ,  $\angle\text{O6-H6B-O16} = 158^\circ$ ,  $d(\text{H6B}\dots\text{O16}) = 1.97\text{\AA}$ ) (cobalt, turquoise; carbon, black; oxygen, red; hydrogen, green; nitrogen, blue)

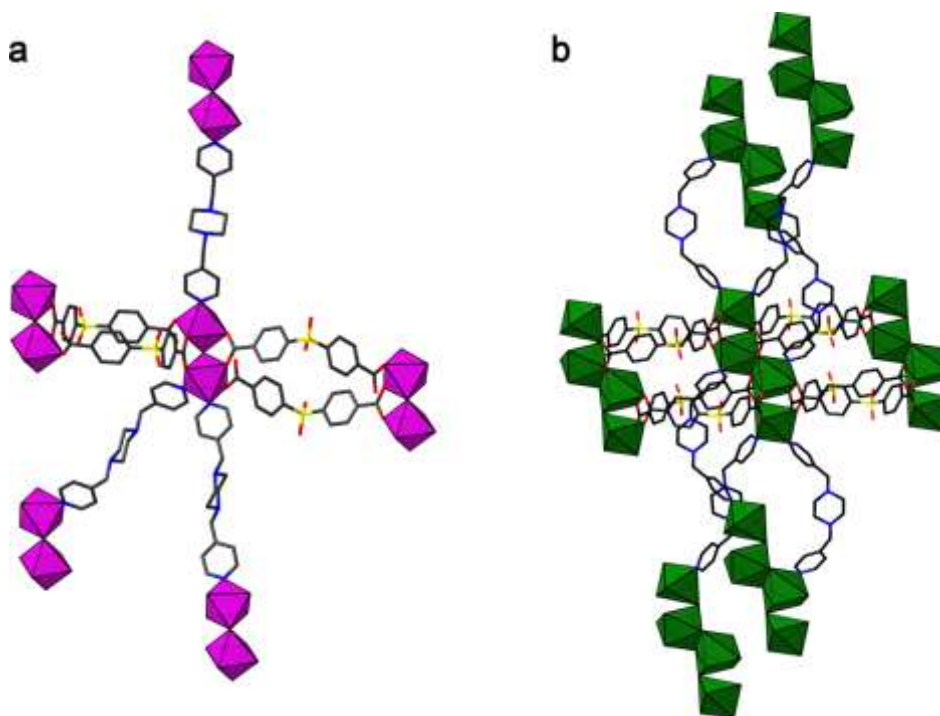


Fig. S5 a  $\text{Co}_2$  clusters in **1** as five-connected nodes; b  $\text{Cd}_4$  clusters in **2** as six-connected nodes.

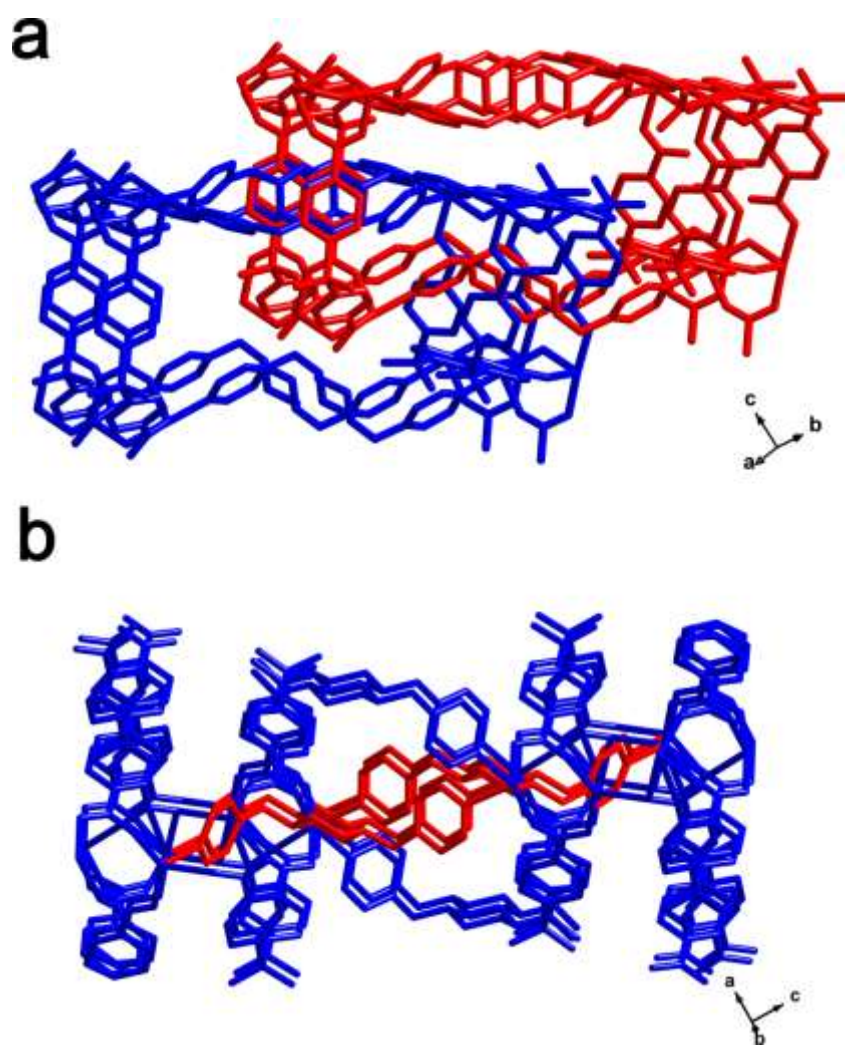


Fig.S6 (a) 2-fold interpenetration in **1**; (b) self-threading like motif in noninterpenetrated framework in **2**.

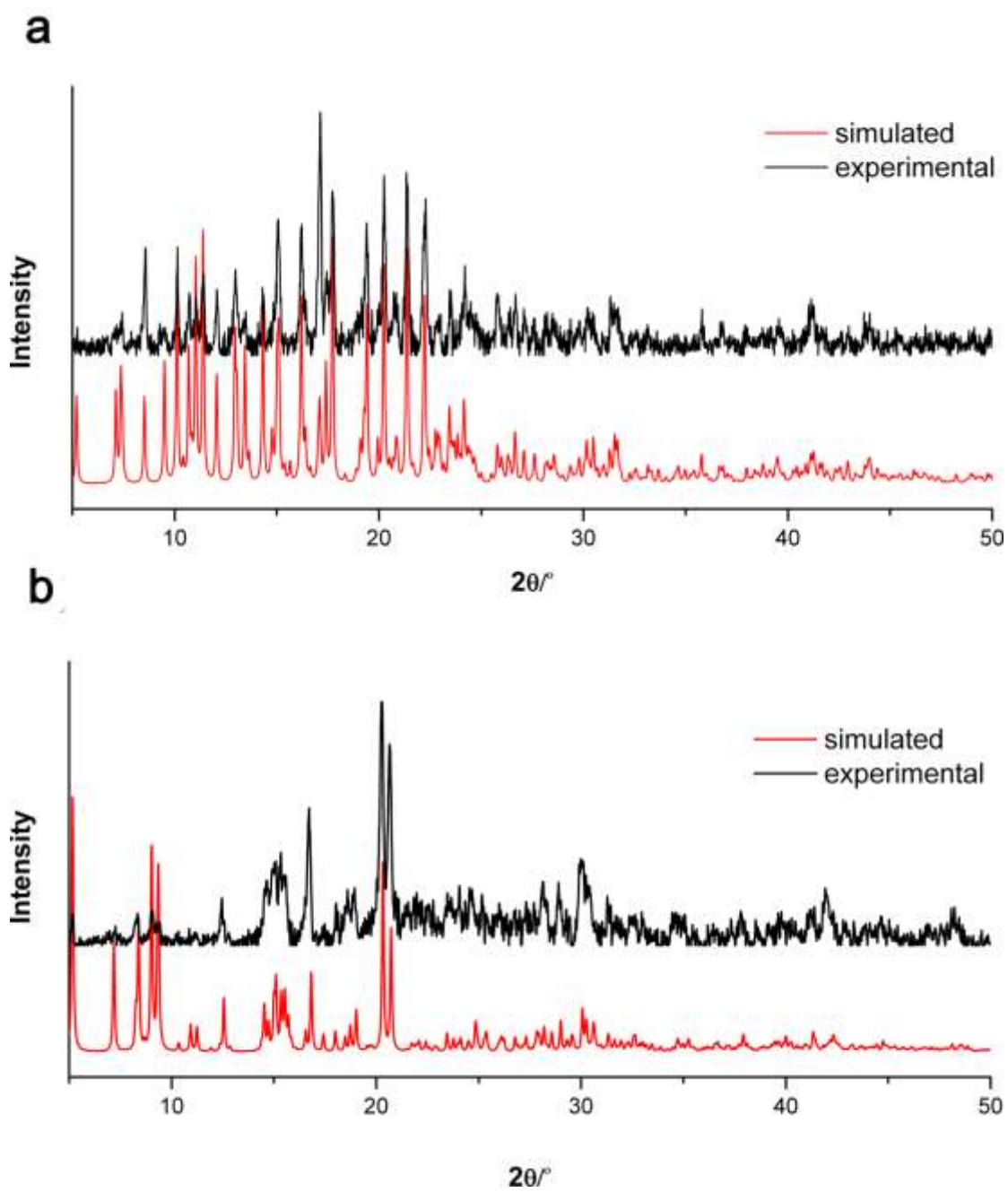


Fig. S7 PXR D patterns of **1(a)** and **2(b)**.

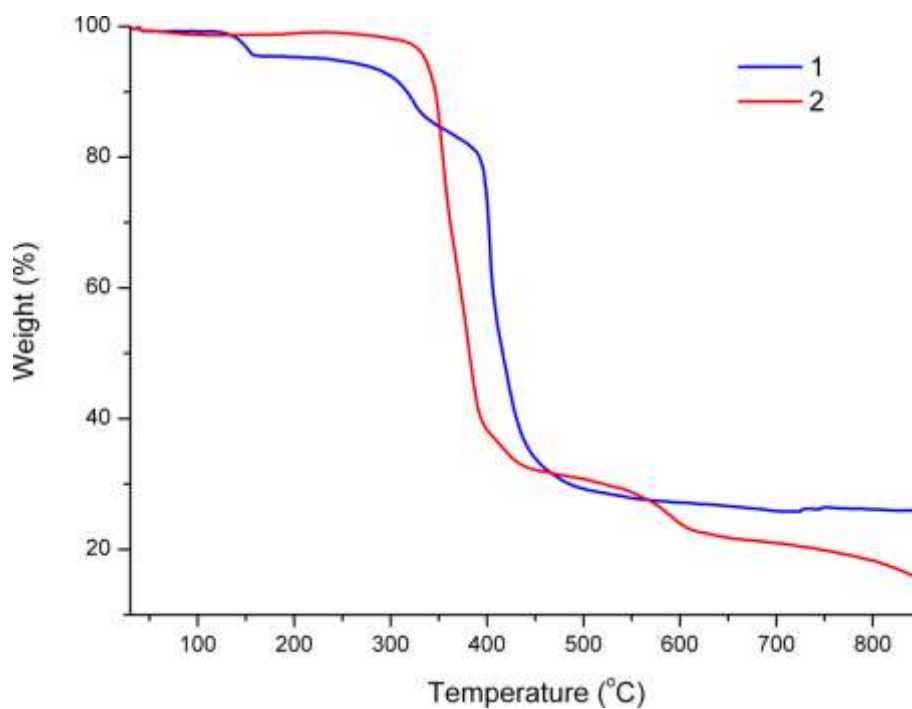


Fig. S8 Thermal gravimetric curves for **1** and **2**.

**1** lost its water solvent and aqua ligands between 120 and 160 °C (4.6% calculated, 4.5% observed), and then the framework undergoes decomposition.

**2** underwent no obvious weight loss before 320 °C, and the compound decomposes rapidly on further heating.

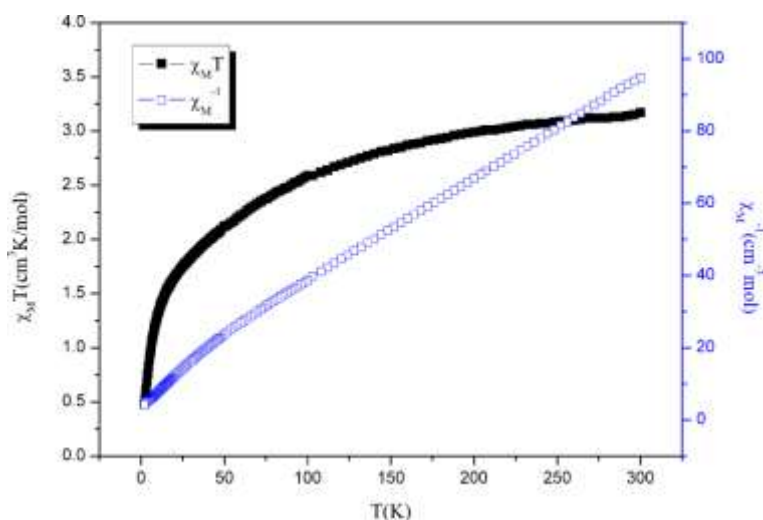


Fig. S9 The temperature dependence of  $\chi_M T$  at 1 kOe for **1**.

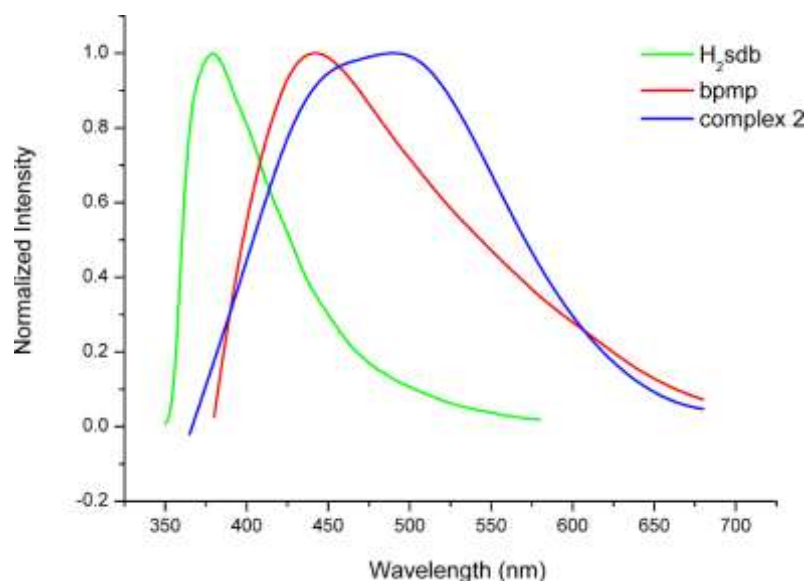


Fig. S10 Solid-state emission spectra of **2**, H<sub>2</sub>sdb and bpmp at room temperature.

Table S1. Selected bond lengths (Å) and angles (°) for complexes **1-2**

Complex 1			
Co1—O1	2.045 (3)	Co2—O2	2.080 (3)
Co1—O3	2.089 (3)	Co2—O4	2.082 (3)
Co1—O6	2.101 (3)	Co2—O15ii	2.137 (3)
Co1—O5	2.107 (3)	Co2—O5	2.153 (3)
Co1—N5	2.136 (3)	Co2—N1	2.156 (3)
Co1—O10i	2.151 (3)	Co2—N3	2.168 (4)
O1—Co1—O3	95.28 (14)	O2—Co2—O4	92.04 (13)
O1—Co1—O6	174.70 (12)	O2—Co2—O15ii	174.47 (12)
O3—Co1—O6	88.19 (13)	O4—Co2—O15ii	87.05 (12)
O1—Co1—O5	95.01 (12)	O2—Co2—O5	97.49 (12)
O3—Co1—O5	85.53 (11)	O4—Co2—O5	89.97 (11)
O6—Co1—O5	89.25 (12)	O15ii—Co2—O5	87.97 (11)
O1—Co1—N5	85.33 (13)	O2—Co2—N1	89.23 (13)
O3—Co1—N5	90.56 (13)	O4—Co2—N1	176.20 (13)
O6—Co1—N5	90.63 (13)	O15ii—Co2—N1	92.02 (12)
O5—Co1—N5	176.10 (12)	O5—Co2—N1	86.31 (12)
O1—Co1—O10i	88.56 (14)	O2—Co2—N3	90.87 (13)
O3—Co1—O10i	175.44 (13)	O4—Co2—N3	91.94 (13)
O6—Co1—O10i	88.16 (13)	O15ii—Co2—N3	83.72 (13)
O5—Co1—O10i	91.68 (12)	O5—Co2—N3	171.36 (12)
N5—Co1—O10i	92.21 (13)	N1—Co2—N3	91.62 (13)
Complex 2			
Cd1—O1	2.2830 (17)	Cd1—Cd2	3.4246 (2)
Cd1—O6i	2.3076 (16)	Cd2—O8	2.2078 (16)



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Cd1—N1	2.3128 (19)	Cd2—O5i	2.2183 (16)
Cd1—O11i	2.3536 (17)	Cd2—N4iii	2.350 (2)
Cd1—O7	2.3854 (17)	Cd2—N5	2.399 (2)
Cd1—O11ii	2.5690 (17)	Cd2—O12i	2.4038 (16)
Cd1—O12i	2.5987 (15)	Cd2—O2	2.4125 (16)
O1—Cd1—O6i	80.87 (6)	O7—Cd1—Cd2	57.19 (4)
O1—Cd1—N1	85.10 (6)	O11ii—Cd1—Cd2	148.48 (4)
O6i—Cd1—N1	154.04 (7)	O12i—Cd1—Cd2	44.46 (3)
O1—Cd1—O11i	175.94 (6)	O8—Cd2—O5i	171.58 (6)
O6i—Cd1—O11i	102.92 (6)	O8—Cd2—N4iii	92.20 (6)
N1—Cd1—O11i	90.84 (6)	O5i—Cd2—N4iii	95.44 (6)
O1—Cd1—O7	87.21 (6)	O8—Cd2—N5	88.87 (6)
O6i—Cd1—O7	126.77 (6)	O5i—Cd2—N5	95.52 (6)
N1—Cd1—O7	73.80 (6)	N4iii—Cd2—N5	83.25 (7)
O11i—Cd1—O7	91.57 (6)	O8—Cd2—O12i	92.03 (6)
O1—Cd1—O11ii	111.13 (6)	O5i—Cd2—O12i	81.34 (6)
O6i—Cd1—O11ii	86.24 (6)	N4iii—Cd2—O12i	166.32 (6)
N1—Cd1—O11ii	78.57 (6)	N5—Cd2—O12i	83.83 (6)
O11i—Cd1—O11ii	68.01 (6)	O8—Cd2—O2	95.88 (6)
O7—Cd1—O11ii	145.29 (6)	O5i—Cd2—O2	82.16 (6)
O1—Cd1—O12i	130.17 (5)	N4iii—Cd2—O2	78.94 (6)
O6i—Cd1—O12i	75.85 (5)	N5—Cd2—O2	161.71 (6)
N1—Cd1—O12i	129.21 (6)	O12i—Cd2—O2	113.54 (5)
O11i—Cd1—O12i	52.89 (5)	O8—Cd2—Cd1	91.80 (4)
O7—Cd1—O12i	73.30 (6)	O5i—Cd2—Cd1	79.95 (4)
O11ii—Cd1—O12i	110.55 (5)	N4iii—Cd2—Cd1	143.55 (5)
O1—Cd1—Cd2	86.32 (4)	N5—Cd2—Cd1	133.05 (5)
O6i—Cd1—Cd2	70.33 (4)	O12i—Cd2—Cd1	49.22 (4)
N1—Cd1—Cd2	130.56 (5)	O2—Cd2—Cd1	64.61 (4)
O11i—Cd1—Cd2	96.28 (4)		

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Symmetry code for **1**: (i) -x, -1-y, -z; (ii) 1-x, 1-y, 1-z; symmetry code for **2**: (i) x, 1+y, z; (ii) -x, -y, 2-z; (iii) 1+x, y, -1+z.

## Reference

- 1 Y. Niu, H. Hou, Y. Wei, Y. Fan, Y. Zhu, C. Du and X. Xin, *Inorg. Chem. Commun.*, 2001, **4**, 358-361.
- 2 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution and Refinement*, 1997, University of Göttingen.