Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPLEMENTARY DATA

for

Single-Crystal-to-Single-Crystal Transformation Involving Release of Bridging Water Molecules and Conversion of Chain Helicity in a Chiral Three-Dimensional Metal-Organic Framework

Dong-Xu Xue,[a] Wei-Xiong Zhang,[a] Xiao-Ming Chen*[a,b] and He-Zhou Wang[b]

[a]MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

Fax: +86-20-84112245; Tel: +86-20-84112074

e-mail: cxm@mail.sysu.edu.cn

[b]State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou 510275, China.

Materials and Measurements:

Solvent and starting materials for synthesis were purchased commercially, and were used as received. H_2bct was prepared according to the literature procedure.[1] Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Thermogravimetric analyses (TGA) were performed at a rate of 10 ºC/min under air using a NETZSCH TG 209 system. Low-temperature DSC analysis was performed on a NETZSCH DSC 204 instrument. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (CuKα, 1.5418 Å). The second harmonic generation (SHG) measurements were performed by the powder Perry and Kurtz method,[2] by placing a powder sample in an intense fundamental beam from a Q-switched Nd:YAG laser of wavelength 1064 nm.

Synthesis of **1**: A reaction of a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol), H_2bct (0.136 g, 0.5 mmol), iso-propyl alcohol (5.0 mL), and water (5.0 mL) in a 12-mL Teflon-lined bomb at 120 °C for 3 days afforded colourless prismatic crystals (yield *ca*. 68%). Anal. calcd (%) for $C_6H_6CdN_2O_5S_3$: C, 18.3; H, 1.5; N, 7.1. Found: C, 18.2; H, 1.5; N, 7.1. IR (KBr pellet, cm^{-1}): 1563(s), 1369(s), 1239(m), 1067(m), 897(m), 770(w), 675(m).

Synthesis of **2**: A single crystal or bulk crystals of **1** were heated at 180 °C for 30 min under vacuum to produce a single crystal and bulk crystals of **2** for single-crystal X-ray diffraction and other measurements, respectively. Anal. calcd (%) for $C_6H_4CdN_2O_4S_3$: C, 19.1; H, 1.3; N, 7.4. Found: C, 19.0; H, 1.3; N, 7.5. IR (KBr pellet, cm^{-1}): 1558(s), 1420(s), 1227(m), 1049(m), 940(m), 891(m), 698(w).

Single-crystal X-ray diffraction measurements for all data were carried out on a Bruker Smart APEX CCD area-detector diffractometer (MoKα, 0.71073 Å) at 293(2) K. Absorption corrections were applied by using multi-scan program SADABS. The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.[3]

Reference

1 X.-H. Lou, Y. Zhu, H. Gao, A.-X. Zhu, Y.-T. Fan, H.-W. Hou, H.-J. Lu, *Chin. J. Inorg. Chem.*, 2005, **21**, 716.

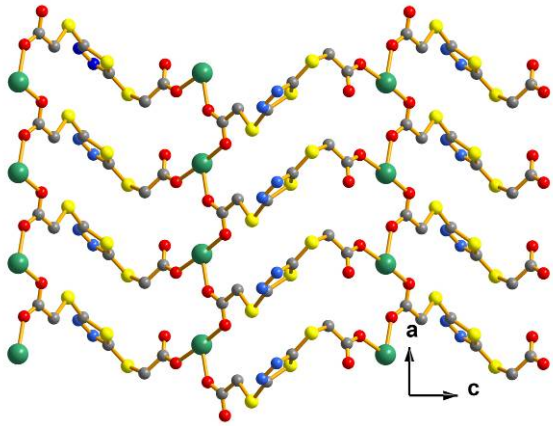
2 S. K. Kurtz, T. T. Perry, *J. Appl. Phys*., 1968, **39**, 3798.

3 (a) SMART Version 5.625, SAINT+ Version 6.22. Bruker Analytical X-ray System, Inc., Madison, Wisconsin, USA, 2001; (b) G. M. Sheldrick, SHELXTL, Version 6.10. Bruker Analytical X-ray System, Siemens Industrial Automation Inc., Madison, Wisconsin, USA, 2000.

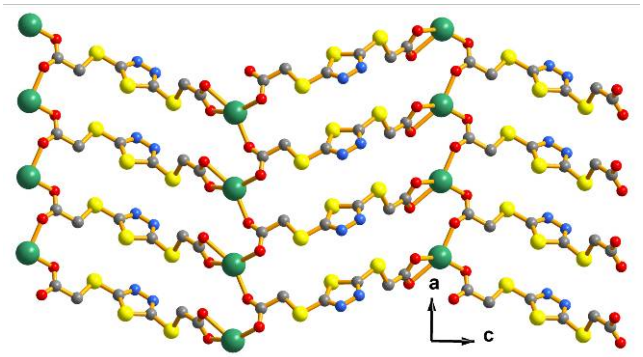
Table S1 Selected Bond Lengths (Å) and Bond Angles (º) for **1**·mpm and **2**·pmm.

1·mpm			
Cd1-O1a	2.2666(2)	Cd1-O1w	2.3954(2)
Cd1-O1wc	2.3909(2)	Cd1-N2b	2.3477(2)
Cd1-O3	2.2276(2)	Cd1-O4d	2.2977(2)
O1w-Cd1-N2b	97.225(4)	N2b-Cd1-O4d	100.686(4)
O4d-Cd1-O1wc	76.302(3)	O1wc-Cd1-O1w	83.947(3)
O3-Cd1-O1w	96.925(4)		
2·pmm			
Cd1-O3	2.256(1)	Cd1-O4	2.532(1)
Cd1-N2b	2.467(1)	Cd1-O4c	2.288(1)
Cd1-O2e	2.315(1)	Cd1-O1a	2.275(1)
O3-Cd1-O4	54.33(1)	O1a-Cd1-O2e	91. 39(1)
O3-Cd1-N2b	88.71(3)	O2e-Cd1-O4c	82.76(1)
N2b-Cd1-O4	119.01(2)	O4c-Cd1-O1a	94.49(2)

Symmetry codes for **1**·mpm: a, -*x* + 1/2, -*y* + 1, *z* + 1/2; b, *x* - 1/2, -*y* + 1/2, -*z*; c, *x* - 1/2, -*y* + 3/2, -*z*; d, *x* - 1, *y*, *z*. For **2**·pmm: a, -*x* - 3/2, -*y*, *z* + 1/2; b, *x* + 1/2, -*y* + 1/2, -*z*; c, *x* + 1/2, -*y* - 1/2, -*z*; e, -*x* - 1/2, -*y*, *z* + 1/2.



(a)



(b)

Fig. S1 Perspective view of the 2-D layer viewed along the *b*-axis in **1**·mpm (a) and **2**·pmm (b).

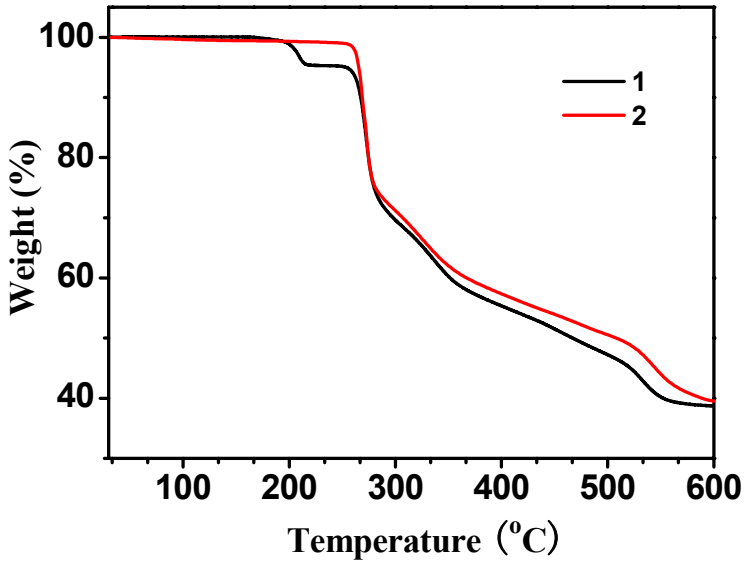


Fig. S2 TGA plots of **1** and **2** recorded in air.

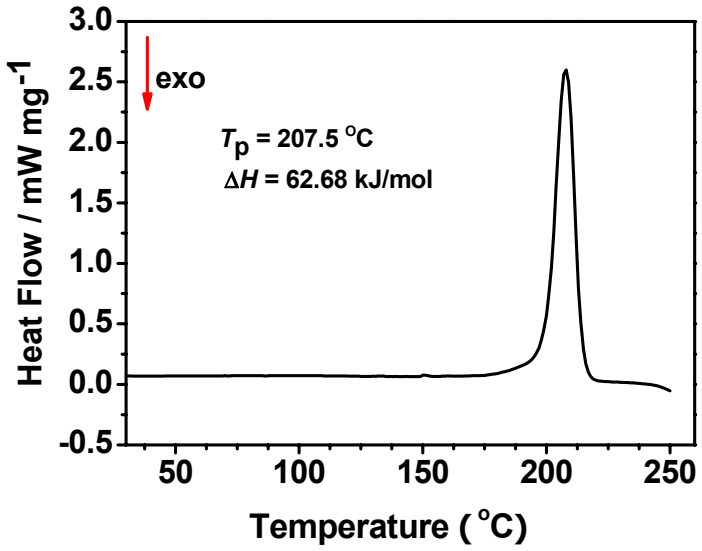


Fig. S3 DSC plot of **1** recorded in nitrogen gas.

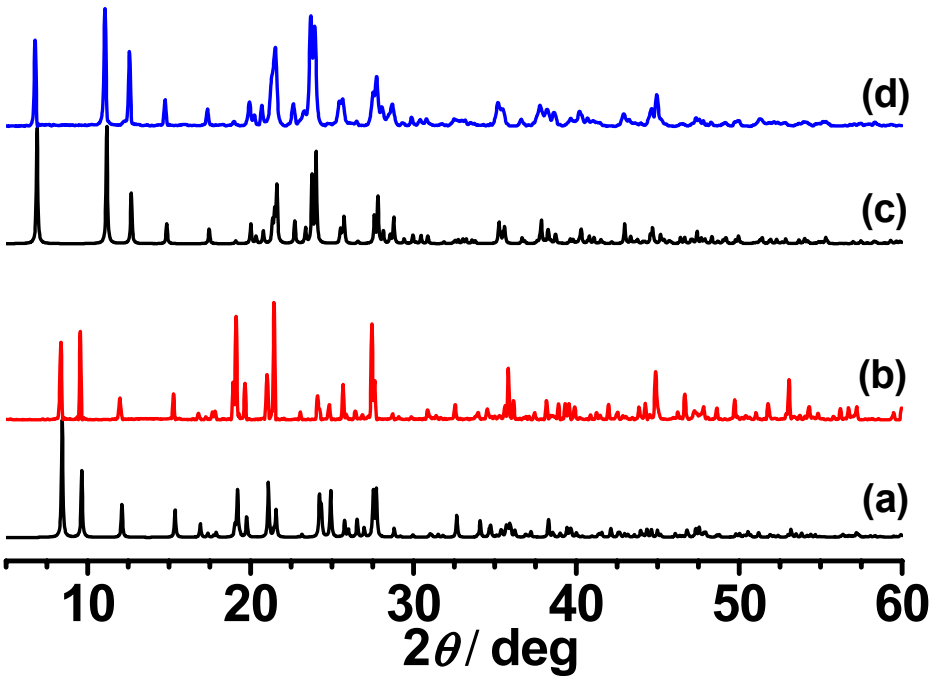
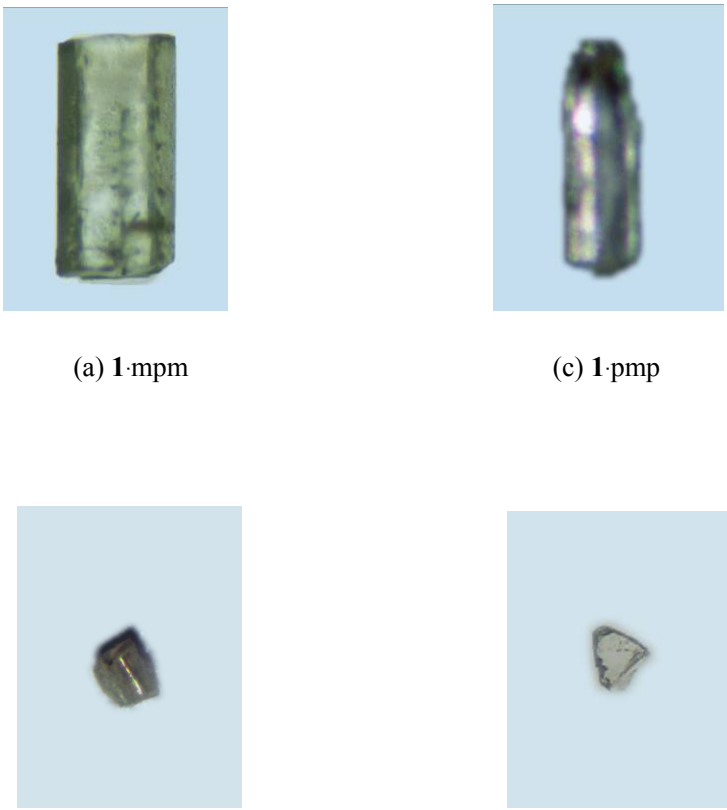


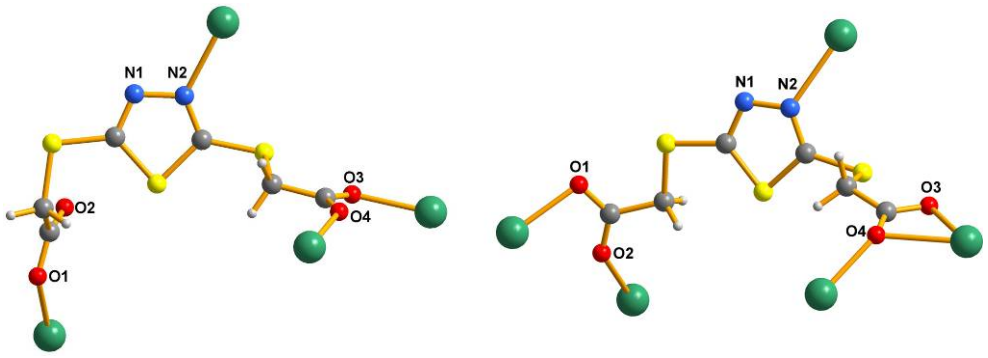
Fig. S4 PXRD patterns for (a) simulated **1**; (b) as-synthesized **1**; (c) simulated **2**; (d) as-synthesized **2** upon heating **1** at 180 °C for 30 minutes under vacuum.



(a) **1**·mpm (c) **1**·pmp

(b) **2**·pmm (d) **2**·mpp

Fig. S5 Photos of the single crystals of **1**·mpm (a), **2**·pmm (b), **1**·pmp (c), and **2**·mpp (d).



(a) μ_4-η^1: η^0: η^1: η^1: η^1(N2)-bridging (b) μ_5-η^1: η^1: η^1: η^2: η^1(N2)-bridging

Fig. S6 Different conformations and corresponding coordination modes of bct in **1**·mpm (a) and **2**·pmm (b).

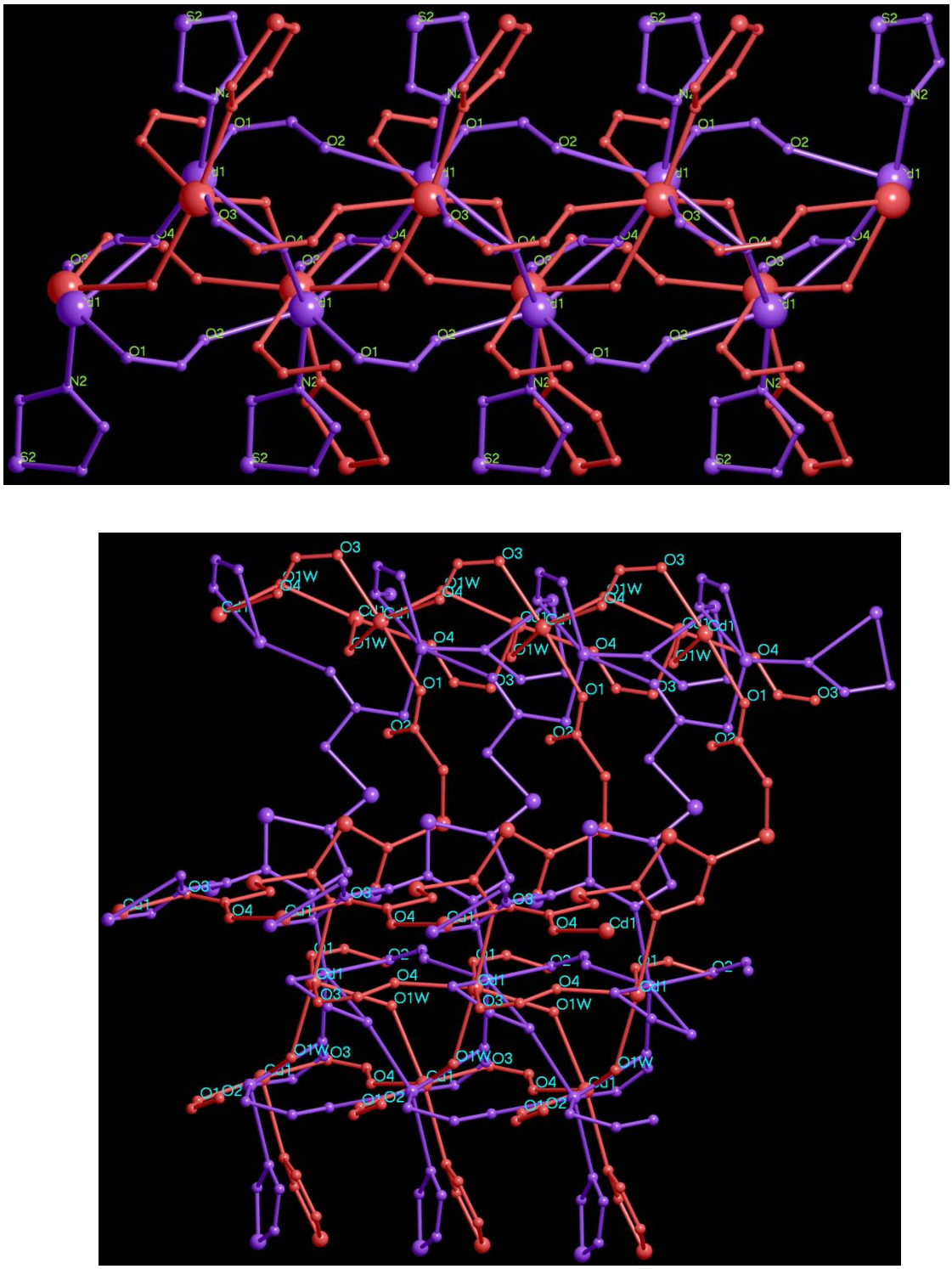


Fig. S7 Perspective views of the structural superpositions of **1**·mpm (red) and **2**·pmm (lavender) in two different directions. Some bct ligands are simplified for clarity in the plots.