Supporting information:

Axially chiral metal-organic frameworks produced from spontaneous resolution with an achiral pyridyl dicarboxylate ligand

Xin Tan, Jixian Zhan, Jianyong Zhang,* Long Jiang, Mei Pan, and Cheng-Yong Su

KLGHEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: zhjyong@mail.sysu.edu.cn

Experimental section

Synthesis of **Cd**. L (0.0254 g, 0.1 mmol) in DMF (4 mL) and $CdCl_2 \cdot 2.5H_2O$ (0.0223 g, 0.1 mmol) in H_2O (1 mL) were mixed and the mixture was heated in a closed container at 80 ^oC. After 1 d, colourless block crystals were obtained (20.2 mg, yield 51%). Microanalysis found (calcd.) for $C_{13}H_{11}NO_6Cd$: C 39.60 (40.07), H 3.05 (2.85), N 3.69 (3.59)%. IR (KBr pellet, cm^{-1}): 3417br (H_2O), 1610m (C=N), 1565s, 1537s (C=O), 1490m, 1450s, 1412s, 1378s, 771m, 730m, 700m, 649m, 581m.

Synthesis of **Zn**. L (0.0254 g, 0.1 mmol) in DMF (4 mL) and $ZnCl_2$ (0.0136 g, 0.1 mmol) in H_2O (1 mL) were mixed and the mixture was heated in a closed container at 80 ^oC. After 1 d, colourless block crystals were obtained (24.3 mg, yield 71%). Microanalysis found (calcd.) for $C_{13}H_{11}NO_6Zn$: C 45.36 (45.57), H 3.32 (3.24), N 4.02 (4.09)%. IR (KBr pellet, cm^{-1}): 3391br (H_2O), 1607s (C=N), 1571m, 1547s (C=O), 1489m, 1454s, 1410s, 1380s, 775m, 728m, 702m, 650m.

Synthesis of **Mn**. L (0.0254 g, 0.1 mmol) in DMF (4 mL) and $MnCl_2 \cdot 4H_2O$ (0.0198 g, 0.1 mmol) in H_2O (1 mL) were mixed and the mixture was heated in a closed container at 80 ^oC. After 1 d, colourless block crystals were obtained (28.7 mg, yield 85%). Microanalysis found (calcd.) for $C_{13}H_{11}NO_6Mn \cdot 0.5H_2O$: C 45.70 (45.77), H 3.47 (3.55), N 4.30 (4.11)%. IR (KBr pellet, cm^{-1}): 3391br (H_2O), 1613m (C=N), 1567s, 1540s (C=O), 1489m, 1451s, 1410s, 1380s, 774m, 732m, 703m, 653m.

Single-crystal X-ray diffraction data were collected on a Rigaku R-Axis Spider Single

Crystal Diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for *M*-**Cd**, *P*-**Cd** and *P*-**Zn** at 298 K and on an Oxford Germini S Ultra diffractometer with Cu Kα radiation (λ = 1.54178 Å) for *M*-**Zn** at 150 K. All the structures were solved by the direct methods following difference Fourier syntheses and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 software.[1] The non-hydrogen atoms were refined anisotropically. The water hydrogen atoms were located from the difference Fourier synthesis and a geometrical calculation, while the other hydrogen atoms were introduced in calculated positions and refined by using a riding model.

(1) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Solution and Refinement*, Göttingen University, Germany, 1997.

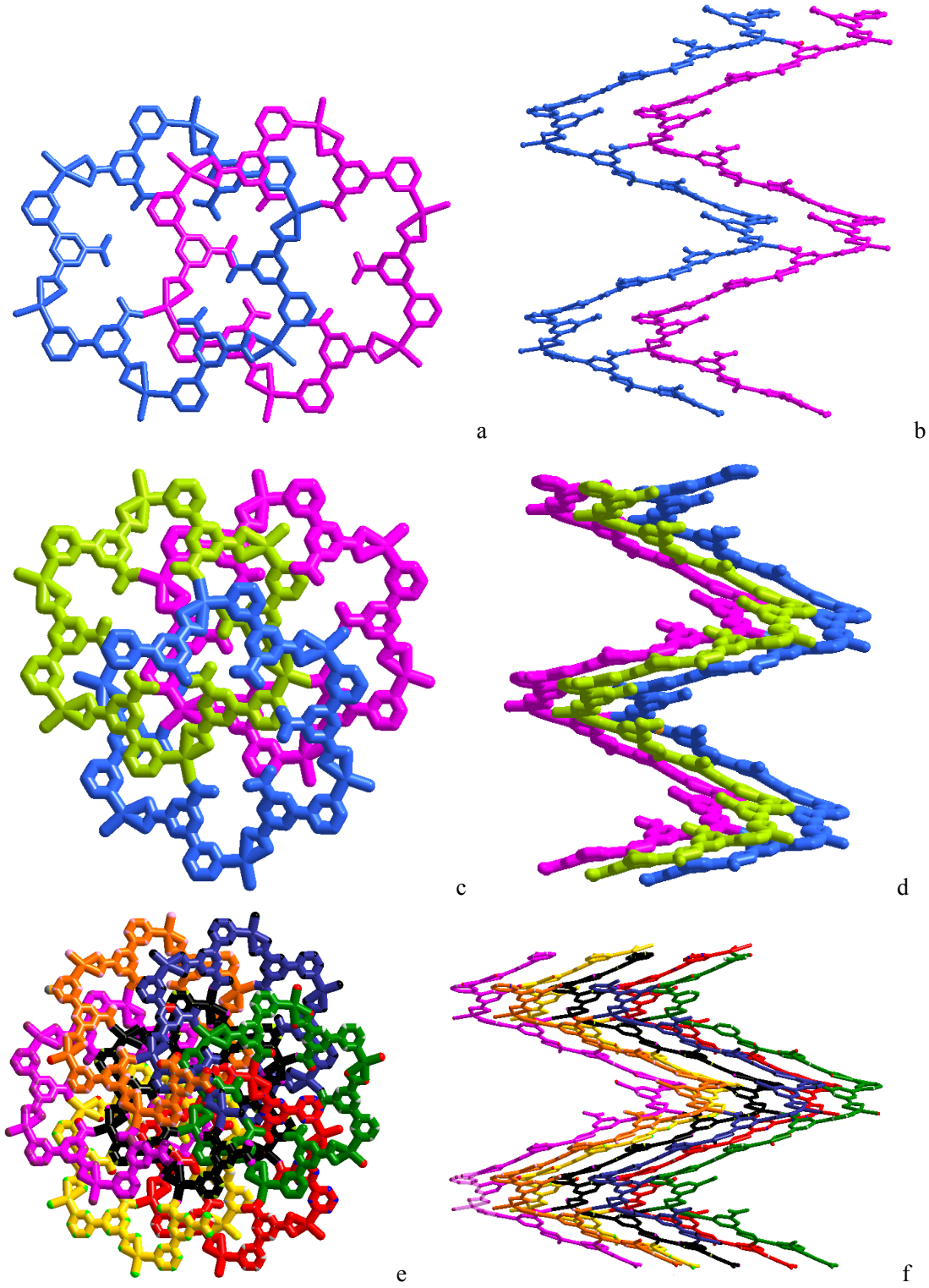

Figure S1. X-ray crystal structures of *P*-**Cd**, a) side view and b) top view of two adjacent helical chains, c) side view and d) top view of three adjacent helical chains, e) side view and f) top view showing connections of one helical chain with six neighbouring helical chains, with coordinated water molecules omitted for clarity.

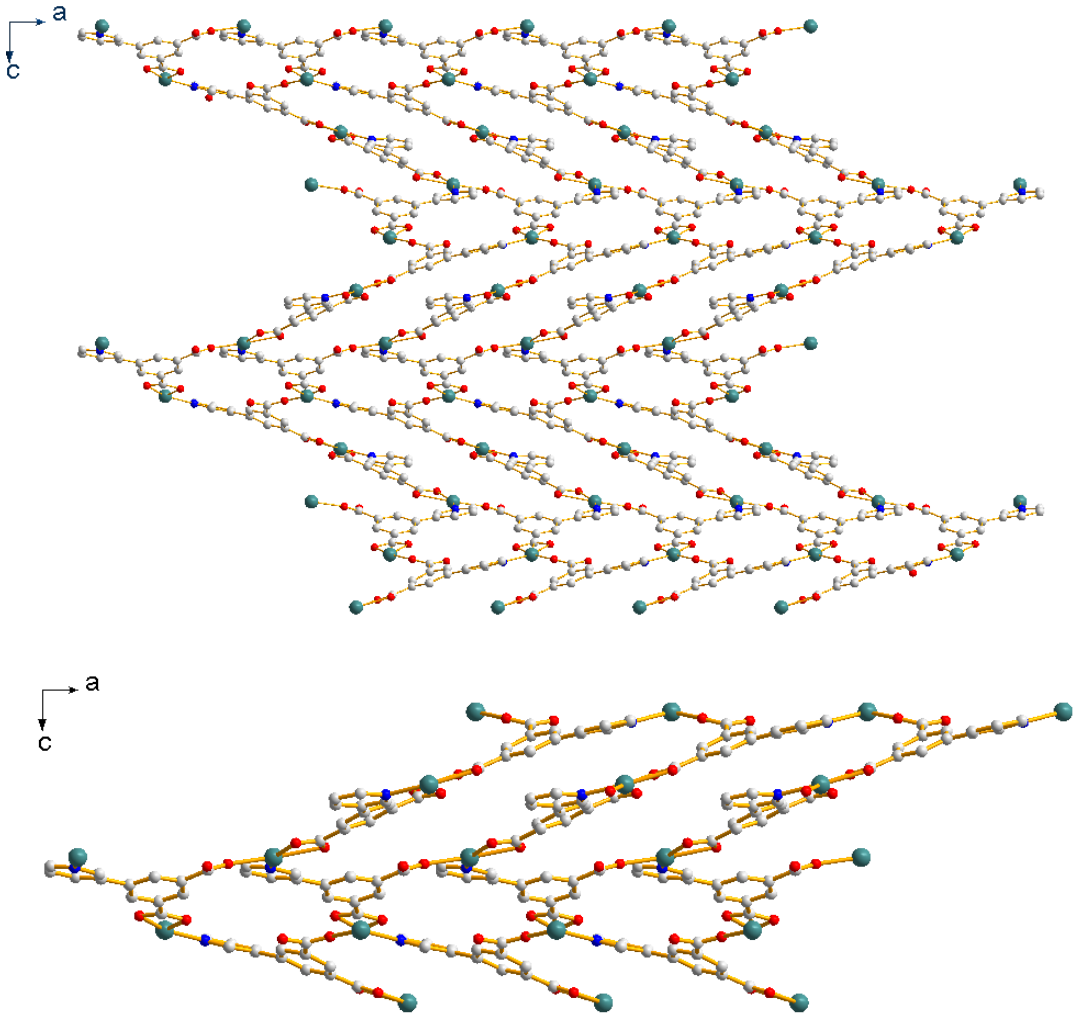

Figure S2. X-ray crystal structures of *P*-**Cd** with a (10,3)-*c* topology, with coordinated water molecules omitted for clarity.

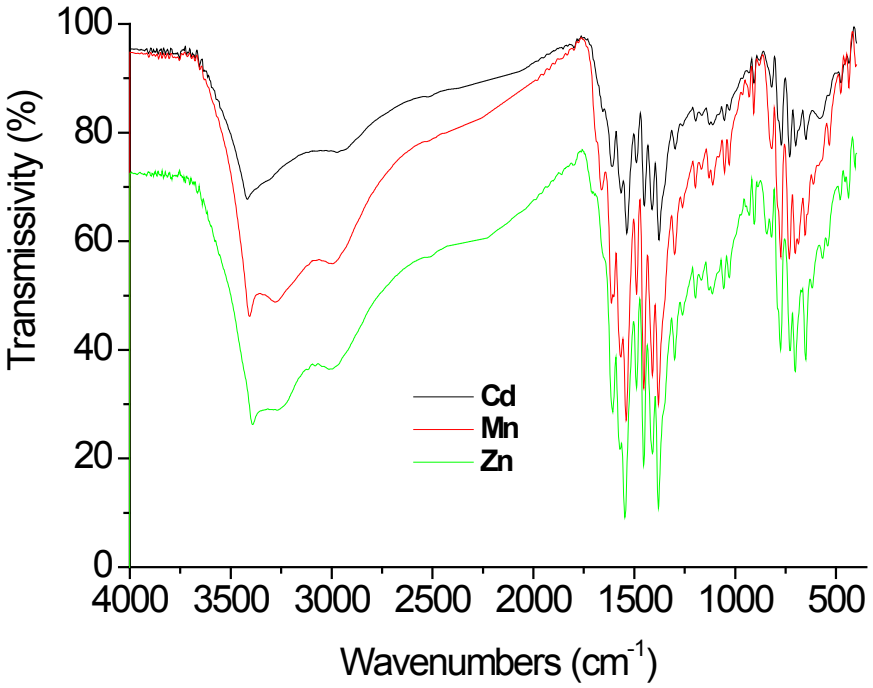

Figure S3. FT-IR spectra of **Cd**, **Zn** and **Mn** showing similar patterns. Broad absorptions at ca. 3400 cm^{-1} is attributed to the presence of water molecules. The absorptions at ca. 1567 and 1540 cm^{-1} are the characteristic $\nu(CO_2^-)$ symmetric stretching vibrations of the coordinated carboxylate groups (protonated COOH νC=O stretch, 1710 cm^{-1}). The characteristic C=N stretching vibration of the pyridyl groups at ca. 1610 cm^{-1}, suggesting the coordination of the N atom of the pyridyl group to the metal centre.

Table S1. Selected bond lengths (Å) and angles (°) for *M*-**Cd**.

Cd1—O3^{i}	2.185(2)	Cd1—O1	2.322(2)
Cd1—N1^{ii}	2.293(3)	Cd1—O2	2.426(2)
Cd1—O1W	2.269(2)	Cd1—O2W	2.322(3)
O3^{i}—Cd1—O1W	91.72(9)	N1^{ii}—Cd1—O2W	87.34(9)
O3^{i}—Cd1—N1^{ii}	96.11(9)	N1^{ii}—Cd1—O2	100.92(8)
O1W—Cd1—N1^{ii}	91.04(9)	O1—Cd1—O2	55.01(8)
O3^{i}—Cd1—O1	107.99(9)	O2W—Cd1—O2	88.37(8)
O1W—Cd1—O1	89.82(8)	O3^{i}—Cd1—O2	162.96(8)
N1^{ii}—Cd1—O1	155.84(9)	O1W—Cd1—O2	87.45(8)
O3^{i}—Cd1—O2W	92.99(10)	O1—Cd1—O2W	89.71(9)
O1W—Cd1—O2W	175.15(9)		

Symmetry codes: (i) 1+y, 1-x+y, 0.16667+z; (ii) y, -x+y, 0.16667+z.

Table S2. Selected bond lengths (Å) and angles (°) for *P*-**Cd**.

Cd1—O4^{i}	2.1864(17)	Cd1—O2	2.3259(16)
Cd1—N1^{ii}	2.2989(16)	Cd1—O1	2.4296(16)
Cd1—O1W	2.2759(18)	Cd1—O2W	2.3218(19)
O4^{i}—Cd1—O1W	92.01(7)	O2W—Cd1—O2	89.92(7)
O4^{i}—Cd1—N1^{ii}	96.18(7)	O4^{i}—Cd1—O1	163.03(6)
O1W—Cd1—N1^{ii}	91.10(7)	O1W—Cd1—O1	87.49(6)
O4^{i}—Cd1—O2W	92.80(8)	N1^{ii}—Cd1—O2	155.77(6)
O1W—Cd1—O2W	175.02(7)	O2—Cd1—O1	55.06(6)
N1^{ii}—Cd1—O2W	87.12(7)	N1^{ii}—Cd1—O1	100.79(6)
O4^{i}—Cd1—O2	107.98(6)	O2W—Cd1—O1	88.28(6)
O1W—Cd1—O2	89.80(6)		

Symmetry codes: (i) 1+x-y, -1+x, 0.16667+z; (ii) 1+x-y, x, 0.16667+z.

Table S3. Selected bond lengths (Å) and angles (°) for *M*-**Zn**.

Zn1—O3A^{i}	1.996(2)	Zn1—O1	2.117(2)
Zn1—N1A^{ii}	2.100(3)	Zn1—O2	2.351(2)
Zn1—O1W	2.077(3)	Zn1—O2W	2.144(2)
O3^{i}—Zn1—O2W	93.60(10)	N1^{ii}—Zn1—O1W	93.44(10)
O3^{i}—Zn1—N1^{ii}	97.49(11)	O1—Zn1—O1W	89.95(10)
O2W—Zn1—N1^{ii}	86.12(11)	O3^{i}—Zn1—O2	165.14(9)
O3^{i}—Zn1—O1	106.67(10)	O2W—Zn1—O2	86.92(9)
O2W—Zn1—O1	87.70(10)	N1^{ii}—Zn1—O2	97.36(10)
N1^{ii}—Zn1—O1	155.38(10)	O1—Zn1—O2	58.49(9)
O3^{i}—Zn1—O1W	93.12(10)	O1W—Zn1—O2	86.48(9)
O2W—Zn1—O1W	173.27(10)		

Symmetry codes: (i) -1+y, 1-x+y, -0.16667+z; (ii) y, 1-x+y, -0.16667+z.

Table S4. Selected bond lengths (Å) and angles (°) for *P*-**Zn**.

Zn1—O3^{i}	1.985(2)	Zn1—O1	2.114(2)
Zn1—N1^{ii}	2.097(3)	Zn1—O2	2.356(2)
Zn1—O1W	2.161(2)	Zn1—O2W	2.082(2)
O3^{i}—Zn1—O2W	93.09(9)	N1^{ii}—Zn1—O1W	85.98(9)
O3^{i}—Zn1—N1^{ii}	97.67(9)	O1—Zn1—O1W	87.66(9)
O2W—Zn1—N1^{ii}	93.52(9)	O3^{i}—Zn1—O2	165.00(9)
O3^{i}—Zn1—O1	106.68(9)	O2W—Zn1—O2	86.57(8)
O2W—Zn1—O1	90.21(9)	N1^{ii}—Zn1—O2	97.32(9)
N1^{ii}—Zn1—O1	155.13(9)	O1—Zn1—O2	58.34(8)
O3^{i}—Zn1—O1W	93.19(10)	O1W—Zn1—O2	87.27(8)
O2W—Zn1—O1W	173.71(9)		

Symmetry codes: (i) -1+y, 1-x+y, -0.16667+z; (ii) y, 1-x+y, -0.16667+z.