Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Two luminescent enantiomorphic 3D metal-organic frameworks with 3D homochiral double helices

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Materials and Methods:

All reagents and solvents used were received from commercial suppliers without further purification. Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS Elemental Analyzer. Metal elemental analyses were carried out on an Ultima-2 ICP Emission Spectrometer. The infrared spectra with KBr pellet were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR Spectrometer. Thermal analyses were performed on a NETZSCH STA 449C instrument from room temperature to 800 ℃ with a heating rate of 10 ℃ min^{-1} under nitrogen flow. The solid-state luminescence emission/excitation spectra were recorded on a FLS920 fluorescence spectrophotometer. Circular dichroism (CD) spectra were conducted on a Jasco J-810 spectrodichrometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX-2500 diffractometer with Cu K_{α}.

Synthesis:

The ligand L- or D-Na_3TTA was prepared according to the described method.[1]

$\{Na_3[Cd_2(L\text{-}TTA)_2(\mu_2\text{-}Cl)](H_2O)_6\}_n$ (**1L**). L-Na_3TTA solution (0.5 mmol, 0.1M) was neutralized with HCl (1.0 M) to pH = 6, and then 5.0 mL of ethanol was added. After 154.3 mg (0.5 mmol) of $Cd(NO_3)\cdot 4H_2O$ was added into the aforementioned aqueous solution, the reaction mixture was stirred at room temperature for half an hour and then placed into a Teflonlined autoclave (20 mL). The autoclave was sealed and heated at 120 °C for 72 h. After the autoclave was cooled to room temperature, large, colorless octahedral crystals of **1L** were separated by filtration, washed with distilled water, and dried in air (yield: ca. 66% based on L-Na_3TTA).

$\{Na_3[Cd_2(D\text{-}TTA)_2(\mu_2\text{-}Cl)](H_2O)_6\}_n$ (**1D**) can also be obtained by the same synthetic procedures as that for **1L** except using D-Na_3TTA instead of L-Na_3TTA as the starting material. Large, colorless octahedral crystals of **1D** were collected in 62% yield on the basis of D-Na_3TTA.

Anal. Calcd for $Na_3Cd_2C_{24}H_{42}N_{12}O_{18}Cl$ **(1L)**: Na, 6.17; Cd, 20.38; C, 25.83; H, 3.79; N, 15.06; found: Na, 6.01; Cd, 20.02; C, 25.58; H, 3.80, N, 14.94%. The IR spectrum of **1L** is shown in **Fig S5**.

Anal. Calcd for $Na_3Cd_2C_{24}H_{42}N_{12}O_{18}Cl$ **(1D)**: Na, 6.17; Cd, 20.38; C, 25.83; H, 3.79; N, 15.06; found: Na, 5.58; Cd, 20.05; C, 25.73; H, 3.85, N, 15.05%. The IR spectrum of **1D** is shown in **Fig S5**.

Crystallographic Analyses:

The structural determination of single crystal was performed on Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. The structures were solved by direct methods and refined by the full-matrix leasts-squares technique on F^2 using the SHELXTL-97 program.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon atoms were generated geometrically (C-H bond fixed at 0.97 Å). Notably, the water molecules in the two complexes were refined by using the pseudo-isotropic “ISOR” restraint to make the ADP values of the disordered oxygen atoms more reasonable.

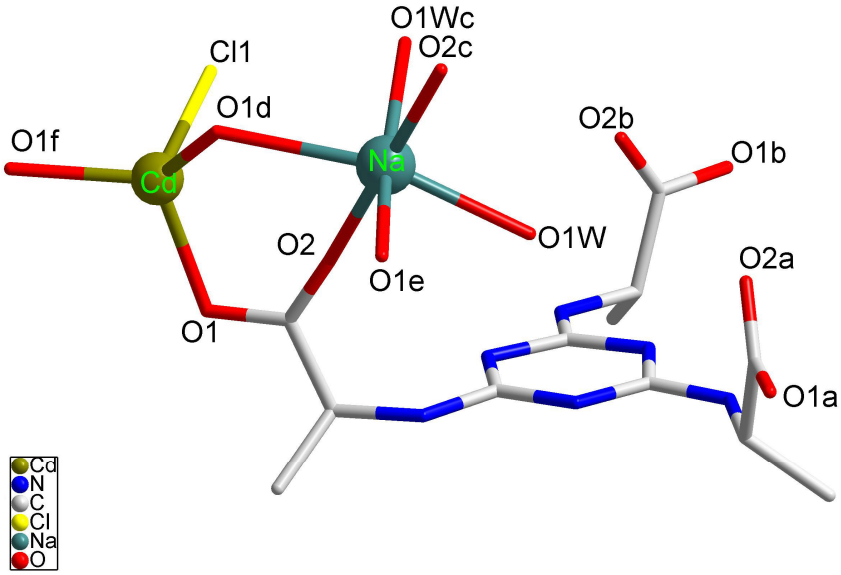

Fig. S1 Coordination environment of the Cd(II) and Na(I) ions in compound **1L**. Symmetry codes for the generate atoms: a, -0.5+y, 0.5-z, -x; b, -z, 0.5+x, 0.5-y; c, -0.25-x, 0.25+z, -0.25+y, d, y, z, x; e, -0.25-y, 0.25+x, -0.25+z; f, z, x, y.

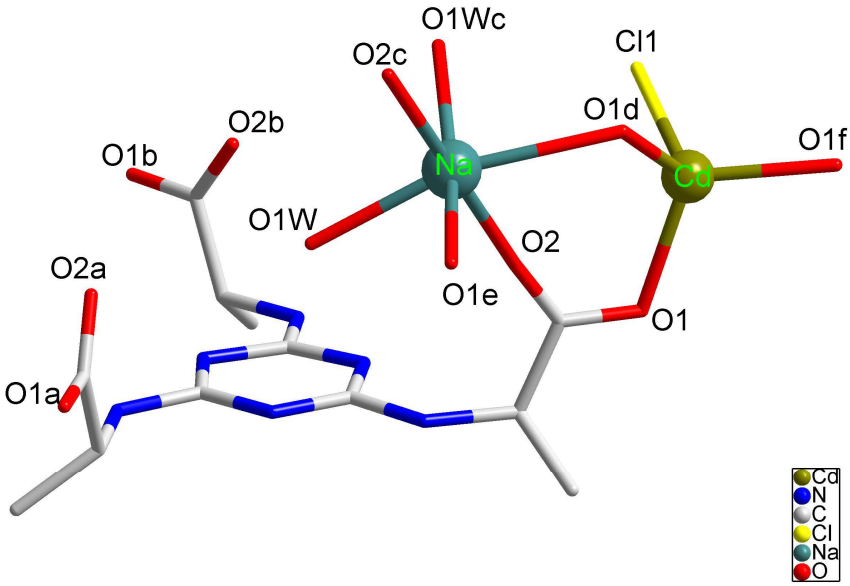

Fig. S2 Coordination environment of the Cd(II) and Na(I) ions in compound **1D**. Symmetry codes for the generate atoms: a, 1-y, 0.5+z, 0.5-x; b, 0.5-z, 1-x, -0.5+y; c, 0.75-x, 0.75-z, 0.75-y, d, 1.5-y, 1-z, -0.5+x; e, -0.75+y, 1.25-x, -0.25+z; f, 0.5+z, 1.5-x, 1-y.

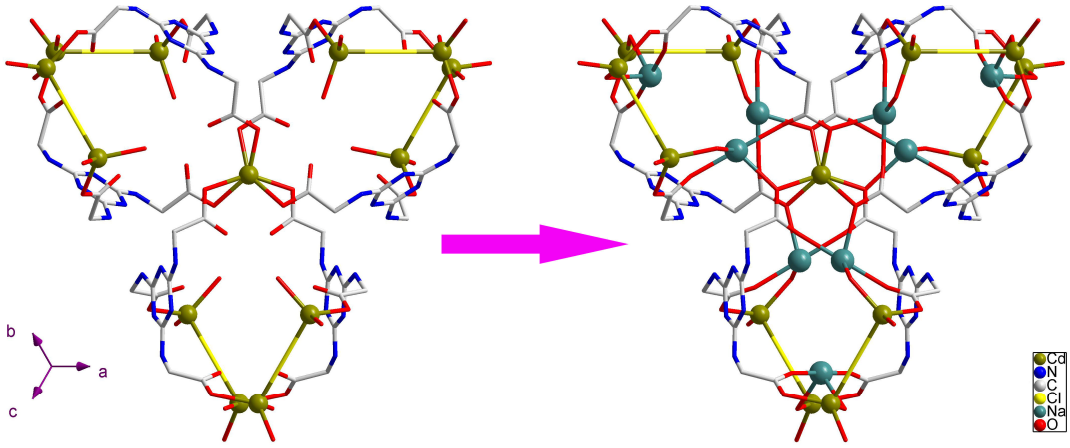

Fig. S3 The views of three cages held together through a Cd(II) ion and arrangement of sodium ions in these cages.

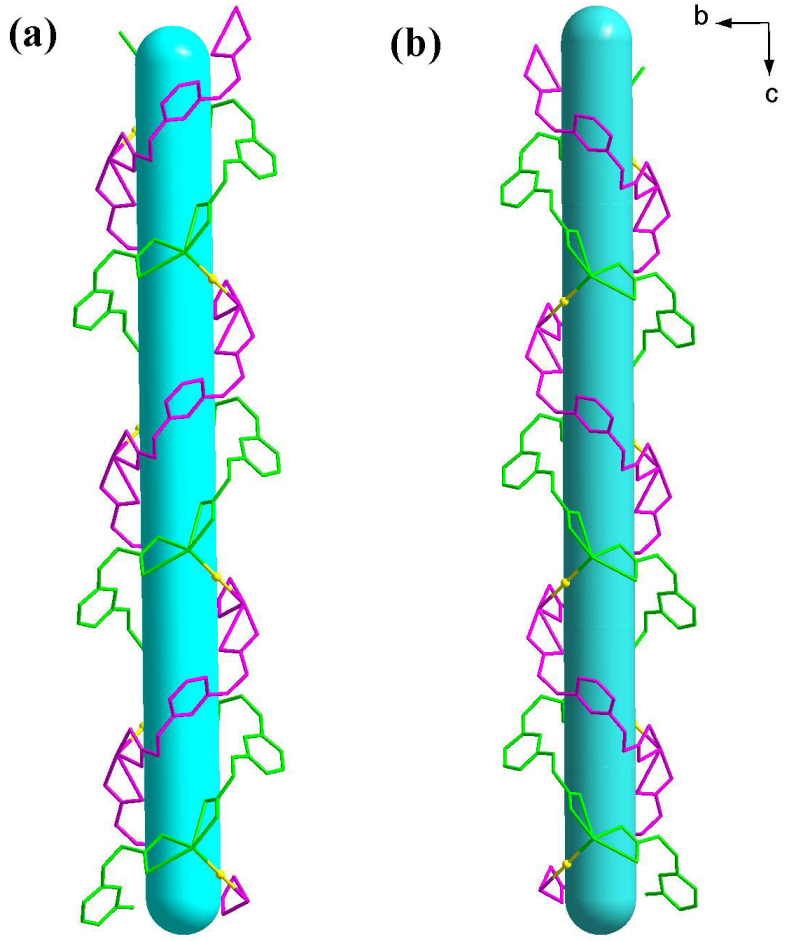

Fig. S4 The twofold homochiral (a) right-handed double helix in **1L** and (b) left-handed double helix in **1D** viewed perpendicular to the *a* axis.

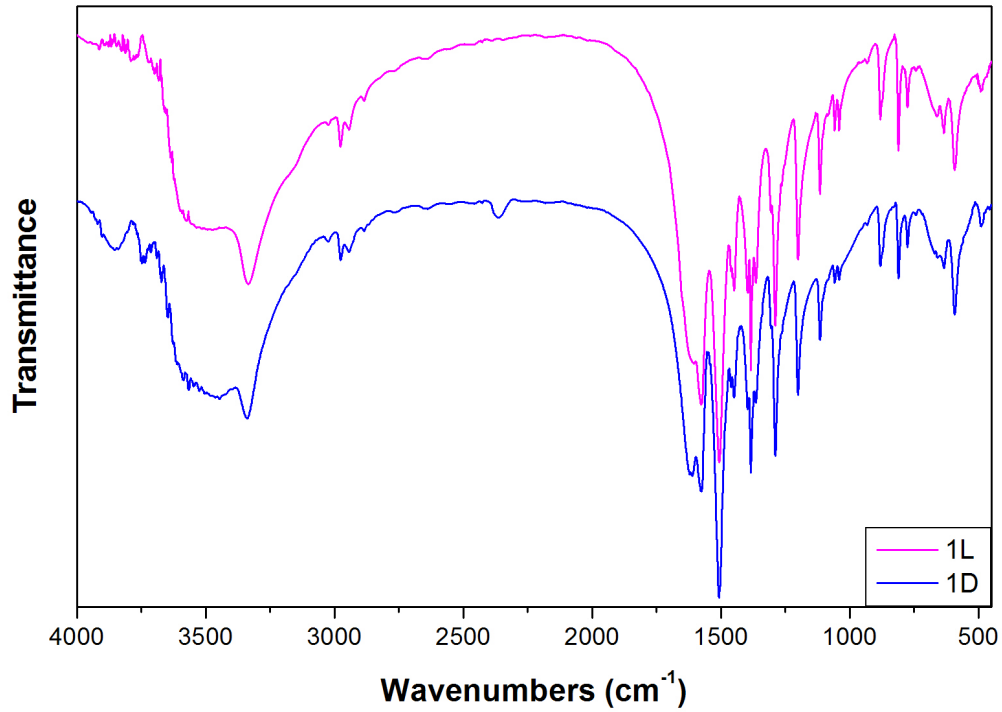

Fig. S5 IR spectra of compounds **1L** and **1D**.

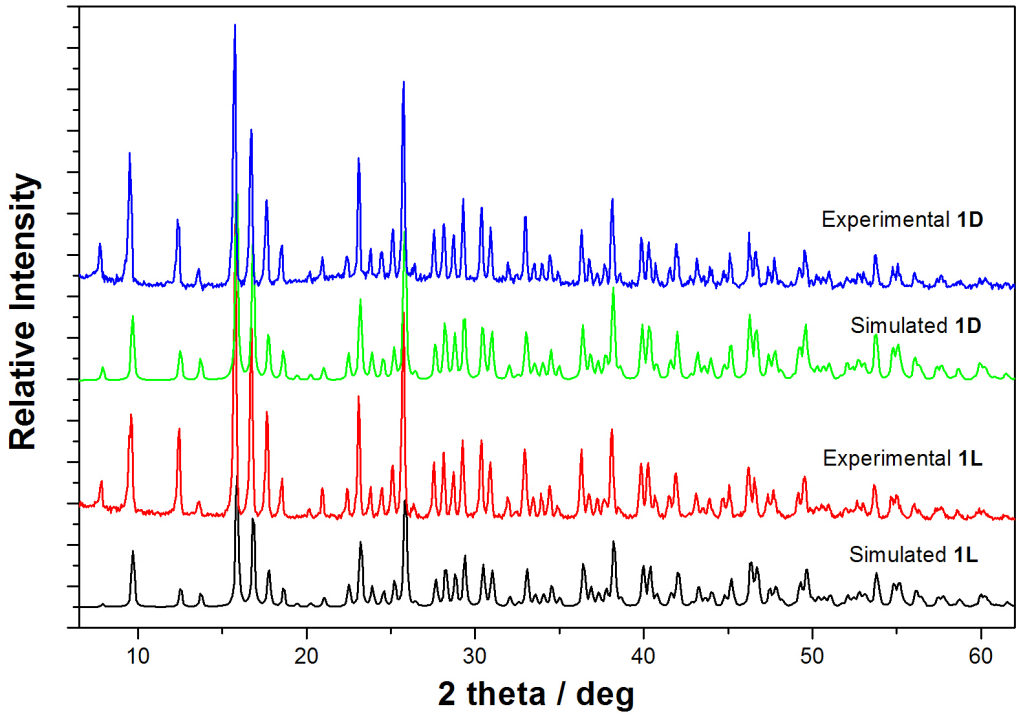

Fig. S6 Powder X-ray diffractions for simulated and experimental **1L** and **1D.**

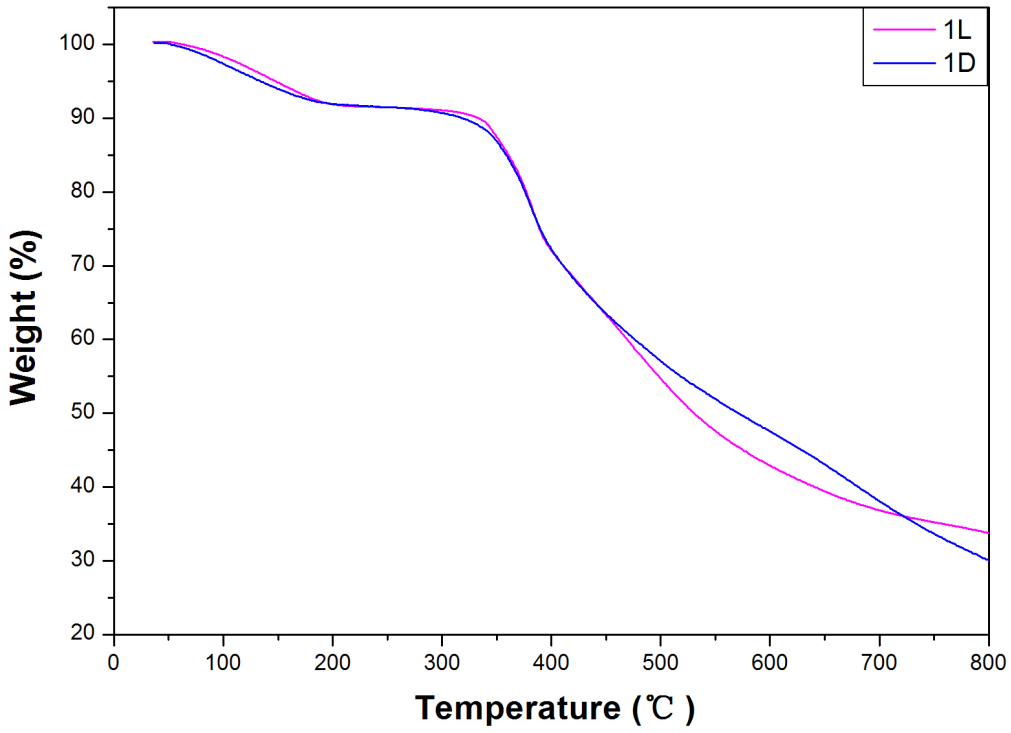

Fig. S7 TGA curves of compounds **1L** and **1D.**

[1] Q. Zhu, T. Sheng, R. Fu, S. Hu, J. Chen, S. Xiang, C. Shen and X. Wu, *Cryst. Growth Des.* 2009, **9**, 5128.
[2] *SHELXTL*, version 5.10; Siemens Analytical X-ray Instruments Inc.: Madison, WI, **1994**.