Electronic Supplementary Information

Vapour-driven crystal-to-crystal transformation showing interlocking switch of the coordination polymers chains between 1D and 3D

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Experimental Section

Materials and Methods.

All chemicals were obtained from commercial sources and were of GR/AR grade. IR spectra (KBr pellets) were obtained on a Nicolet iS10 FT-IR spectrometer. Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 1/1100 analyzer under air atmosphere with a heating rate of 20 °C min^{-1} from 25 to 800°C. PXRD patterns were obtained using a BrukerD8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). The elemental analysis (C, H, N) was performed using Vario EL III CHNOS elemental analyzer.

Synthesis Procedures

The ligand HBCbpeCl (HBCbpeCl = 1-(4-carboxybenzyl)-4-[2-(4-pyridyl)-vinyl]pyridinium chloride) was synthesized according to the previously reported literature from us.[1] The general procedures for the preparation of two compounds were as follows:

Synthesis of [Cd(BCbpe)Cl$_2$]·DMF·H$_2$O (1): The starting materials of $CdCl_2$ (0.5 mL, 0.1 mol/L) and HBCbpeCl (4.4 mg, 0.0125 mmol) were added in a mixed solvents (H_2O/DMF, v/v = 1: 2), and stirred for 30 min, then evaporated at room temperature for 7 days, cuboid-shaped colourless single crystals were obtained with a yield of 77% (based on HBCbpeCl). Calcd for $CdCl_2C_{23}N_3O_4H_{25}$(590.76): 46.76; H, 4.26; N, 7.11. Found: C, 46.92; H, 3.94; N, 7.14.

Synthesis of [Cd(BCbpe)Cl$_2$]·5H$_2$O (2): Compound (**2**) was obtained in a similar fashion to (**1**), but the water used instead of mixed solvents. Long pink needle crystals were collected after 7 days and dried in air (62% yield). Calcd for $CdCl_2C_{20}N_2O_7H_{26}$(589.73): C, 40.73; H, 4.44; N, 4.75. Found: C, 40.57; H, 4.74; N, 4.75.

Synthesis of [Cd(BCbpe)$_2$(H$_2$O)$_2$Cl$_2$]·2BCbpe·8H$_2$O (1a): The **1a** was crystalized in a few hours by dropping 50-150 microliters water onto the crystal of **1** with a yield of 71%, and it is needed to maintain the crystal in water environment during the whole process. Calcd for $CdCl_2C_{80}N_8O_{18}H_{84}$ (1628.85): C, 58.99; H, 5.20; N, 6.88. Found: C, 58.63; H, 5.26; N, 6.81.

X-ray Crystallographic Analysis

The X-ray diffraction data for crystal **1** were collected on an Agilent Diffraction SuperNova dual diffractometer with Cu Kα radiation (λ = 1.54178 Å). Single-crystal X-Ray diffraction data for **2** and **1a** were collected using Mo Kα (λ = 0.7107 Å) radiation and Cu Kα radiation (λ = 1.54178 Å) on a Gemini A ultra diffractometer equipped with a CCD area detector, respectively. The structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by using SHELXL-2017 program.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters except for the individual lattice water in compound **2** and **1a**. In all compounds, allowance for the hydrogen atoms of the water molecules were not included in final refinements. Compound **1** has some 15% disorder at the central ethylenic C6=C7 bond but no major change in the overall structure, and its difference map is calculated and provided at Fig. S12. In compound **2**, the asymmetric unit has half-occupancy and four unit-occupancy water molecules in general positions and half of a water molecule on a twofold axis, leading to the reported formula with "·5H$_2$O". The effective free volume in **1** and **2**, which are calculated by PLATON analysis without consideration of the free molecules, are 25.8% (1294.5 Å^3 per unit) and 29.7% (5055.8 Å^3 per unit), respectively.

Crystallographic data for (1). $CdCl_2C_{23}N_3O_4H_{25}$; M_r = 590.76; space group *P*-1; a = 8.4809(3) Å, b = 12.3920(6) Å, c = 12.8512(6) Å, α = 92.174(4)°, β = 99.176(4)°, γ = 103.153(4)°; T = 293(2) K; Z = 2; V = 1294.46(10) Å^3;-D_c = 1.516 g cm^{-3}; μ = 8.930 mm^{-1}; F(000) = 596; 8815 reflections collected, of which 5089 unique (R_{int} = 0.0547); GOF = 1.013; R_1 = 0.0546 and ωR_2 = 0.1446 [$I > 2\sigma(I)$]. CCDC 1816177

Crystallographic data for (2). $CdCl_2C_{20}N_2O_7H_{26}$; M_r = 589.73; space group *C*2/c; a = 29.9946(12) Å, b = 12.7727(9) Å, c = 13.3844(6) Å, β = 98.122(4)°; T = 293(2) K; Z = 8; V = 5076.3(5) Å^3; D_c = 1.543 g cm^{-3}; μ =

1.111 mm^{-1}; F(000) = 2384; 14724 reflections collected, of which 6042 unique (R_{int} = 0.0263); GOF = 1.043; R_1 = 0.0485 and ωR_2 = 0.1387 [I>2σ (I)]. CCDC 1816178

Crystallographic data for (1a). $CdCl_2C_{80}N_8O_{18}H_{84}$; M_r = 1628.85; space group $P2_1$/n; a = 9.4764(2) Å, b = 18.9403(2) Å, c = 22.1540(3) Å, β = 91.056(2)°; T = 293(2) K; Z = 2; V = 3975.65(11) Å^3; D_c = 1.361 g cm^{-3}; μ = 3.425 mm^{-1}; F(000) = 1692; 31722 reflections collected, of which 7087 unique (R_{int} = 0.0371); GOF = 1.046; R_1 = 0.0664 and ωR_2 = 0.1929 [I>2σ (I)]. CCDC 1825689

The Experiment Details of the Crystal-to-Crystal Transformation

Since the saturated vapour pressure of DMF is low at room temperature, all conversion experiments from **2** to **1** were performed in a DMF vapour environment by heating DMF solvent at 40 °C.

Additional Data and Figures

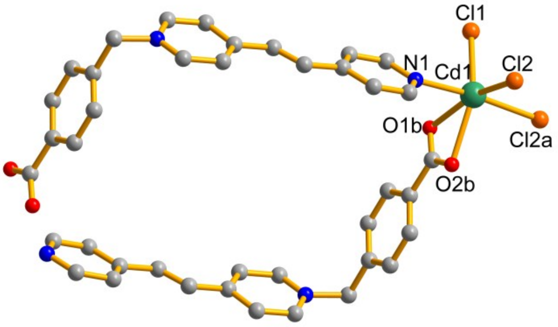


Fig. S1. The coordination environment of **1**. Symmetry codes: a (2-x, -y, 2-z); b (1-x, 1-y, 1-z). All hydrogen atoms and guest molecules are omitted for clarity.

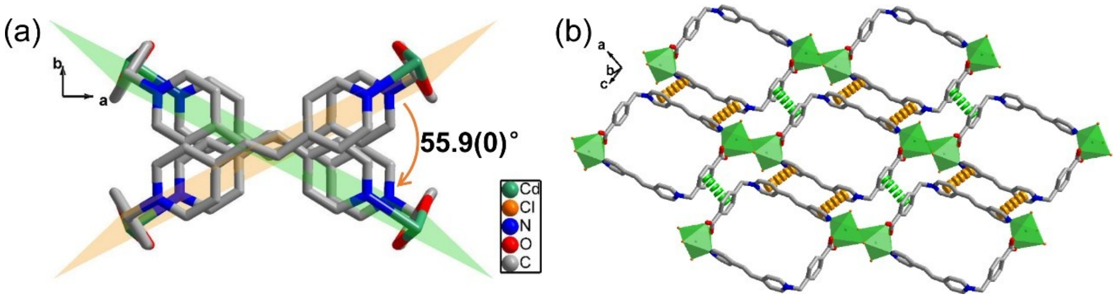


Fig. S2. (a) The angle between the planes where the two interlocked rings are located is 55.9(0)°. Take the four vertices of the rectangular ring as a plane. (b) The interaction between the parallel 1D chains in compound **2**. The golden dashed lines and the green dashed lines represent cation-π interactions (centroid-centroid distances: 3.877(2) Å; angle: 15.6(2)°) and π–π stacking interactions (centroid-centroid distances: 3.742(3) Å; angle: 0°) respectively. All hydrogen atoms and guest molecules are omitted for clarity.

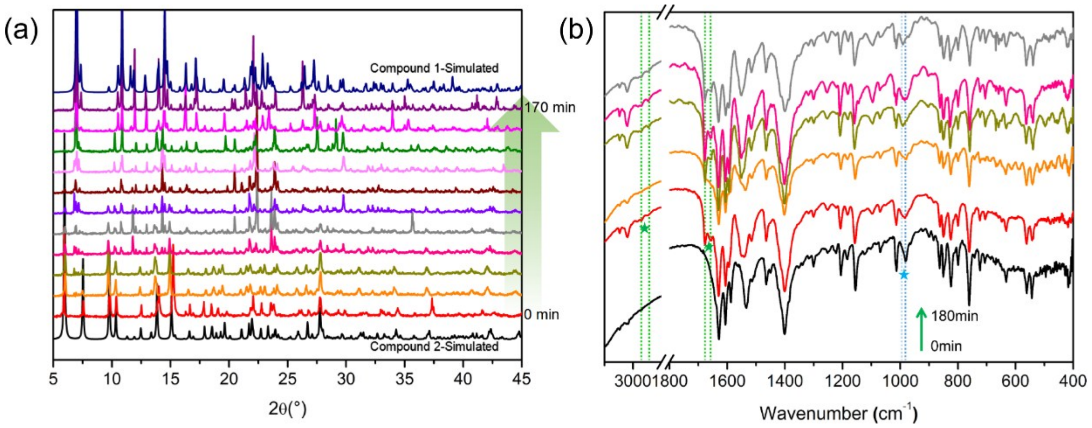
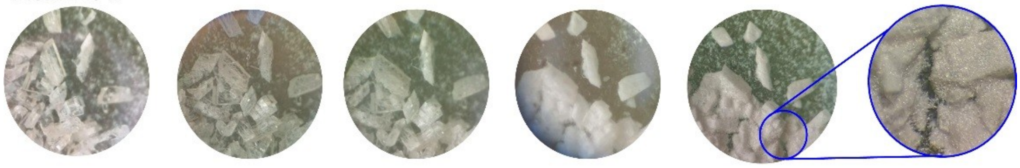


Fig. S3 The PXRD patterns (a) and IR spectra (b) of transformation processes from **2** to **1**. In (b) the color of the star: green, and blue represents the new appearance, and the blue shift respectively.

From **1** to **2**



From **2** to **1**

Fig. S4 Photographs of changes in crystal morphology during conversion. The series diagrams above are the conversion process from **1** to **2**, and the diagrams below are from 2 to 1.

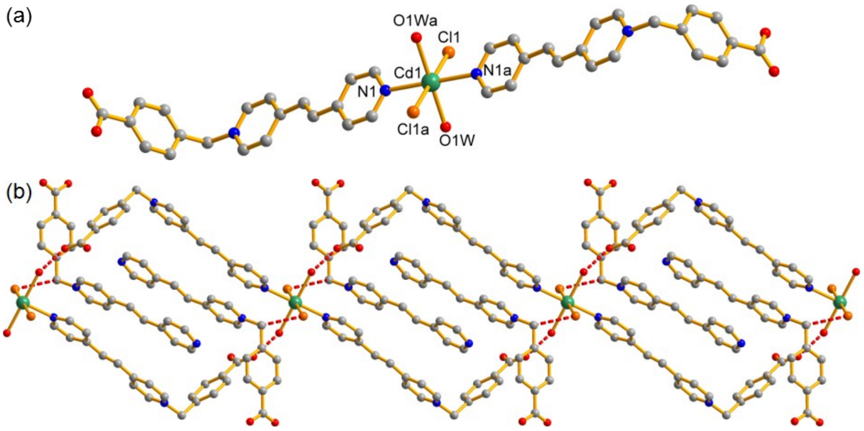


Fig. S5 (a) The coordination environment of **1a**. (b) The 1D supramolecular chain of **1a**. **1a** is a zero-dimensional coordination compound, the center Cd^{II} ion is six-coordinated by two N atoms from the BCbpe ligands, two O atoms from coordinated water molecules and two Cl$^-$ anions.

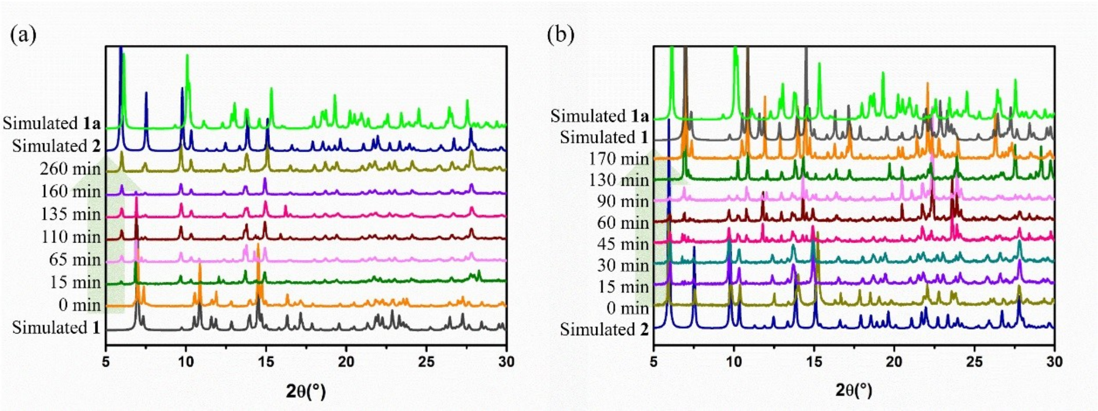


Fig. S6 The PXRD patterns of **1a** compared with the peaks appearing and disappearing during the conversion.

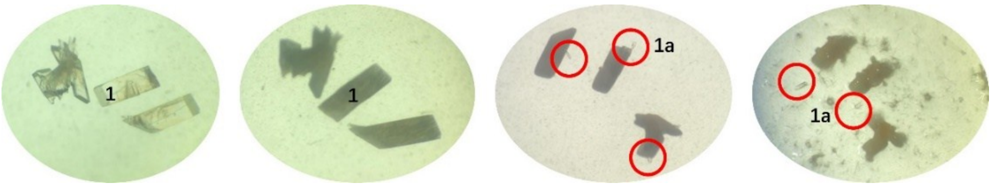


Fig. S7 Photographs of changes in crystal morphology during conversion from **1** to **1a**.

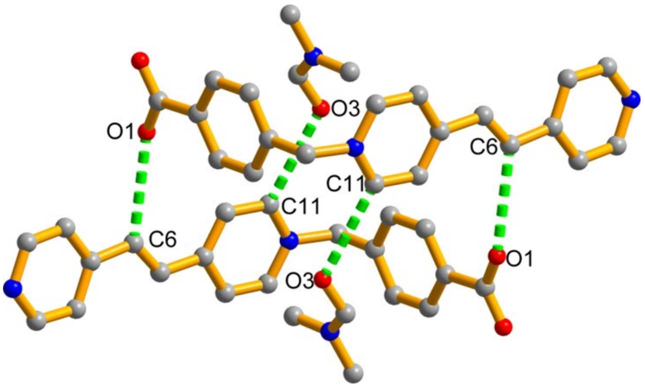


Fig. S8. The hydrogen bonds between O1 and C6 from adjacent BCbpe (D-H...A distance: 3.230(9) Å; angle: 162°); Another hydrogen bond interactions between C11 from Bcbpe and O3 from DMF (D-H...A distance: 3.172(18) Å; angle: 158°) in compound **2**.

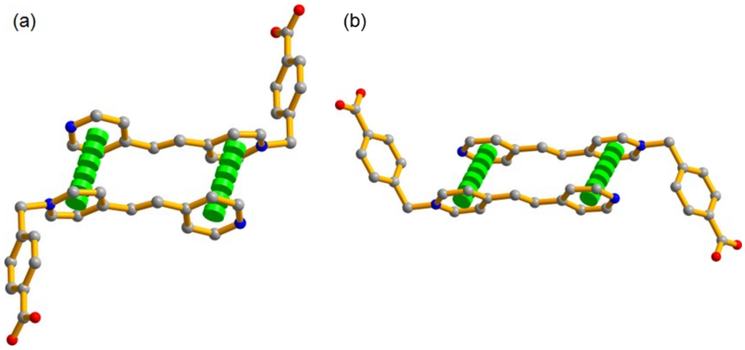


Fig. S9 (a) The head-to-tail fashion of BCbpe in the subunit of compound **2**; (b) The head-to-tail fashion of guest BCbpe in compound **1a**. Both of the pictures also show the cation-π interactions between pyridinium and pyridine rings. All hydrogen atoms and guest molecules are omitted for clarity.

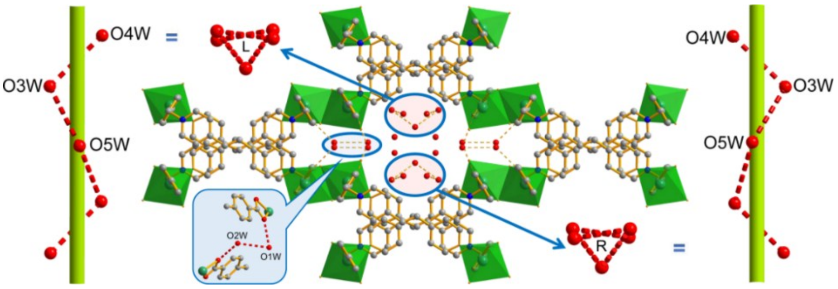


Fig. S10 The distribution of water molecules in the compound **2**. The O1W, O2W and carboxylate oxygen atoms are connected with each other via hydrogen bonds (O1 W...O2W 3.090 Å; O1W...O2 2.798 Å; and O2w...O1 2.794 Å) at the acute parts of the rhombic channels to prop up the rhombic channels. Interestingly, unprecedented spiral water sections containing five water molecules were observed at the obtuse portion of the rhombic channels, and the R-hand and L-hand helical sections arranged above or below in one channel(O4W...O3W 2.936 Å; O3W...O5W 2.937 Å).

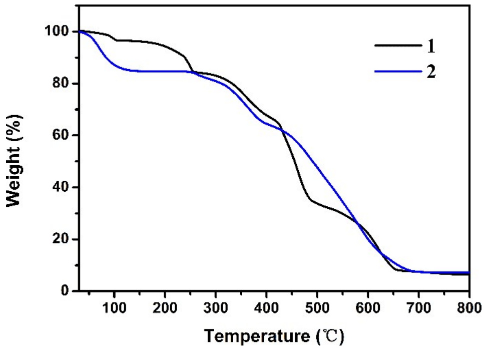


Fig. S11 The TG Plots of compound **1** (black) and **2** (blue). The TGA curve of compound **1** shows two steps weight loss of dissociative molecules, the first step to lose one water 3.36% from 30 to 110 °C (Calcd: 3.05%), and the second step shows a 12.20% mass loss corresponding to the release of one DMF from 110 to 256 °C (Calcd: 12.36%). Compound **2** shows a 15.33% mass loss from 40 to 120 °C, which is associated with framework desolvations (Calcd: 15.22%).

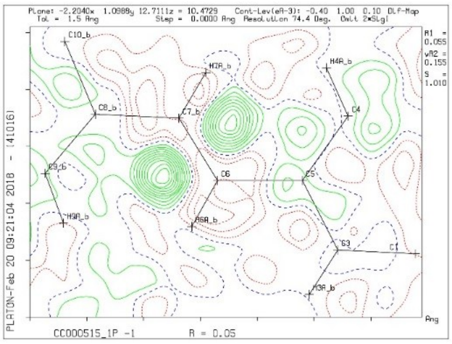


Fig. S12 Difference map calculated for compound **1**.

References

1. J. K. Sun, W. Li, C. Chen, C. X. Ren, D. M. Pan and J. Zhang, *Angew. Chem. Int. Ed.*, 2013, **52**, 6653-6657.
2. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.