

Supporting Information for

Hydrogen bond-organized two-fold interpenetrating homochiral pcu net

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Crystal structure determination

Single-crystal X-ray diffraction analysis of **2** was performed by using a Bruker Smart CCD diffractometer equipped with graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected at 296(2) K within the limits of $1.37^\circ \leq \theta \leq 25.05^\circ$. Starting model for structure refinement was solved by direct methods using SHELXS-97,^{S1} and the structural data were refined by full-matrix least-squares methods on F^2 using the WINGX^{S2} and SHELX-97^{S1} program packages. The molecular structure of **2** was solved in the monoclinic chiral space group $P2_1$. The asymmetric unit consists of two copper atoms, two D-H₂Cam ligands, four 4-ptz ligands, and two coordination water molecules. Anisotropical thermal factors were assigned to most of non-disordered non-hydrogen atoms except those (O4, O4', C26, C27, C32, C24', C26', C31', and C32') showing severe disorder as explained below. Carbon-bound hydrogen atoms were generated geometrically and assigned isotropic thermal parameters. Oxygen-bound hydrogen atoms were structurally evident in difference Fourier maps and refined isotropically in the riding-model approximation with bond length and angles restrains. In **2**, the first crystallographically distinct D-H₂Cam ligand (C1–C10) has a non-disordered hydrocarbon skeleton, thus it was well-solved in its absolute structure (D-configuration). One of the carboxylic acid oxygens (O4 and O4') of this non-disordered D-H₂Cam ligand was split over two positions, which were refined isotropically with refined site-occupation factors (SOF) of 0.575 and 0.425. On the other hand, the second crystallographically distinct D-H₂Cam ligand (C23–C32) was disordered over two occupied sites with refined SOF of 0.65 and 0.35, in which several disordered carbon atoms (C26, C27, and C32 in the major-occupied part, and C24', C26', C31', and C32' in the minor-occupied part) were refined isotropically. Although this D-H₂Cam ligand is disordered, its absolute structure of D-configuration was determined very well as indicated by the Flack parameter of 0.02(3).^{S3} When checking the missing symmetry by the ADDSYM subroutine of PLATON,^{S4} an additional (pseudo) symmetry operation of c -glide is detected; this suggests an alternative space group ($P2_1/c$) assignment. Therefore solving the structure of **2** was further done in the centrosymmetric space group $P2_1/c$. Model in $P2_1/c$ space group contains one copper atom, one H₂Cam ligand, two 4-ptz ligands, and one coordination water molecule in the asymmetric unit. In the model, structure was refined in mixed isotropic/anisotropic approximation: isotropic for the disordered carbon atoms and anisotropic for the rest non-hydrogen atoms. The H₂Cam ligand was disordered over two occupied sites with refined SOF of 0.775 and 0.225. Structure refinement showed that the disorder model for the H₂Cam molecule has had more than disorder of the α -methyl group at the C1 and C3 atoms. Refinement of the occupancies of the α -methyl group at C1/C3 gave values of 0.449/0.326 and 0.122/0.103 in the major- and minor-occupied parts, respectively, of the disordered model with reasonable equivalent isotropic displacement parameters. As a result, the ratio of D-/L-configuration or L-/D-configuration of the H₂Cam ligand is 0.552:0.448 in the final refinement. However, refinement (goodness-of-fit on $F^2 = 1.118$, final $R_1 = 0.0479$ and $wR_2 = 0.0958 [I > 2\sigma(I)]$, and $R_1 = 0.0664$ and $wR_2 = 0.1052$ (all data)) does not lead to a more reasonable result significantly over than those (goodness-of-fit on $F^2 = 1.039$, final $R_1 = 0.0456$ and $wR_2 = 0.0932 [I > 2\sigma(I)]$, and $R_1 = 0.0739$ and $wR_2 = 0.1120$ (all data)) in space group $P2_1$ (Table S1). Further, refinement in the chiral space group $P2_1$ assigns a reasonable absolute structure parameter (the Flack parameter = 0.02(3))

properly, suggesting a well-solved *D*-configured structure of the H₂Cam ligand, even though the extreme conditions in the hydrothermal synthesis may induce isomerization of *D*-H₂Cam ligand. Therefore, on the basis of the refinements, solving the structure of **2** in the chiral space group *P2*₁ is preferred over than in the centrosymmetric space group *P2*₁/*c*, and the absolute configuration of **2** was determined unambiguously due to the use of the enantiopure *D*-H₂Cam ligand.

Table S1 Crystallographic data for **2**

	Non-centrosymmetric model for 2	Pseudo-centrosymmetric model for 2
Empirical formula	C ₂₂ H ₂₆ CuN ₁₀ O ₅	C ₂₂ H ₂₆ CuN ₁₀ O ₅
<i>M</i> _w	574.07	574.07
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2</i> ₁	<i>P2</i> ₁ / <i>c</i>
<i>a</i> /Å	15.262(3)	15.262(3)
<i>b</i> /Å	13.046(3)	13.046(3)
<i>c</i> /Å	13.058(3)	13.058(3)
<i>α</i> /°	90.00	90.00
<i>β</i> /°	102.54(3)	102.54(3)
<i>γ</i> /°	90.00	90.00
<i>V</i> /Å ³	2537.9(9)	2537.9(9)
<i>Z</i>	4	4
<i>T</i> /K	296(2)	296(2)
<i>λ</i> /Å	0.71073	0.71073
<i>D</i> _{calc} /g cm ⁻³	1.502	1.502
<i>μ</i> /mm ⁻¹	0.915	0.915
<i>F</i> ₀₀₀	1188	1188
Refl. collected	19536	19057
Unique refl. (<i>R</i> _{int})	8693 (0.0446)	4492 (0.0519)
Obs. refl. (<i>I</i> > 2σ(<i>I</i>))	6108	3440
Parameters	710	354
Restraints	1	3
GOF	1.039	1.118
<i>R</i> ₁ ^{<i>a</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0456	0.479
<i>wR</i> ₂ ^{<i>b</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0931	0.958
<i>R</i> ₁ ^{<i>a</i>} (all data)	0.0739	0.664
<i>wR</i> ₂ ^{<i>b</i>} (all data)	0.1120	0.1052
Δρ _{max} , Δρ _{min} /e Å ⁻³	0.395, -0.451	0.721, -0.468
Flack parameter	0.02(3)	–

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\| \cdot ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

References:

- (S1) Sheldrick, G. M. *SHELX-97* (including *SHELXS* and *SHELXL*); University of Göttingen: Göttingen, Germany, 1997.
- (S2) *WINGX*: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
- (S3) Flack, H. D. *Acta Crystallogr., Sect. A: Foundations of Crystallography*, 1983, **39**, 876.
- (S4) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

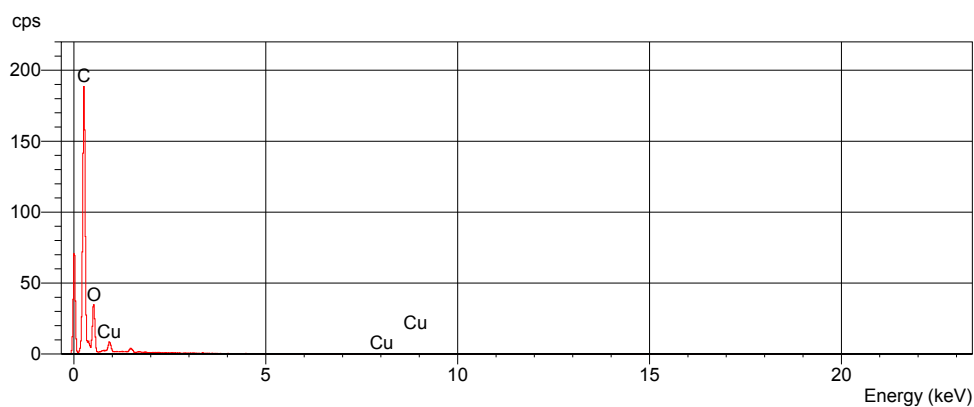


Fig. S1 Energy-dispersive X-ray (EDX) spectrum of **2**.

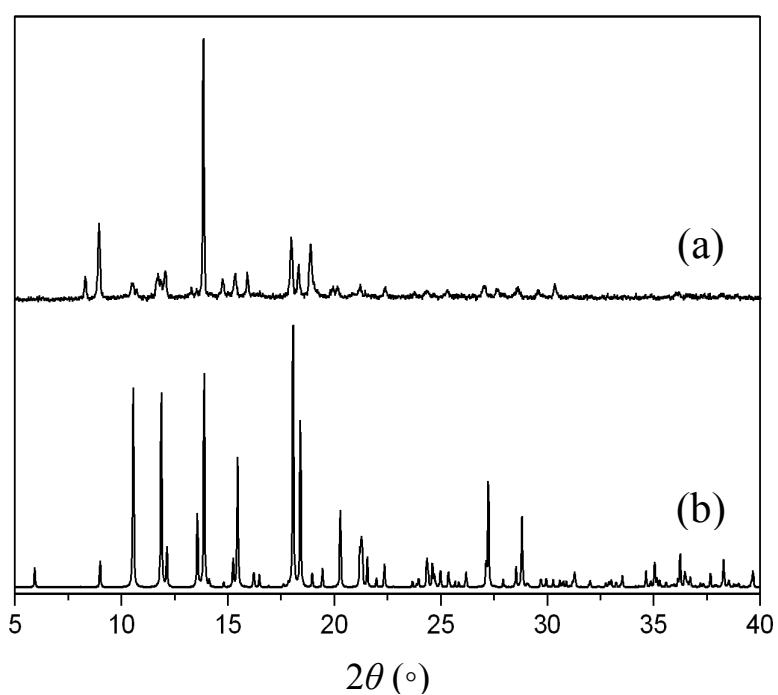


Fig. S2 Powder X-ray diffraction (PXRD) patterns of **2**: (a) a freshly grounded sample at room temperature; (b) simulated from the single-crystal data.

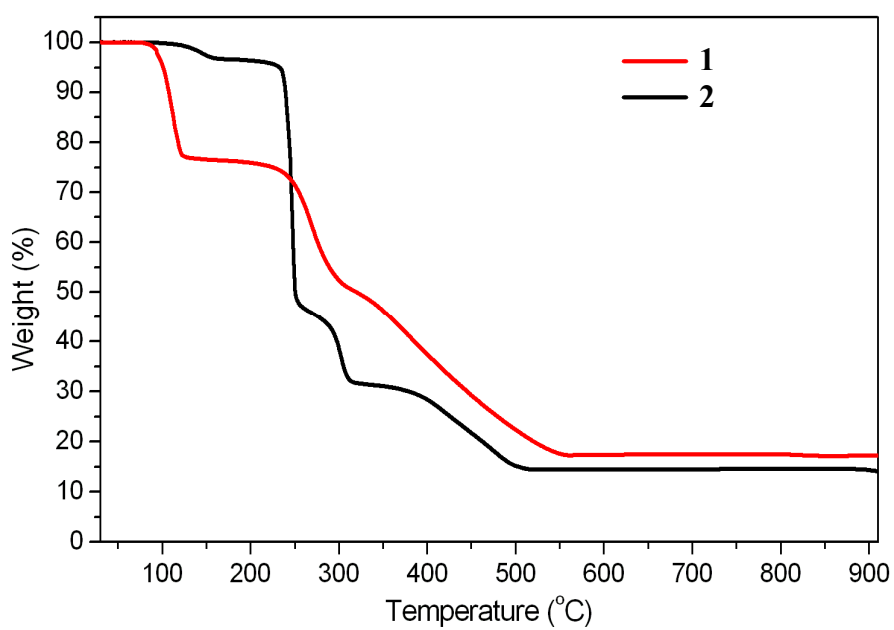


Fig. S3 Thermogravimetric (TG) traces of **1** and **2**.