Supporting information

$LiCu_2[BP_2O_8(OH)_2]$: enantioenriched open-framework copper borophosphate via spontaneous asymmetrical crystallization

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1. Synthesis

$LiCu_2[BP_2O_8(OH)_2]$ was prepared by the boric acid flux method. Typically, 0.5 g H_3BO_3, 0.2 g $Cu(OAc)_2 \cdot H_2O$ and 0.208 g LiH_2PO_4 were charged into a 15 mL Teflon-stainless steel autoclave directly. The vessel was heated under autogenous pressure at 200°C for 5 days, and then cooled to room temperature. The final product containing large rectangular single crystals with blue color was washed with distilled hot water for several times, and then dried in air.

2. Characterization:

The powder X-ray diffraction (XRD) data were recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.54059 Å) operating at 40 mA and 40 kV. The experimental X-ray diffraction (XRD) pattern and the simulated pattern based on structure analysis were shown in Fig. S1. Inductively coupled plasma (ICP) analysis was performed on Perkin-Elmer Optima 2000 DV ICP Spectrometer. It gives the contents of Cu, P, B and Li as 34.62, 17.25, 2.98 and 2.00 wt %, respectively (calcd: Cu: 34.51, P: 16.89, B: 2.95 and Li: 1.89 wt %). The thermal analysis was performed on a TA Q-600 analyzer with a temperature-programmed rate of 5 K/min under an air flow of 100 mL/min. TG-DSC measurements as shown in Fig. S2 showed a weight loss of 4.4% occurring at from 140 °C to 400 °C ascribed to the removal of H_2O molecules dehydrated from OH groups (calcd: 4.88 wt %).

3. Determination of crystal structure:

A suitable blue single crystal in the form of rectangular, with dimensions 0.15 × 0.14 × 0.13 mm^3, was selected for single-crystal X-ray diffraction analysis. Intensity data were collected on a Bruker SMART Apex II CCD system equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 20°C ± 2°C. The structure was solved in the space group $P2_12_12_1$ (No. 19) by direct methods[1] and refined by a full-matrix least-squares procedure using SHELXTL crystallographic software package[2]. All non-hydrogen atoms Cu, P, B, O and Li could be unambiguously located from the difference Fourier map and refined with

anisotropic thermal parameters. Two H atoms attached to two O atoms connected with B and Cu, respectively, can be located from the difference Fourier map. A summary of the crystallographic data are presented in Table S1.

4. Properties measurements:

The circular dichroism (CD) spectra were recorded on a MOS-450 spectropolarimeter with KBr pellets (1mg sample, 50mg KBr).

Temperature-dependent magnetic susceptibility data were recorded on a commercial 14T-PPMS-VSM system (Quantum Design, USA).

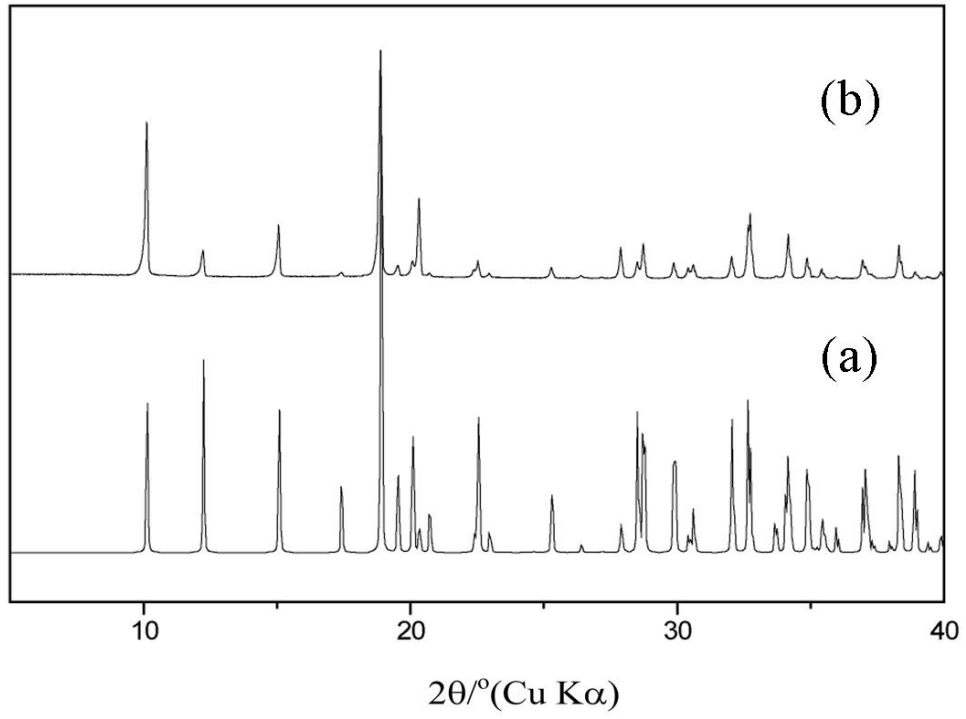

Fig. S1 The simulated XRD pattern (a) and experimental one (b) for compound **1**.

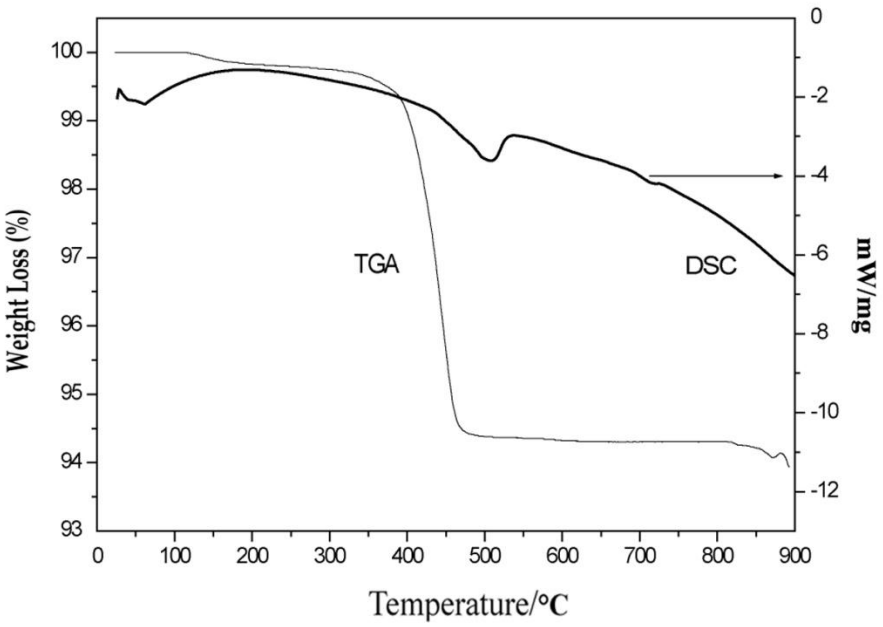

Fig. S2 TG-DSC curves for compound **1**.

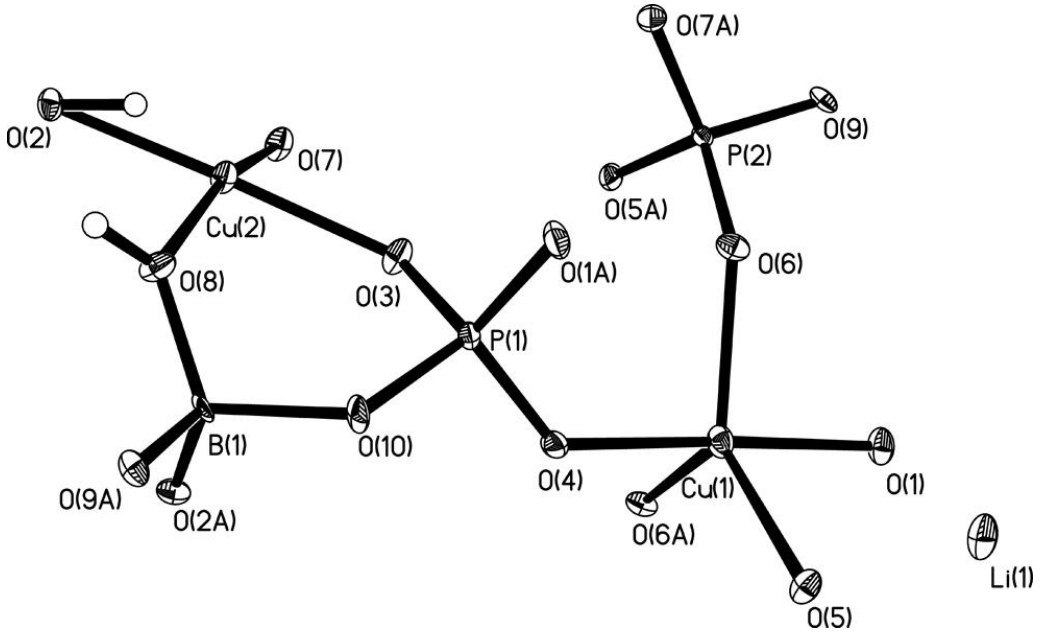

Fig. S3 Thermal ellipsoid plot (with 50% probability) and atomic labeling scheme.

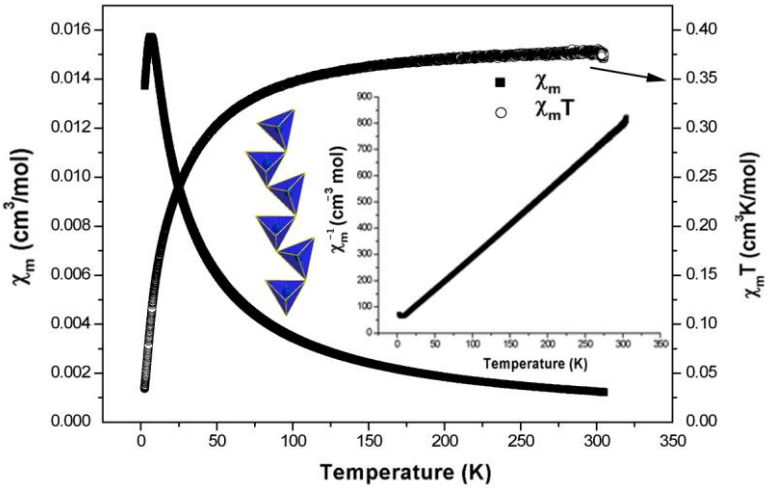

Figure S4. The χ_m vs. T and $\chi_m T$ vs. T plots. The insets are $1/\chi_m$ vs. T plot and the $Cu(1)O_5$ polyhedra chain extending along the [100] direction.

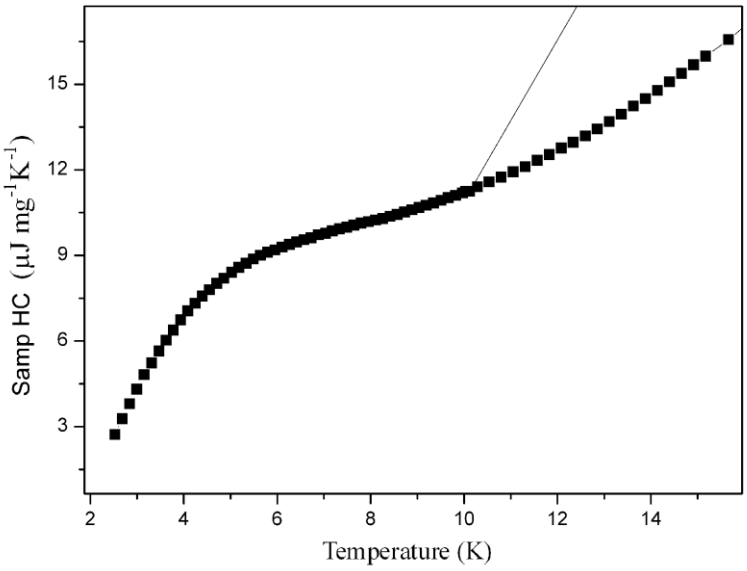

Fig. S5 Heat capacity of compound **1**.

Table S1 Crystallographic data and refinement results of compound **1**.[a]

Empirical formula	$H_2BCu_2LiO_{10}P_2$
Formula weight	368.79
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1(19)$
Unit cell dimensions	a = 5.3195(10) Å, α = 90°
	b = 7.9352(15) Å, β = 90°
	c = 17.464(3) Å, γ = 90°
Volume	737.2(2) $Å^3$
Z, Calculated density	4, 3.323 Mg/m^3
Absorption coefficient	6.248 mm^{-1}
F(000)	712
Crystal size	0.15 × 0.14 × 0.13 mm^3
Theta range for data collection	2.33 to 28.32 º
Limiting indices	$-7 \le h \le 6$, $-10 \le k \le 10$, $-23 \le l \le 14$
Reflections collected / unique	5399/ 1828 [R(int) = 0.0206]
Completeness to theta = 28.00	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1828 / 1/ 146
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R_1 = 0.0172, wR_2 = 0.0468
R indices (all data)	R_1 = 0.0178, wR_2 = 0.0470
Absolute structure parameter	0.010(11)
Extinction coefficient	0.0098(7)
Largest diff. peak and hole	0.322 and -0.487 e $Å^{-3}$

[a] $R_1=\sum(\Delta F/\sum(F_o))$; $wR_2=(\sum[w(F_o^2-F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w=1/\sigma^2(F_o^2)$