

Supplementary Information

Zn(1, 3-DAP)[B₄O₇]: A Rarely Chiral Zeolitic Framework Constructed by Four-connected [B₄O₉] Cluster with Single- stranded Helical Channel

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Experimental Section

Materials and physical measurements: All chemicals were purchased commercially and used without further purification. FTIR spectra were recorded in the 400-4000cm⁻¹ range using an ABB Bomem MB102 spectrometer in a KBr pellet in room temperature. Thermo-gravimetric and Differential Scanning Calorimetry were performed using a Mettler TGA/SDTA851 thermal analyzer under air atmosphere with a heating rate of 10°C·min⁻¹ in the temperature region of 25-990 °C. Powder X-ray diffraction (PXRD) patterns were recorded in the angular range of 2θ = 5-50 ° a Bruker D8 advance diffractometer using CuKα radiation. The luminescence spectra was recorded by Fluoro Max-4 at room temperature. Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 900 UV/Vis spectrophotometer at room temperature over the range of 200-2000 nm. The band structure and DOS calculation were made by using the computer code CASTEP. Density functional theory calculations were performed by using Gaussian03 suite of programs. Single point energy calculations were carried out with B3LYP hybrid functional.

Crystalline **1** was prepared by solvothermal reaction. A powder mixture of H₃BO₃ (0.5243 g), Zn(OH)₂ (0.145 g), 1,3-diaminopropane (denoted 1,3-DAP, 1 ml), and N, N- dimethyl formamide (3 ml) with a mole ratio of 6.0 : 0.7 : 50.9 : 37.2 : 2.6 : 0.42 was stirred to homogeneity for 1 hour at room temperature, and then sealed in a Teflon-lined autoclave and heated at 180 °C for 8 days under autogenous pressure, and then cooled to room temperature. Colorless transparent block crystals were recovered by filtration, washed with distilled water, and dried in air. The yield of **1** is about 65% according to H₃BO₃. The yield of **1** is about 65% according to H₃BO₃. Elemental analysis (%) for **1** calcd: C 12.26, H 3.09, N 9.54, Found: C 12.83, H 2.90, N 8.59. The experimental and simulated powder X-ray diffraction patterns corresponded well in position, indicating the phase purity of the sample. The FTIR spectrum of **1** is shown in **Figure S8**. The bands at 3320, 3200 and 3140 cm⁻¹ are stretching modes of NH₂ groups. The band at 1590 cm⁻¹

might be due to the bending mode of N–H bonds. The sharp peaks at 2950 and 2890 cm^{-1} are characteristic of stretching vibrations of C–H bonds. The bands at 1470, 1420 and 1330 cm^{-1} are assigned as the asymmetric and symmetric stretching modes of B–O bond in BO_3 groups. The band at 960 cm^{-1} and 930 cm^{-1} might be the asymmetric and symmetric stretching modes of B–O in BO_4 . The peaks at 680 cm^{-1} can be assigned to asymmetric Zn–O stretching of the ZnO_3N_2 groups. The bands at 540 cm^{-1} are due to symmetric Zn–O stretching.

Structure Determination: The single crystal of title compound with the dimensions of $0.35 \times 0.25 \times 0.20 \text{mm}^3$ was carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. **1** crystallizes in the tetragonal space group $P4_32_12$ (No. 96), $a = 8.670(4) \text{\AA}$, $b = 8.670(4) \text{\AA}$, $c = 12.722(13) \text{\AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 956.2(12) \text{\AA}^3$, $Z = 4$, $\mu = 2.591 \text{mm}^{-1}$, $D_c = 2.040 \text{g/cm}^3$, 5272 reflections measured, 853 unique ($R_{\text{int}} = 0.0657$). The final $wR(F^2)$ (all data) was 0.0482 and $R(F)$ ($I > 2s(I)$) was 0.0159. The flack parameter was 0.016(17). Diffraction data were measured on a Bruker diffractometer using graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073 \text{\AA}$) radiation at room temperature. All absorption corrections were performed using the multi-scan program. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 and SHELX-97 programs,^[1] respectively. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. CCDC-955550 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. Pore sizes of L and R-helical 8-M channels.

Figure S2. From the topological point of view, framework of **1** has the same topology as diamond if B_4O_9 units act as four-connected nodes with vertex symbols $6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2$.

Figure S3. UV- vis optical diffuse reflectance spectra for **1**.

Figure S4. Density of states (left) and energy bands (right) for **1**.

Figure S5. Emission spectra of **1**.

Figure S6. TG-DSC curve of **1**.

Figure S7. Heated, experimental and simulated powder X-ray diffraction pattern of **1**.

Figure S8. FTIR spectrum of **1**.

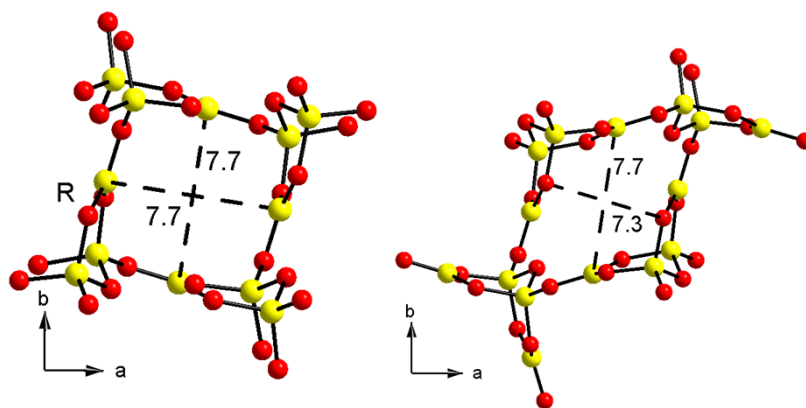


Figure S1. Pore sizes of L and R-helical 8-M channels. Clore codes: B atom yellow; O atom red.

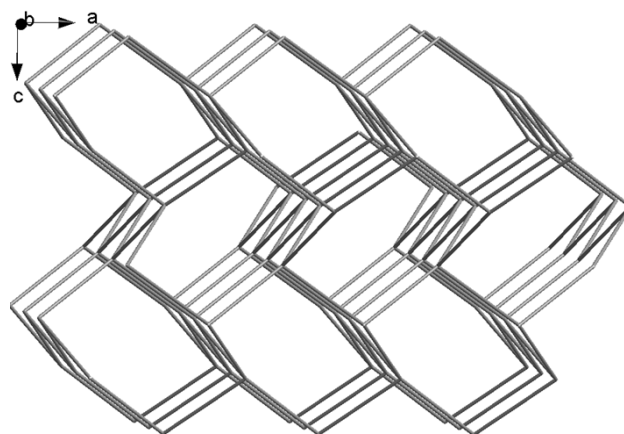


Figure S2. From the topological point of view, framework of **1** has the same topology as diamond if B_4O_9 units act as four-connected nodes with vertex symbols $6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2$.

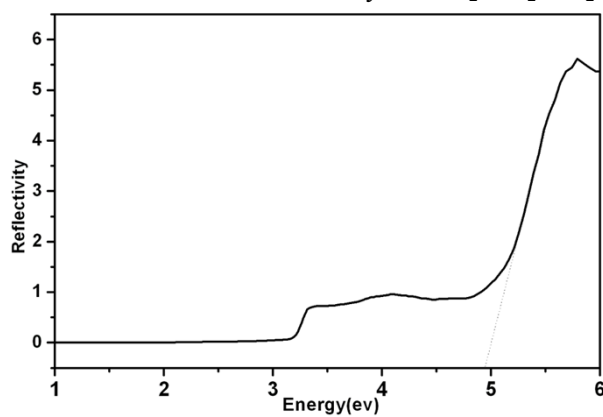


Figure S3. UV- vis optical diffuse reflectance spectra for **1**.

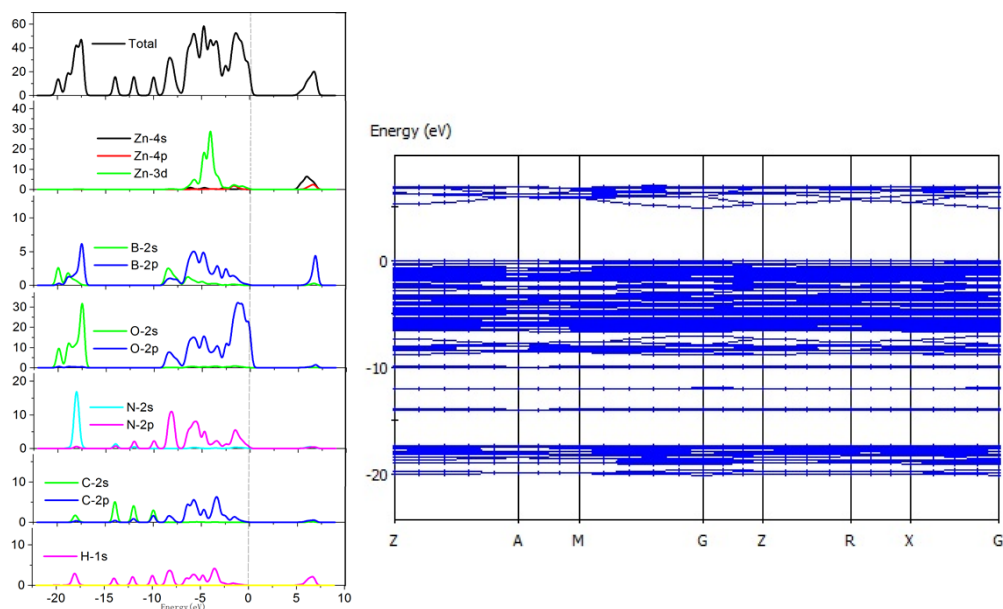


Figure S4. Density of states (left) and energy bands (right) for **1**.

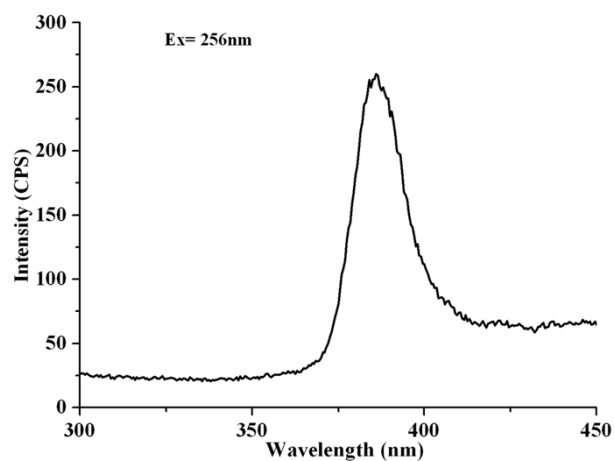


Figure S5. Emission spectra of **1**.

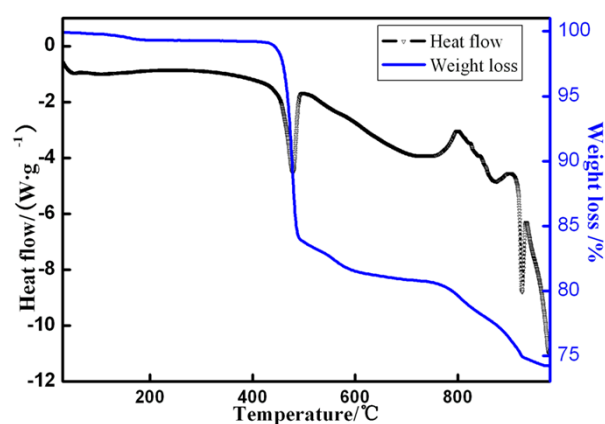


Figure S6. TG-DSC curve of **1**.

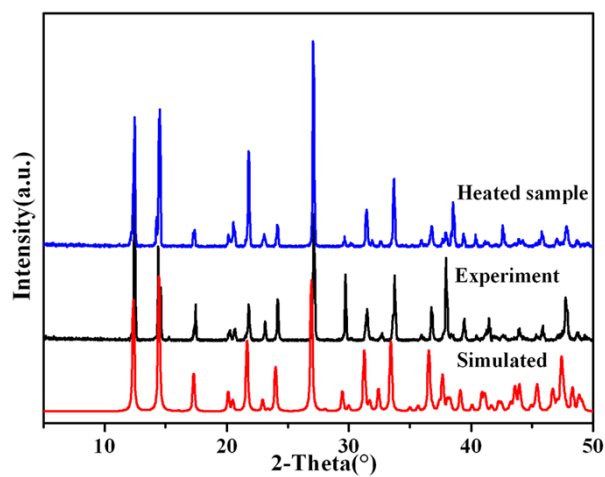


Figure S7. Heated, experimental and simulated powder X-ray diffraction pattern of **1**.

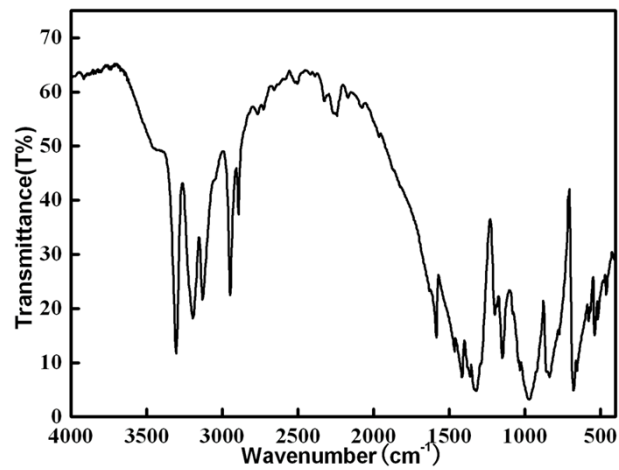


Figure S8. FTIR spectrum of **1**.

Reference

1 a) G. M. Sheldrick, in *Sheldrick SHELXS97 Program for Solution of Crystal Structures*, University of Göttingen, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, in *SHELXL97 Program for the Refinement of Crystal Structures* University of Göttingen, Germany, **1997**.