Electronic Supplementary Information

Luminescent Boracite-Like Metal-Organic Frameworks Constructed by Cu-centered CuCu₄ Tetrahedra and CuCu₃ Triangles with Acentric Cubic Superlarge Cell

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Experimental Section

General. All the starting materials were purchased of commercially reagent grade and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded from KBr pellets in the range 400–4000 cm⁻¹ on a Nicolet 5DX spectrometer. Thermogravimetric analysis (TGA) was carried out in an air stream using SETARAM LABSYS equipment with a heating rate of 10°C/min. Photoluminescence analyses were performed on an Edinburgh FLS920 luminescence spectrometer. Approximate estimation of second-order NLO intensity was obtained by a comparison of the results from a powdered samples with those obtained for KDP (S. K. Kurtz and T. T. Perry, J. Appl. Phys., 1968, 39, 3798). A pulsed Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532-nm radiation.

Synthesis of [Cu₃₁X₄(H₁.55amtz)₂₄](SO₄)₈·xDMF [X = Cl, Br for 1, 2, 3] A mixture of CuCl₂·2H₂O (0.068g, 0.4 mmol)/CuBr₂ (0.090g, 0.4 mmol)/CuI (0.076g, 0.4 mmol) H₂amtz (0.044g, 0.4 mmol) and DMF (5 mL) in a mole ratio of 1:1:162 was sealed in a 15 mL Teflon-lined stainless container, which is heated to 160°C for 120 h. After cooling to room temperature, yellow block-like crystals were obtained in the yield of
60% (based on H$_2$amtz). Anal. Calcd for C$_{144}$H$_{308}$Cl$_4$Cu$_{31}$N$_{128}$O$_{64}$S$_{32}$ ([Cu$_{31}$X$_4$(H$_{1.55}$amtz)$_{24}$](SO$_4$)$_8$·32DMF): C, 21.63; H, 3.88; N, 22.43; S, 12.83. Found: C, 21.46; H, 3.95; N, 22.28; S, 12.64. IR(KBr, cm$^{-1}$): 3439 w, 3312 w, 1630 s, 1495 s, 1221 m, 1113 s, 1010 s, 827 m, 724 m, 633 s.

**X-ray Crystallography.** The crystal structures 1-3 were determined by single-crystal X-ray crystallography. Data collections were performed using a Bruker-AXS SMART CCD area detector diffractometer with Mo-K$_\alpha$ radiation with an $\omega$-scan mode ($\lambda = 0.71073$Å). The structures were solved by direct methods and refined by full-matrix least squares refinements based on $R^2$. Multi-scan corrections were applied using SADABS. All non-hydrogen atoms were anisotropically refined. Structure solutions and refinements were performed with the SHELXL-97 package (G. M. Sheldrick, *SHELXS-97* and *SHELXL-97*, Göttingen University, Göttingen, Germany, 1997).

![Fig. S1a. XRPD patterns for 1. (A– simulated, B– experimental)](image1)

![Fig. S1b. XRPD patterns for 2. (A– simulated, B– experimental)](image2)
Fig. S1c. XRPD patterns for 3. (A – simulated, B – experimental)

Fig. S2. The three-dimensional framework of 1.

Fig. S3. The TG curve of 1.
Fig. S4a. The building block Cu₄Cl(Hamtz)₆ selected for TD-DFT computation in 1.

Fig. S4b. The building block Cu₅(Hamtz)₈ selected for TD-DFT computation in 1.