Electronic Supplementary Information for

An Unusual Case of Symmetry-Preserving Isomerism

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Synthesis of PCN-16 (Cu₂(H₂O)₂(ebdc)·3DMA·6H₂O): A mixture of H₄ebdc (0.01 g), Cu(NO₃)₂·2.5H₂O (0.02 g) and 2 drops of HBF₄ in 1.5 mL DMA was sealed in a Pyrex tube under vacuum and heated at a constant rate of 1 °C/min to 75°C, kept at that temperature for 3 days, and then cooled to room temperature at a constant rate of 0.1°C/min. The resulting blue block crystals were washed with DMA (yield: 50% based on ebdc ligand). Anal. Calcd (%): C, 40.81; H, 5.59; N, 4.76 %. Found: C, 40.43; H, 5.71; N, 4.59 %.

Synthesis of PCN-16' ($Cu_2(H_2O)_2(ebdc)$ ·3DMF·6H₂O): A mixture of H₄ebdc (0.01 g), $Cu(NO_3)_2$ ·2.5H₂O (0.02 g), and HBF₄ (1 drop) was dissolved in 1.5 mL of a DMF / EtOH mixture (2:1 volume ratio), and sealed in a Pyrex tube under vacuum. The tube was heated at 1 °C/min to 65 °C. After 24 hr at 65 °C, the tube was cooled to room temperature at 0.1 °C/min. The resulting blue block crystals were washed with DMF (yield: 60% based on ebdc ligand).. Anal. Calcd (%): C, 38.57; H, 5.15; N, 5.00 %. Found: C, 38.86; H, 5.11; N, 4.92 %.

Single-crystal X-ray crystallographic studies: Single crystal X-ray data of PCN-16 were collected on a Bruker Smart Apex^[1] diffractometer equipped with an Oxford Cryostream low temperature device and a fine-focus sealed-tube X-ray source (Mo-K_a radiation, $\lambda = 0.71073$ Å, graphite monochromated) operating at 45 kV and 35 mA. Frames were collected with 0.3° intervals in φ and ω for 30 s per frame such that a hemisphere of data was collected. Single crystal x-ray structure determination of PCN-16' was performed on a specially configured diffractometer based on the Bruker-Nonius X8 Proteum using focused Cu-K α radiation ($\lambda = 1.54178$ Å). Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT+ and corrected for Lorentz and polarization effects.^[2] The structure were solved by using the direct method and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters during the final cycles. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. Absorption corrections were applied using SADABS after the formula of

the compound is determined approximately.^[2] Solvent molecules in the structure were highly disordered and were impossible to refine using conventional discrete-atom models. To resolve these issues, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.[4]

X-ray Crystal data for PCN-16 (CCDC-709273): C81H45Cu9O45, Mr = 2310.0; blue block, $0.11 \times 0.10 \times 0.08$ mm, T = 213(2) K, trigonal, space group R-3m, a = b = 18.824 (2) Å, c = 32.126 (7), $\alpha = \beta = 90.00 \circ \gamma = 120.00 \circ$, V = 9858 (3) Å3, Z = 2, dcalcd = 0.778 g/cm3; R1 (I > 2 σ (I)) = 0.0445, wR2 (all data) = 0.1046, GOF = 1.012; PCN-16' (CCDC-709274): C81H45Cu9O45, Mr = 2310.0; blue block, 0.12 × 0.09 × 0.07 mm, T = 213(2) K, trigonal, space group R-3m, a = b = 23.773 (3) Å, c = 19.072 (4), $\alpha = \beta = 90.00 \circ \gamma = 120.00 \circ, V = 9335$ (3) Å3, Z = 2, dcalcd = 0.943 g/cm3; R1 (I > 2 σ (I)) = 0.0898, wR2 (all data) = 0.2243, GOF = 1.069.



Fig. S1. The two kinds of cages (a, b) in PCN-16; PCN-16' has similar cages but the -3m (in space group *R*-3*m*) channels (c) projected on the *ab* plane in PCN-16' are larger than those in PCN-16.



Fig. S2. The two kinds of cages connected by sharing three Cu_2 SBUs (aqua blue) in PCN-16.



Fig. S3. View of PCN-16 showing the arrangement of the two kinds of cages through the extended crystal lattice. Alternatively, the structure can also be viewed as consisting of three parallel sets of squashed-honeycomb-nets connected through the dimetal paddlewheel units (aqua blue).



Fig. S4.



Fig. S5.



(a)





Fig. S6. PXRD patterns: (a) PCN-16; (b) PCN-16'. (Sim. = Simulated; Dehyd. = dehydrated; Outgassed temperature is 120 °C)

Low-Pressure Adsorption Measurements. Low pressure volumetric gas adsorption measurements involved in this work were performed at 77 K, maintained by a liquid nitrogen bath, with pressures ranging from 10^{-3} to 760 Torr. Each sample was soaked in methanol for 24 h, and the extract was discarded. Fresh methanol was subsequently added, and the crystals were allowed to stay in methanol for an additional 24 h to remove solvates (DMA or DMF and H₂O). The sample was treated further with dichloromethane to remove methanol solvates. After decanting the dichloromethane extract, the sample was dried under a dynamic vacuum (< 10^{-3} Torr) at room temperature overnight. Before adsorption measurement, the sample was activated using the "outgas" function of the surface area analyzer for 2 h at 120 °C. In the hydrogen adsorption measurement, high-purity hydrogen (99.9995%) was used. The regulator and pipe were flushed with hydrogen before connecting to the analyzer. The internal lines of the instrument were flushed three times utilizing the "flushing lines" function of the program to ensure the purity of hydrogen.

High-Pressure Gas Adsorption Measurements and Analysis: High-pressure hydrogen and methane sorption isotherm measurements on PCN-16 and PCN-16' were performed using a home-built fully computer-controlled Sievert apparatus at NIST. The detailed specifications of the Sievert apparatus, data analysis, and discussion of excess adsorption can be found in a recently published work.^[5] Scientific/research-grade hydrogen and methane were used for the high-pressure measurements with purities of 99.9999% and 99.999%, respectively. Prior to measurements, solvent-exchanged samples were activated in two stages. First, the samples were outgassed under vacuum (~10⁻⁶ torr) overnight at room temperature, followed by heating at 120 °C for at least 4 h. Approximately 150 mg of activated sample was loaded into the high-pressure cell in a helium glove box, valved off with a He atmosphere, and then transported to the cryostat for measurement.

[1] Note: Certain commercial suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

[2] *SAINT*+, version 6.22; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.

[3] G. M. Sheldrick, *SHELX-97*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.

[4] A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.

 [5] W. Zhou, H. Wu, M. R. Hartman, T. Yildirim, J. Phys. Chem. C 2007, 111, 16131-16137.