

Supplementary information

Introduction of Cavities up to 4 nm into a Hierarchically-Assembled, Metal-Organic Framework Using an Angular, Tetratopic Ligand

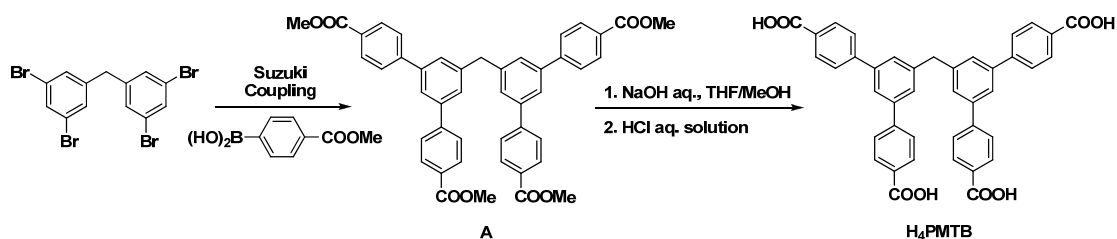
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General Information. Commercially available reagents were used as received without further purification. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. The powder X-ray diffraction patterns (PXRD) were recorded on a Bruker D8 Discover diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of 1 s deg^{-1} . Powder samples were dispersed on low-background quartz discs (G. M. Associates, Inc., Oakland, California) for analyses. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via internet at <http://www.iucr.org>. FT-IR data were recorded on an IRAffinity-1 instrument. Thermogravimetry analyse (TGA) was obtained under N₂ atmosphere on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of $2 \text{ }^{\circ}\text{C min}^{-1}$.



Scheme 1

Synthesis of tetramethyl diphenylmethane-3,3',5,5'-tetrakis(3,5-bis(benzoate)), (A). Bis(3,5-dibromophenyl)methane (2.00 g, 4 mmol),¹ 4-(Methoxycarbonyl)phenylboronic acid (4.50 g, 25 mmol), CsF (2.00 g, 13 mmol) and Pd(PPh₃)₄ (0.20 g, 0.5 mmol) were mixed in a 500 mL Schlenk flask. The flask was pumped under vacuum and refilled with N₂ for three times, and then 200 mL of degassed 1,2-dimethoxyethane was added through

a canula. The mixture was heated to reflux under nitrogen atmosphere for 96 hours. After removal of organic solvent, the residue was dissolved in chloroform (200 mL) and washed with water (150 mL). The organic phase was eluted with chloroform through a short silica gel column and then dried to yield a light yellow powder **A**, 2.02 g (yield, 69 %). ¹H NMR (300 MHz, CDCl₃): σ = 7.95 (*d*, 8H); 7.76 (*d*, 8H); 7.67 (*s*, 4H); 7.43 (*s*, 2H); 3.98 (*s*, 2H); 3.89 (*s*, 12H).

Synthesis of diphenylmethane-3,3',5,5'-tetrakis(3,5-bis(benzoic acid)), (H₄PMTB). Compound **A** (2.02 g, 2.84 mmol) was suspended in 50 mL tetrahydrofuran/methanol (*v* : *v* = 1 : 1), to which 30 mL 10 % NaOH solution was added. The mixture was stirred at room temperature overnight. After tetrahydrofuran and methanol were removed using a rotary evaporator, 10 % hydrochloric acid aqueous solution was added to the remaining aqueous solution until the pH value was adjusted to approximately 2. The resulting white precipitate was collected by filtration, washed with water, and dried under vacuum to give white solid H₄PMTB, 1.65 g (yield, 90 %). ¹H NMR (300 MHz, DMSO-*d*⁶): σ = 11.50 (*br*, 4H); 8.03 (*d*, 8H); 7.90 (*d*, 8H); 7.84 (*s*, 4H); 7.49 (*s*, 2H); 3.98 (*s*, 2H).

X-ray Crystallography. Single crystal X-ray data of PCN-21 were collected on beamline 15ID-C at the Advanced Photon source in Argonne National Laboratory. Adsorption corrections were applied using the *SADABS* routine. The structure was solved by direct methods and refined by full-matrix least-squares on *F*² with anisotropic displacement using the *SHELXTL* software package.² Non-hydrogen atoms (except some in coordinated solvents) were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters. In PCN-21, free solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these residual solvent molecules were removed from the data set using the *SQUEEZE* routine of *PLATON* and refined further using the data generated.³ The contents of the solvent region are not represented in the unit cell contents in crystal data. Attempts to determine the final formula of such compound from the *SQUEEZE* results combined with elemental analysis and TGA data were not successful because the volatility of the crystallization solvents during measurements prevented accurate data from being obtained. The details for data collection and refinement are included in the CIF file in the Supplementary Information.

Gas Sorption Measurements. Gas sorption isotherm measurements were performed on an ASAP 2020 Surface Area and Pore Size Analyzer. An as-isolated sample of PCN-21 was immersed in methanol for 72 h, and the extract was decanted. Fresh methanol was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the non-coordinated solvent molecules. The sample was collected by decanting and treated with dichloromethane similarly to remove methanol solvates. After

the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum at room temperature overnight. Before the measurement, the sample was dried again by using the “degas” function of the surface area analyzer for 6 h at 100 °C. UHP-grade nitrogen (99.999%) gas source was used in the nitrogen sorption measurement. In the hydrogen sorption measurement, high purity hydrogen (99.9995%) was used. High purity oxygen (99.999%) was used in the oxygen sorption measurement. The temperature was maintained at 77 K with liquid nitrogen throughout the whole measurement.

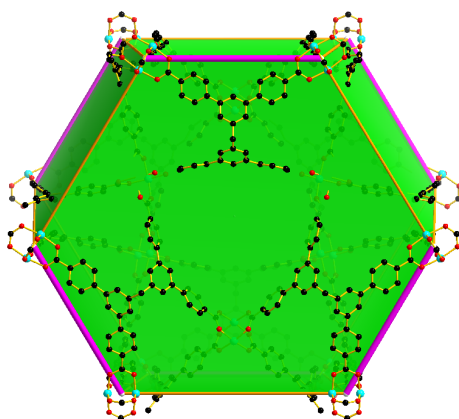


Fig. S1 (a) The structure of a quaternary building unit (QBU) with D_{3d} symmetry, purple (16.3 Å) and orange (20.9 Å) lines represent different length edges of the pseudo-hexagonal tertiary building unit (TBU), respectively.

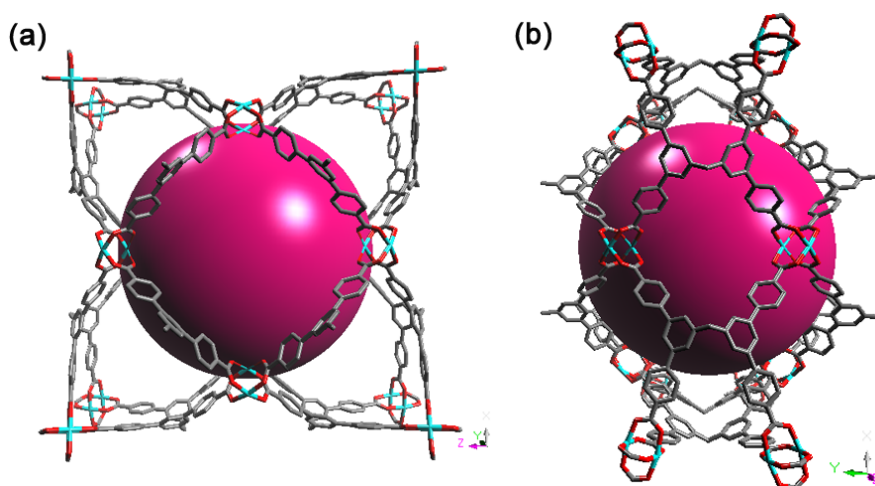


Fig. S2 The structure of smaller cavity in PCN-21, purple sphere shows the internal diameter of 24 Å: (a) viewed along the a -axis; (b) viewed along the c -axis.

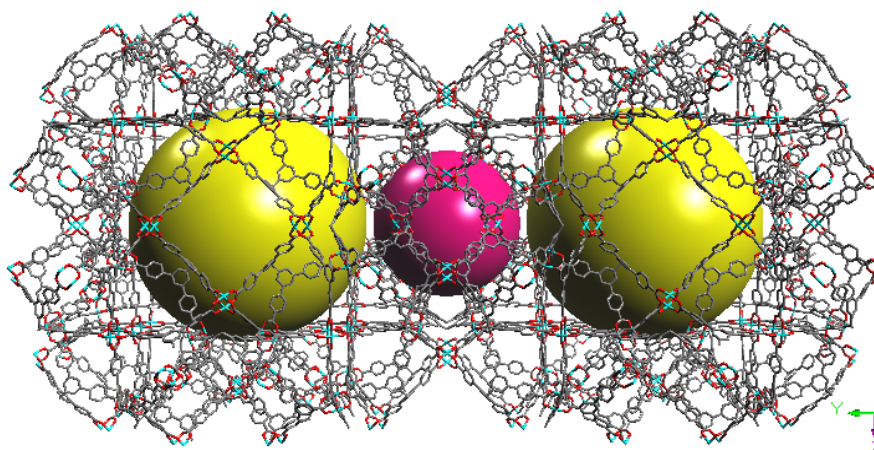


Fig. S3 The connection model of two types of cavities (yellow and purple spheres) in PCN-21 (viewed along the *a*-axis).

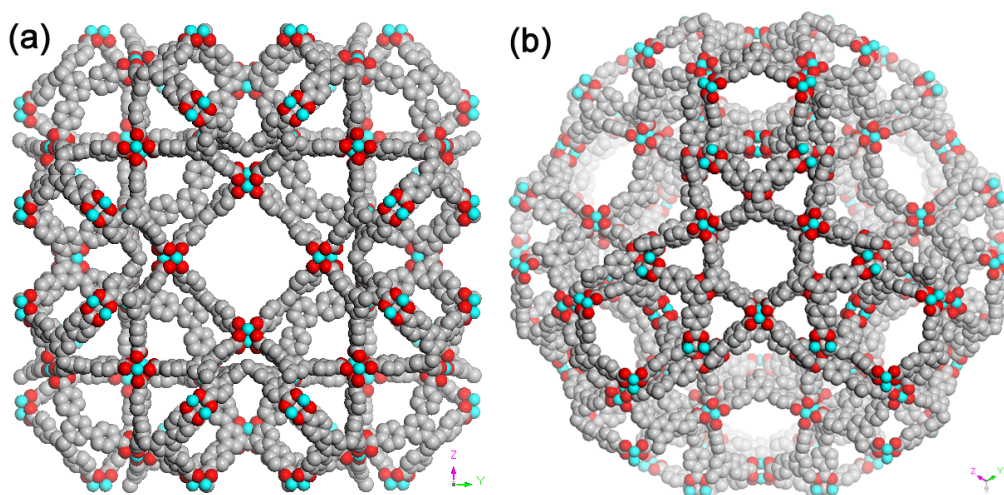


Fig. S4 The space-filling model of a unit cell showing open channels: (a) viewed along the $[1\ 0\ 0]$ direction and (b) viewed along the $[1\ 1\ 1]$ direction.

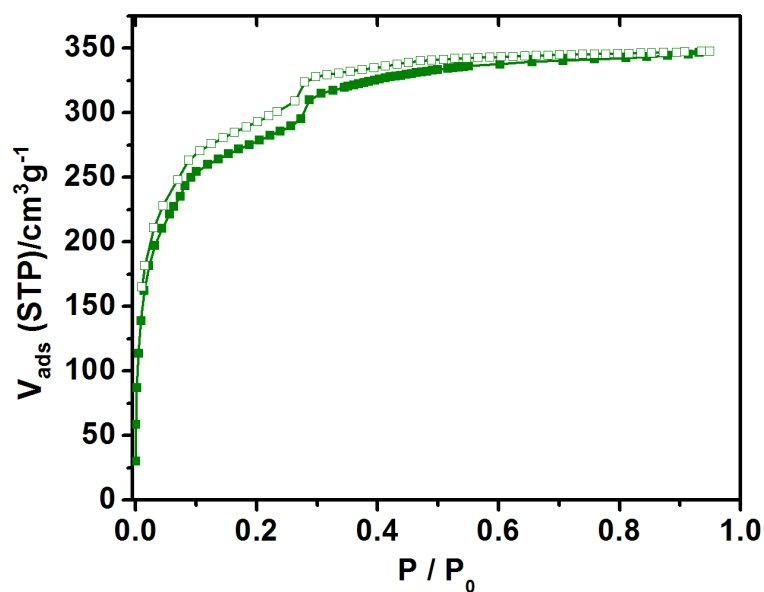


Fig. S5 Nitrogen gas sorption isotherms at 77 K after activation by using the supercritical CO₂ drying method (solid symbols, adsorption; open symbols, desorption).

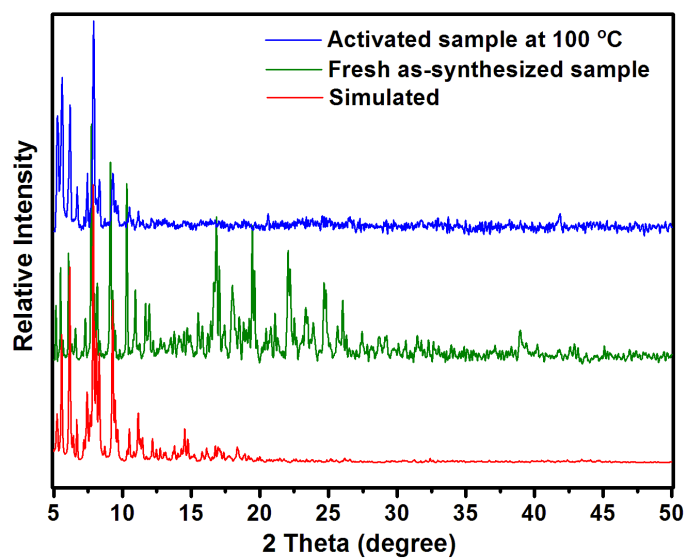


Fig. S6 Powder X-ray diffraction patterns of PCN-21.

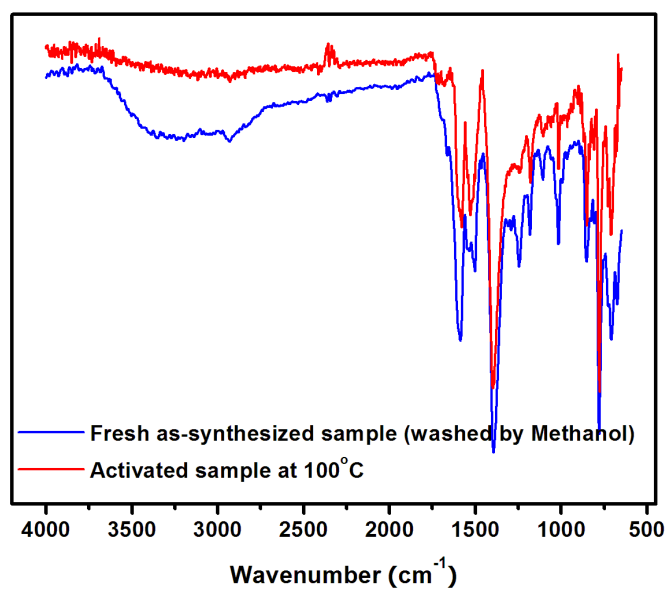


Fig. S7 IR of PCN-21.

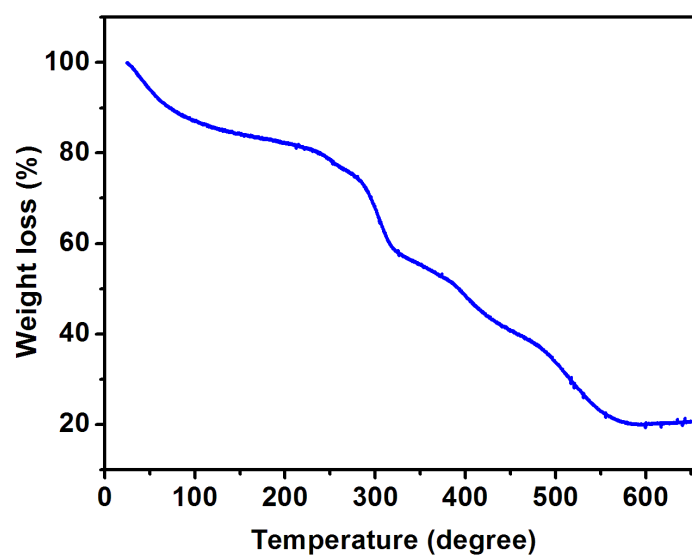


Fig. S8 TGA of fresh as-synthesized sample of PCN-21.

References

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2. G. M. Sheldrick, *Acta Crystallogr. Section A*, 2008, **64**, 112.
3. A. Spek, L. J. *Appl. Crystallogr.* 2003, **36**, 7.