Supporting Information

A NbO-type metal-organic framework derived from a polyne-coupled di-isophthalate linker formed *in situ*

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Experimental Details

Materials and Methods. Commercially available reagents were used as received without further purification. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 MHz NMR spectrometer. Fourier transform infrared spectroscopy (FTIR) data were collected on a SHIMADZU IRAffinity-1 FTIR Spectrophotometer. Elemental analyses (C, H, and N) were obtained from Canadian Microanalytical Service, Ltd. Thermogravimetry analyses (TGA) were performed under N_2 on a SHIMADZU TGA-50 TGA, with a heating rate of 5 °C min^{-1}.

Synthesis of 5-ethynylisophthalic acid, H_2ei. Diethyl-5-(trimethylsilylethynyl)isophthalate[1] (6.363 g, 20 mmol) was suspended in 150 mL of THF/methanol (1/1) mixed solvent, to which 100 mL of 1 M KOH aqueous solution was added. The mixture was stirred at room temperature for 3 hours. Organic solvent was removed under vacuum, and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic (pH = 2). The precipitate was collected by filtration, washed with water, and dried under vacuum at 80 °C to give H_2ei as a white solid. ν_{max}(neat)/cm^{-1} 3545, 3076, 1712, 1450, 1205 and 916; δ_H(300 MHz; DMSO-d_6; Me_4Si) 13.27 (2 H, br), 8.42 (1 H, t, J 3), 8.12 (2 H, d, J 3) and 4.37 (1 H, s); δ_C(300 MHz; DMSO-d_6; Me_4Si) 165.80, 135.93, 132.01, 130.09, 122.71, 82.63 and 81.60; *m/z* (ESI) 188.9861 (M^-, 34%), 224.9597 (27), 378.9674 (100) and 535.0992 (7).

Synthesis of PCN-46. H_2ei (50 mg, 2.63×10^{-4} mol) and cupric acetate (125 mg, 6.26×10^{-4} mol) were dissolved in 20 mL of dimethylacetamide (DMA) in a vial, to which 10 drops of HBF_4 were added. The vial was tightly capped and placed in a 85 °C oven for 72 h to yield 102 mg of green block crystals (yield: 77% based on H_2ei). ν_{max}(neat)/cm^{-1} 3414, 2933, 1620, 1371 and 1014. The crystal has a formula of $[Cu(H_2O)]_2(bdi)\cdot 5DMA\cdot 2H_2O$, which was derived from crystallography data, elemental analysis (% calc/found: C 47.61/47.41, H 5.89/5.98, N 6.94/7.25), and TGA.

X-ray Crystallography. Single crystal X-ray structure determination of PCN-46 was performed at 173(2) K on the Advanced Photon Source on beamline 15ID-B in Argonne National Laboratory. Raw data for the structure were processed using SAINT and absorption corrections were applied using SADABS[2]. Structures were solved by direct method and refined by full-matrix least-squares on F^2 using *SHELXTL*[3]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The solvent molecules are highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the *SQUEEZE* routine of *PLATON*[4]; structures were then refined again using the data generated.

Sample Activation. As-synthesized PCN-46 crystals were immersed in methanol for 3 days to remove the nonvolatile solvates (DMA and water), and the extract was decanted every day and fresh methanol was replaced. The sample was collected by decanting and treated with dichloromethane for 3 days similarly to remove methanol. After the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum at room temperature overnight.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) pattern of as-synthesized PCN-46 was obtained on a Bruker-AXS D8 Advanced Bragg-Brentano X-ray Powder Diffractometer using Cu-K_α radiation. Due to the instability of activated PCN-46 in the air, its PXRD pattern was obtained by sealing the sample in 0.6 mm standard Lindeman capillary under an argon atmosphere and collecting the data on a Bruker GADDS three-circle X-ray Diffractometer (Cu-Kα radiation).

Low-Pressure Gas Sorption Measurements. The low-pressure gas sorption isotherm measurements were performed at 77 K (liquid nitrogen bath) or 87 K (liquid argon bath) on a Micromeritics ASAP 2020 surface area and pore size analyzer. Before measurements, the activated sample was degassed for 10 h at 100 °C. UHP grade (99.999%) N_2, He, H_2, and Ar were used for all measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

High-Pressure Gas Sorption Measurements. High pressure excess adsorption of H_2, CH_4 and CO_2 were measured using an automated controlled Sieverts' apparatus (PCT-Pro 2000 from Setaram) at 77 K (liquid nitrogen bath) or 298 K (room temperature). About 600 mg of activated sample were loaded into sample holder under an argon atmosphere. Before measurements, the sample was degassed at 100 °C overnight. The free volume was determined by the expansion of low-pressure He (<5 bar) at room temperature. The temperature gradient between the gas reservoir and sample holder was corrected by applying a correction factor to the raw data, which was obtained by replacing the sample with a polished stainless-steel rod and measuring the adsorption isotherm at the same temperature over the requisite pressure regime. The total gas uptake was calculated by: $N_{\text{total}} = N_{\text{excess}} + \rho_{\text{bulk}}V_{\text{pore}}$, where ρ_{bulk} equals to the density of compressed gases at the measured temperature and pressure, and V_{pore} was obtained from the N_2 sorption isotherm at 77 K.

References

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(2) Sheldrick, G.M. SADABS v.2008/1, *Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA 1998.
(3) Sheldrick, G.M. SHELXTL v. 5.10, *Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.
(4) A.L.Spek, J.Appl.Cryst. 2003, 36, 7-13.

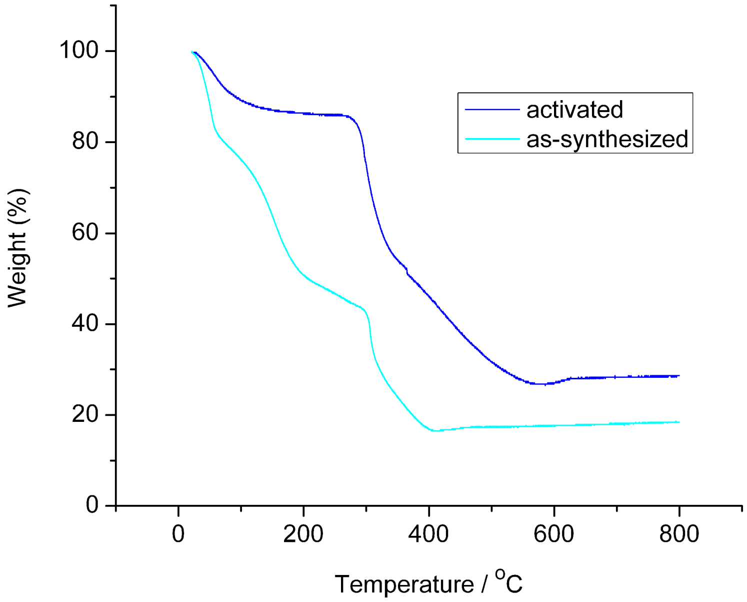

Figure S1. TGA curves of PCN-46 (activated: blue; as-synthesized: azure).

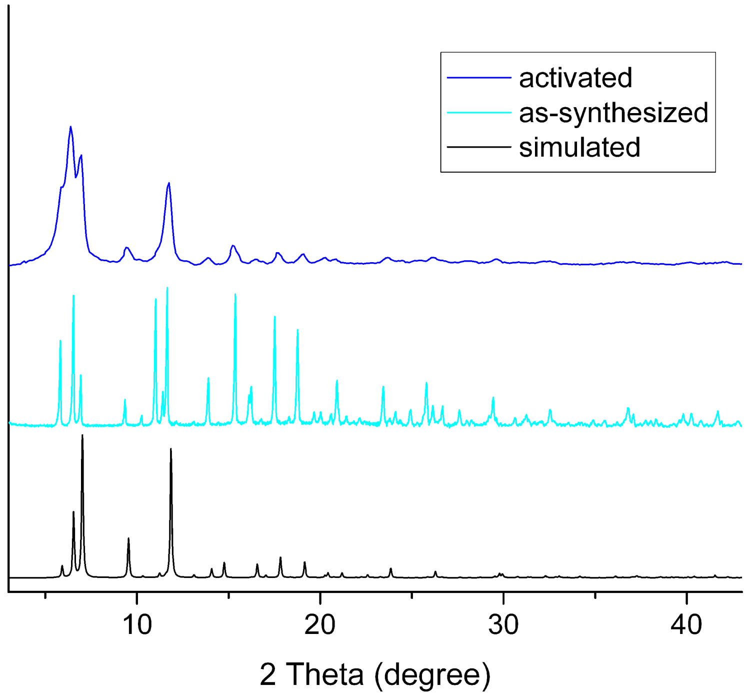

Figure S2. PXRD of PCN-46 (activated: blue; as-synthesized: azure; simulated: black).

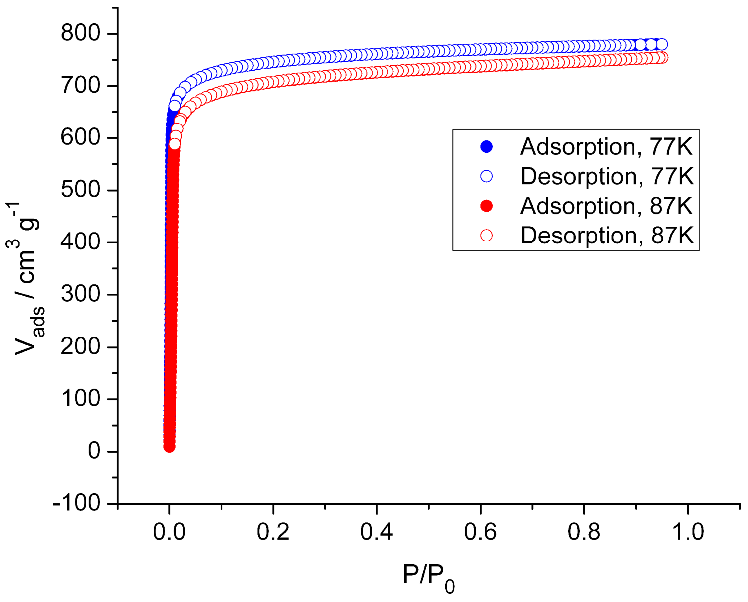

Figure S3. Ar sorption isotherms of PCN-46 (solid symbols: adsorption; open symbols: desorption; 77 K isotherms: blue; 87 K isotherms: red).

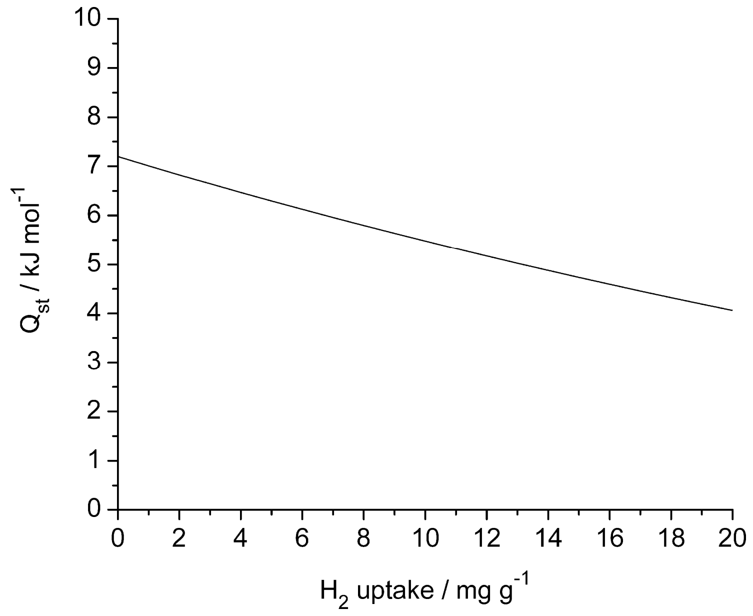

Figure S4. H_2 isosteric adsorption enthalpy of PCN-46