

# Supporting Information

“Stabilization of Metal-Organic Frameworks with High Surface Areas by the Incorporation of Mesocavities with Microwindows”

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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 Bruker Avance 200 MHz NMR spectrometer. Elemental analyses (C, H, and N) were obtained from Canadian Microanalytical Service, Ltd. Thermogravimetry analyses (TGA) were performed under N<sub>2</sub> on a PerkinElmer TGA 7, with a heating rate of 5 °C min<sup>-1</sup>. X-ray powder diffraction (XRPD) patterns were obtained on a Scintag X1 powder diffractometer system using Cu-K<sub>α</sub> radiation with a variable divergent slit, solid-state detector, and a routine power of 1400 W (40 kV, 35 mA). Scanning electron microscopy (SEM) images were taken on a Zeiss Supra 35 VP FEG SEM or a JEOL JSM-840A SEM. The samples were coated with gold before observation.

**Synthesis of 1,3,5-tris(2-diethyl isophthalate-1-ethynyl)benzene, 1.** 1,3,5-tribromobenzene (2.00 g, 6.35 mmol), diethyl-5-(ethynyl)isophthalate (6.25 g, 25.4 mmol),<sup>1</sup> Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (442 mg, 0.63 mmol), PPh<sub>3</sub> (330 mg, 1.26 mmol), and CuI (240 mg, 1.26 mmol) were mixed in a 500 mL three neck Schlenk flask. The flask was pumped under vacuum and refilled with N<sub>2</sub> for three times, and then 200mL of freshly distilled and degassed triethylamine was added. The mixture was heated to reflux under nitrogen atmosphere for 64 hours. After removal of organic solvent, the residue was dissolved in chloroform (150 mL) and washed with water (100 mL). The aqueous layer was back-extracted with chloroform (3 × 50 mL), and the combined organic layers were dried over MgSO<sub>4</sub> and filtered. The solvent was removed and the crude product was purified by column chromatography on silica gel with 40:1 chloroform/EtOAc to give compound **1** as a pale yellow solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 8.69 (t,

3H,  $J = 1.6$  Hz), 8.41 (d, 6H,  $J = 1.6$  Hz), 7.78 (s, 3H), 4.47 (q, 12H,  $J = 7.1$  Hz), 1.48 (t, 18H,  $J = 7.1$  Hz).

**Synthesis of 5,5',5''-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalic acid), H<sub>6</sub>btei.** Compound **1** (5.00 g, 6.17 mmol) was suspended in 100 mL of THF, to which 150 mL of 1 M KOH aqueous solution was added. The mixture was stirred under reflux for 4 hours. THF was removed using a rotary evaporator, and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic. The precipitate was collected by filtration, washed with water and dried under vacuum to give H<sub>6</sub>btei as a yellow solid. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 13.63$  (br, 6H), 8.50 (t, 3H,  $J = 1.6$  Hz), 8.33 (d, 6H,  $J = 1.6$  Hz), 8.01 (s, 3H).

**Synthesis of hexaethyl 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl))-triisophthalate, 2.** Tris(4-ethynylphenyl)amine (1.69 g, 5.0 mmol),<sup>2</sup> diethyl-5-(iodo)isophthalate (6.96 g, 20.0 mmol),<sup>1</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> (580 mg, 0.50 mmol), and CuI (95 mg, 0.50 mmol) were mixed in a 250 mL three neck Schlenk flask. The flask was pumped under vacuum and refilled with N<sub>2</sub> for three times, and then 100 mL of freshly distilled and degassed triethylamine was added. The mixture was heated to reflux under nitrogen atmosphere for 72 hours. After removal of organic solvent, the residue was dissolved in chloroform (200 mL) and washed with water (150 mL). The aqueous layer was back-extracted with chloroform (3  $\times$  50 mL), and the combined organic layers were dried over MgSO<sub>4</sub> and filtered. The solvent was removed and the crude product was purified by column chromatography on silica gel with chloroform to give compound **2** as a green solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.60$  (s, 3H), 8.34 (s, 6H), 7.47 (d, 6H,  $J = 8.7$  Hz), 7.12 (d, 6H,  $J = 8.7$  Hz), 4.42 (q, 12H,  $J = 7.2$  Hz), 1.43 (t, 18H,  $J = 7.2$  Hz).

**Synthesis of 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl))triisophthalic acid, H<sub>6</sub>ntei.** Compound **2** (3.00 g, 6.13 mmol) was suspended in 50 mL of THF and 50 mL of methanol, to

which 50 mL of 3 M KOH aqueous solution was added. The mixture was stirred under reflux for 4 hours. THF was removed using a rotary evaporator, and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic. The precipitate was collected by filtration, washed with water, and dried under vacuum to give H<sub>6</sub>ntei as a yellow solid. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.35 (br, 6H), 8.43 (s, 3H), 8.23 (s, 6H), 7.61 (d, 6H, *J* = 8.7 Hz), 7.13 (d, 6H, *J* = 8.7 Hz).

**Synthesis of PCN-60.** H<sub>6</sub>btei (100 mg,  $1.6 \times 10^{-4}$  mol) and ZnBr<sub>2</sub> (300 mg,  $1.3 \times 10^{-3}$  mol) were dissolved in 15 mL of DMF in a vial. The vial was tightly capped and placed in a 75 °C oven for 72 h to yield 86 mg of amber block crystals (yield: 34% based on H<sub>6</sub>btei). The crystal has a formula of [Zn(H<sub>2</sub>O)]<sub>3</sub>(btei)·9DMF·5H<sub>2</sub>O, which was derived from crystallographic, elemental analysis (% calc/found: C 46.29/46.32, H 5.61/5.02, N 7.71/7.76), and TGA.

**Synthesis of PCN-61.** H<sub>6</sub>btei (100 mg,  $1.6 \times 10^{-4}$  mol) and Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (300 mg,  $1.3 \times 10^{-3}$  mol) were dissolved in 15 mL of DMF with 9 drops of HBF<sub>4</sub> in a vial. The vial was tightly capped and placed in a 75 °C oven for 72 h to yield 218 mg of turquoise block crystals (yield: 94% based on H<sub>6</sub>btei). The crystal has a formula of [Cu(H<sub>2</sub>O)]<sub>3</sub>(btei)·5DMF·4H<sub>2</sub>O, which was derived from crystallographic data, elemental analysis (% calc/found: C 46.45/46.97, H 4.66/4.88, N 5.31/5.21), and TGA.

**Synthesis of PCN-66.** H<sub>6</sub>ntei (50 mg,  $6.2 \times 10^{-5}$  mol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (150 mg,  $8.8 \times 10^{-4}$  mol) were dissolved in 15 mL of DMA with 20 drops of HBF<sub>4</sub> in a vial. The vial was tightly capped and placed in a 85 °C oven for 72 h to yield 80 mg of turquoise block crystals (yield: 42% based on H<sub>6</sub>ntei). The crystal has a formula of [Cu(H<sub>2</sub>O)]<sub>3</sub>(ntei)·21DMA·10H<sub>2</sub>O, which was derived from crystallographic data, elemental analysis (% calc/found: C 51.84/51.82, H 7.78/7.56, N 10.08/10.05), and TGA.

**X-ray Crystallography.** Single crystal X-ray data of PCN-60 and PCN-61 were collected on a Bruker AXS Proteum-R 6000 X-ray diffractometer outfitted with a Cu rotating-anode X-ray source

(FR-591) (Cu K $\alpha$  radiation,  $\lambda = 1.54178$  Å) and a Smart6000 CCD detector equipped with an Oxford Cryostream low temperature device. The *Proteum II* software suite was used for data collection, cell refinement, reduction, and absorption correction. Single crystal X-ray data of PCN-66 were collected on beamline 15ID-C at the Advanced Photon source in Argonne National Laboratory. Structures were solved by direct method and refined by full-matrix least-squares on  $F^2$  using *SHELXTL*. 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*; structures were then refined again using the data generated. Crystal data are summarized in Table S1.

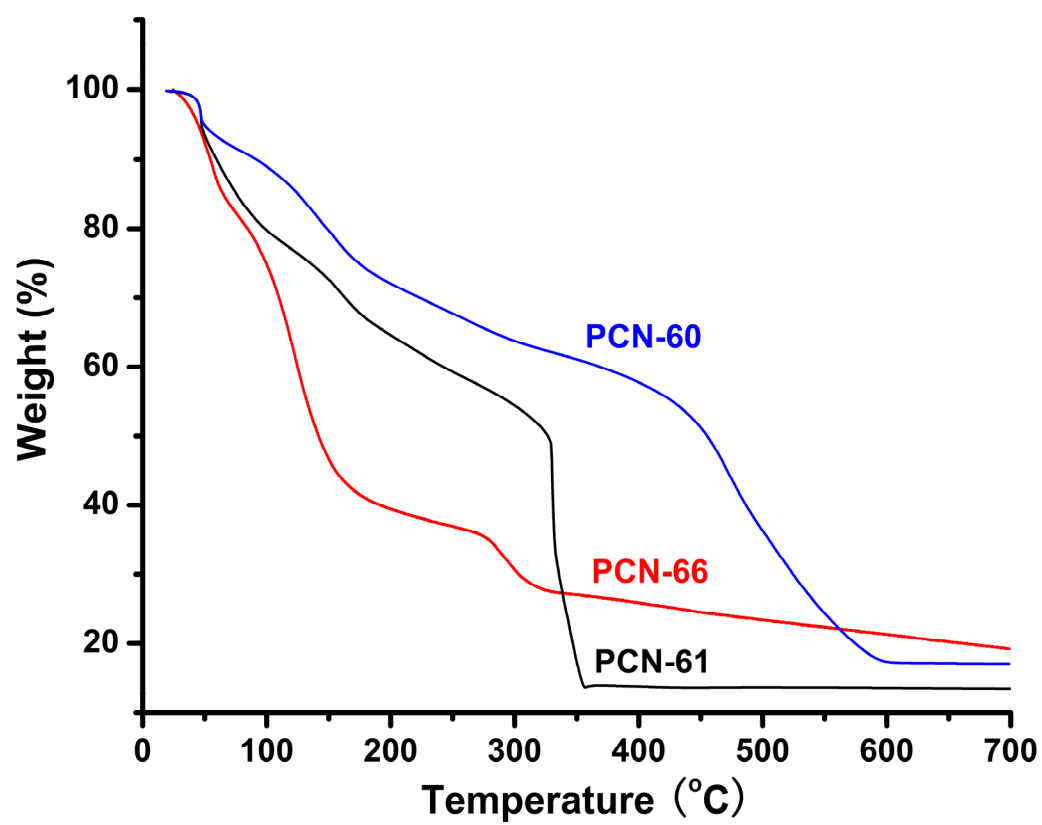
**Low-Pressure Nitrogen Sorption Measurements.** The low-pressure nitrogen sorption isotherm measurements were performed at 77 K and 0-760 Torr on a ASAP 2020 surface area and pore size analyzer. An as-isolated sample of PCN-61 or PCN-66 was immersed in methanol for 24 h, and the extract was decanted. Fresh methanol was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile solvates (DMF/DMA and water). 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 “outgas” function of the surface area analyzer for 12 h at 150 °C. Nitrogen isotherms at 77 K were measured in liquid nitrogen baths using UHP-grade (99.999%) gas source. 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.

## Reference

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- (2) McIlroy, S. P.; Cló, E.; Nikolajsen, L.; Frederiksen, P. K.; Nielsen, C. B.; Mikkelsen, K. V.; Gothelf, K. V.; Ogilby, P. R. *J. Org. Chem.* 2005, 70, 1134-1146.

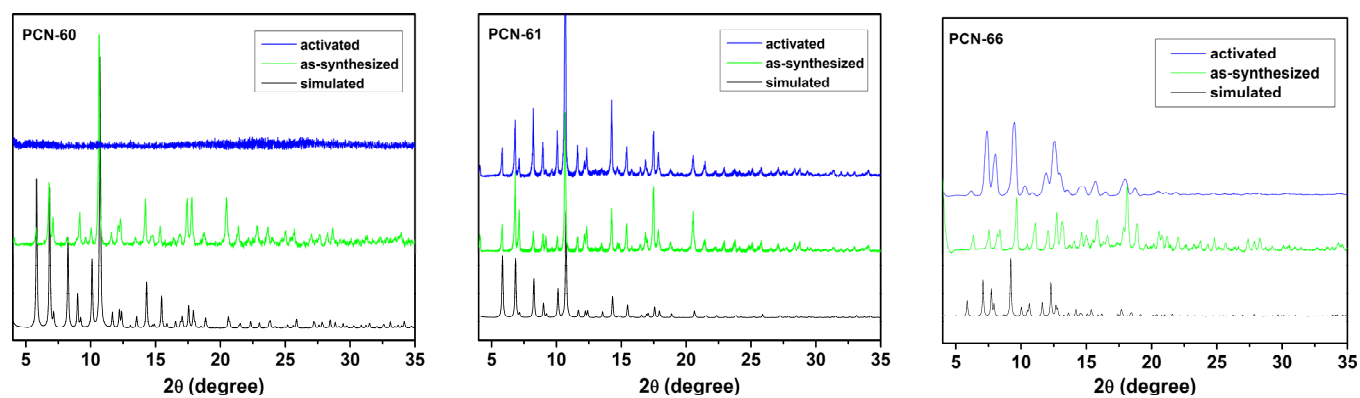
**Table S1.** Crystal Data for PCN-60, PCN-61, and PCN-66

	PCN-60	PCN-61	PCN-66
formula	C <sub>12</sub> H <sub>6</sub> O <sub>5</sub> Zn	C <sub>12</sub> H <sub>6</sub> CuO <sub>5</sub>	C <sub>48</sub> H <sub>27</sub> Cu <sub>3</sub> NO <sub>15</sub>
fw	295.54	293.71	1048.33
cryst size, mm <sup>3</sup>	0.15 × 0.13 × 0.12	0.08 × 0.07 × 0.03	0.08 × 0.06 × 0.05
cryst syst	cubic	cubic	cubic
space group	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>Fm-3m</i>
<i>a</i> , Å	42.8434(3)	42.7958(6)	49.112(4)
<i>V</i> , Å <sup>3</sup>	78641.5(10)	78379.7(19)	118458(18)
<i>Z</i>	96	96	32
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	0.599	0.597	0.470
<i>F</i> <sub>000</sub>	14208	14112	16928
<i>T</i> , K	173(2)	173(2)	110(2)
reflns collected	44736	33881	118332
independent reflns	1381 ( <i>R</i> <sub>int</sub> = 0.038)	740 ( <i>R</i> <sub>int</sub> = 0.056)	2903 ( <i>R</i> <sub>int</sub> = 0.1743)
GOF ( <i>F</i> <sup>2</sup> )	1.116	1.130	1.104
<i>R</i> 1, <i>wR</i> 2	0.050, 0.16	0.042, 0.12	0.1204, 0.3423
data/restraints/params	1325/9/99	702/9/99	1259/63/127
$\mu$ , mm <sup>-1</sup>	1.086	0.989	0.237

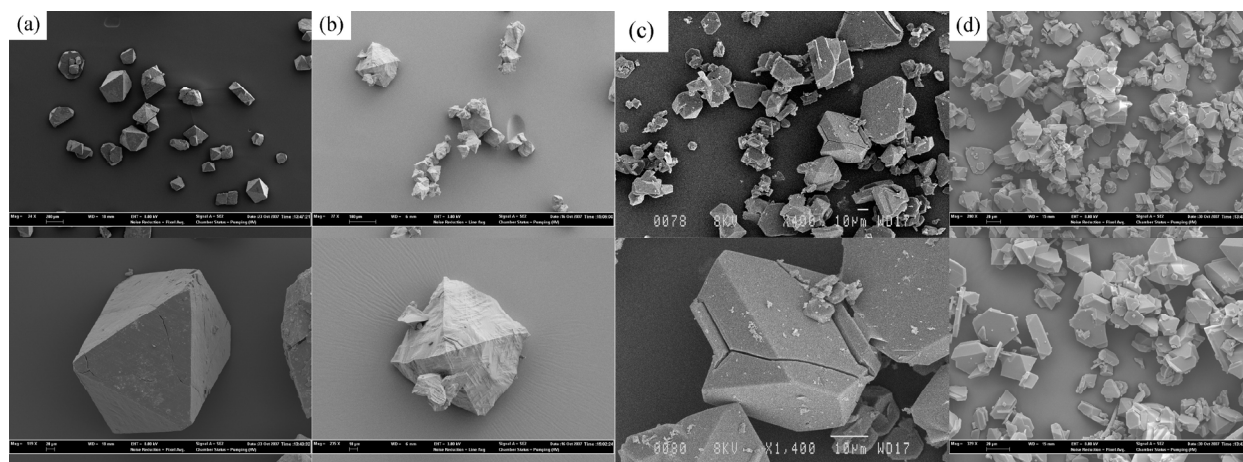


**Figure S1.** TGA curves of PCN-60 (blue), PCN-61 (black), and PCN-66 (red).

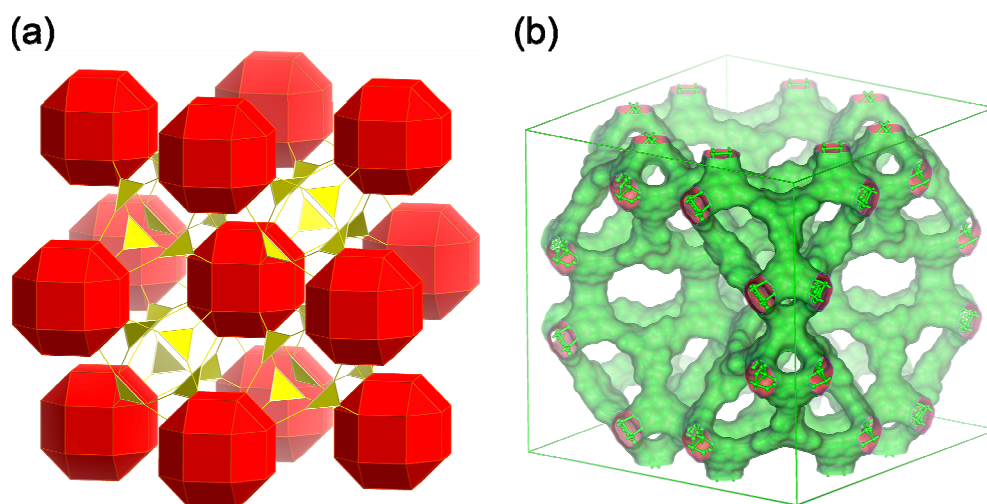




**Figure S2.** XRPD of PCN-60 (left), PCN-61 (middle), and PCN-66 (right) (activated: blue, as-synthesized: green, simulated: black).



**Figure S3.** SEM images of PCN-60 and PCN-61 (a: as-synthesized PCN-60; b: activated PCN-60; c: as-synthesized PCN-61; d: activated PCN-61).



**Figure S4.** (a) Polyhedra as building units in PCN-66. (b) Solvent accessible surface area in PCN-66.

Complete author list of Ref 9c:

Park, Y. K.; Choi, S. B.; Kim, H.; Kim, K.; Won, B. H.; Choi, K.; Choi, J. S.; Ahn, W. S.; Won, N.; Kim, S.; Jung, D. H.; Choi, S. H.; Kim, G. H.; Cha, S. S.; Jhon, Y. H.; Yang, J. K.; Kim, J. *Angew. Chem.-Int. Edit.* **2007**, *46*, 8230-8233.