

Ligand-elaboration as a strategy for engendering structural diversity in porous metal-organic framework compounds

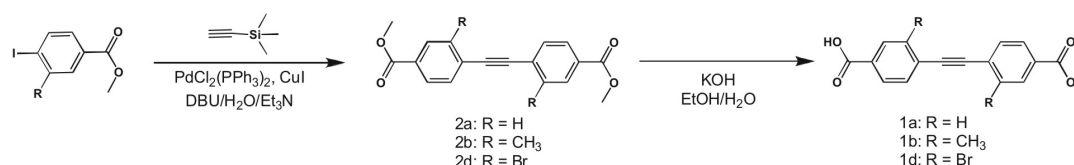
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Materials. All chemicals were used as received from commercial sources unless otherwise noted. 4-Iodo-3-methylbenzoic acid methyl ester (TCI America Organic Chemicals), methyl-p-iodobenzoate (City Chemical), 3-bromo-4-iodobenzoic acid methyl ester (Focus Synthesis), dichlorobis(triphenylphosphine)palladium (Strem Chemicals), copper iodide (Strem Chemicals), and *N,N'*-dimethylamine (Fisher Scientific) were purchased from commercial sources. Zinc nitrate hexahydrate, 4,4-dipyridyl (BIPY), trimethylsilylacetylene, triethylamine, DBU, dichloromethane, ethyl acetate, and ethanol were purchased from Aldrich Chemicals. Triethylamine was distilled under nitrogen over potassium hydroxide and kept under nitrogen in a Straus flask. DBU were freeze-pump-thawed three times and stored under nitrogen in a Straus flask. Deionized, water (ultrapure, 18.2 MΩ•cm resistivity, obtained from a Millipore system) was degassed with a stream of nitrogen for 15 minutes prior to addition into the Sonigashira couplings. For convenience, a 0.15-mol% solution of water in DBU can be prepared, freeze-pump-thawed three times, stored under nitrogen in a Straus flask, and used as demanded.

Characterization. Elemental analyses were performed by Atlantic Microlabs, Inc. (Norcross, GA) after drying under vacuum at 100 °C overnight. ¹H NMR and ¹³C NMR spectra were recorded on a Varian INOVA 500 NMR spectrometer (500 MHz for ¹H, 125 MHz for ¹³C). NMR chemical shifts were reported in ppm against residual solvent resonance as the internal standard (δ(CHCl₃) = 7.27 ppm (¹H), 77.2 ppm (¹³C); δ(DMSO) = 2.50 ppm (¹H), 39.5 ppm (¹³C)). ¹H NMR data were reported as follows: chemical shift (multiplicity (s = singlet, d = doublet), integration, assignment). Gas Chromatography-Mass Spectrometry (GC-MS) analyses were performed on a Hewlett-Packard 6890 GC interfaced to a HP 5972 Mass Selective Detector Quadrupole Mass Spectrometer. Electrospray-ionization mass spectrometry (ESIMS) was conducted in negative ionization mode on a Micromass Quattro II triple quadrupole HPLC-MS-MS mass spectrometer. Laser desorption mass spectrometry was performed on a PE Voyager DE-Pro MALDI-TOF mass spectrometer in positive ionization mode, using 2-hydroxy-1-naphthoic acid as a matrix.

Synthetic Procedures

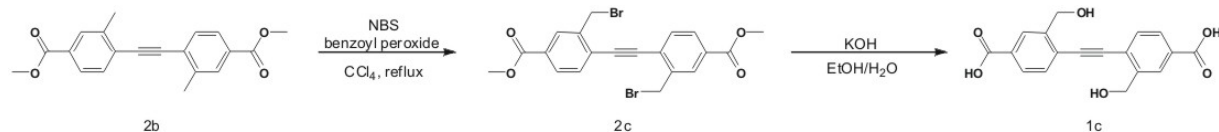


General procedure for the syntheses of 2a, 2b, and 2d via Sonogashira coupling. Inside a nitrogen-filled drybox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stir bar was charged with PdCl₂(PPh₃)₂ (7 mg, 1 mol%), CuI (6 mg, 3 mol%), and the organic iodide (1 equiv, 1 mmol). Triethylamine (2 mL, 27 mmol) and DBU (1 mL, 6.6 equiv) were then added. The vial was capped with a screw cap fitted with a Teflon-coated rubber septum, and trimethylsilylacetylene (70 μL, 0.50 equiv) was added via a gas-tight syringe to start the reaction. Next, the vial was taken out of the drybox, and degassed, deionized water (7 μL, 40 mol%) was added via a gas-tight syringe. The reaction vial was then covered up with aluminum foil and allowed to stir at ambient temperature for 2 h, over which time the reaction became darker in color and the product precipitated out of solution. Upon completion, triethylamine was removed under reduced pressure, and water (~ 2 mL) was added to the remaining slush to precipitate more of the product. The mixture was then filtered over a Buchner funnel and the collected solid was air-dried overnight before being recrystallized.

4,4'-(1,2-ethynediyl)bis(benzoic acid) dimethyl ester (2a). Recrystallized from EtOAc to give a white solid (151 mg, 94%). Characterization data matches those reported in the literature.¹

4,4'-(1,2-ethynediyl)bis(3-methylbenzoic acid) dimethyl ester (2b). Recrystallized from EtOAc to give a white solid (151 mg, 94%). ¹H NMR (500 MHz, CDCl₃): δ 7.92 (s, 2H, ArH), 7.84 (d, 2H, *J* = 7.6 Hz, ArH), 7.55 (d, 2H, *J* = 7.6 Hz, ArH), 3.91 (s, 3H, OCH₃), 2.55 (s, 3H, CH₃). ¹³C NMR (500 MHz, CDCl₃): δ 166.9, 140.5, 132.2, 130.7, 130.0, 127.6, 127.0, 94.5, 52.4, 21.1. GC-MS(ED): *m/z* (%) 322 (100, [M]⁺), 323 (20).

4,4'-(1,2-ethynediyl)bis(3-bromobenzoic acid) dimethyl ester (2d). Recrystallized from EtOAc to give a white solid (135 mg, 60%). ¹H NMR (500 MHz, CDCl₃): δ 8.30 (d, 2H, *J* = 0.5 Hz, ArH), 7.97 (dd, 2H, *J*₁ = 0.50 Hz, *J*₂ = 8.0 Hz, ArH), 7.67 (d, 2H, *J* = 8.0 Hz, ArH), 3.94 (s, 3H, OCH₃). ¹³C NMR (500 MHz, CDCl₃): δ 165.4, 134.1, 133.6, 131.7, 129.2, 128.3, 125.8, 94.5, 52.9. GC-MS(ED): *m/z* (%) 450 (51, [M]⁺), 452 (100), 454 (50), 453.



Bromination of 2b to yield 4,4'-(1,2-ethynediyl)bis[3-(bromomethyl)benzoic acid] dimethyl ester (2c). A 500-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with **2b** (3.1 g, 9.6 mmol), NBS (3.43 g, 19.2 mmol), and benzoyl peroxide (470 mg, 1.92 mmol). Approximately 200 mL of CCl_4 was added, and a water-cooled reflux condenser was then attached to the flask. The mixture was allowed to stir under reflux overnight, after which it was allowed to cool to room temperature. Hexanes were added to the mixture to precipitate the crude product. The mixture was then filtered over a Buchner funnel and washed with cold EtOAc before being recrystallized from EtOAc to give a white solid (1.42 g, 30%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.16 (s, 2H, ArH), 8.01 (d, 2H, $J = 8.0$ Hz, ArH), 7.70 (d, 2H, $J = 8.0$ Hz, ArH), 4.83 (s, 2H, CH_2Br), 3.96 (s, 3H, OCH_3). $^{13}\text{CNMR}$ (500 MHz, CDCl_3): δ 166.1, 139.9, 133.3, 131.2, 131.1, 129.8, 127.1, 94.2, 52.7, 31.5. MALDI-MS: m/z 478.9 $[\text{M}+\text{H}^+]$, 480.9, 482.9.

General procedure for the syntheses of 1a, 1b, 1c and 1d via hydrolysis. A 30-mL vial equipped with a Teflon-coated magnetic stir bar was charged with the appropriate methyl ester precursor (1 equiv), KOH (10 equiv), and an EtOH/ H_2O (9:1 v/v) mixture to give a 0.2-M solution of the diester. The vial was capped and the mixture was allowed to stir at 35 °C with occasional monitoring by TLC (CH_2Cl_2). The reaction was stopped when starting material completely disappears (~ 1 h). Upon completion, ethanol was removed under reduced pressure, and distilled H_2O was added to the remaining slush until the entire mixture becomes homogeneous. The resulting aqueous solution was washed with CH_2Cl_2 (20 mL), and then acidified with concentrated aqueous HCl until no more solid precipitates out. The mixture was filtered over a Buchner funnel and the collected solid was washed with deionized water until the filtrate is no longer acidic. The solid product was then dried on a Schlenk line overnight.

4,4'-(1,2-ethynediyl)bisbenzoic acid (1a). White solid (96% yield from 8 mmol of **2a**). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 13.21 (s, 2H, COOH), 7.98 (d, 2H, $J = 8.0$ Hz, ArH), 7.67 (d, 2H, $J = 8.0$ Hz, ArH). $^{13}\text{CNMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 167.3, 132.4, 131.6, 130.3, 126.7, 91.7. ESIMS: m/z 265.1 $[\text{M}-\text{H}^-]$.

4,4'-(1,2-ethynediyl)bis[3-methylbenzoic acid] (1b). White solid (92% yield from 5 mmol of **2b**). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 13.21 (s, 2H, COOH), 7.89 (s, 2H, ArH), 7.79 (d, 2H, $J = 8.0$ Hz, ArH), 7.64 (d, 2H, $J = 8.0$ Hz, ArH), 2.52 (s, 3H, CH_3). $^{13}\text{CNMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 167.5, 140.7, 132.7, 131.5, 131.0, 127.5, 126.9, 94.6, 21.09. ESIMS: m/z 293.1 $[\text{M}-\text{H}^-]$.

4,4'-(1,2-ethynediyl)bis[3-(hydroxymethyl)benzoic acid] (1c). Pale yellow solid (74% yield from 1.3 mmol of **2c**). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 13.13 (br s, 2H, COOH), 8.07 (s, 2H, ArH), 7.91 (d, 2H, $J = 8.0$ Hz, ArH), 7.72 (d, 2H, $J = 8.0$ Hz, ArH), 4.75 (s, 4H, CH_2OH). $^{13}\text{CNMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 166.9, 140.5, 132.2, 130.7, 130.0, 127.6, 127.0, 94.5, 52.4, 21.1. ESIMS: m/z 324.9 $[\text{M}-\text{H}^-]$.

4,4'-(1,2-ethynediyl)bis[3-bromobenzoic acid] (1d). White solid (87% yield from 2.17 mmol of **2d**). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 13.55 (s, 2H, COOH), 8.19 (s, 2H, ArH), 7.98 (d, 2H, $J = 8.0$ Hz, ArH), 7.83 (d, 2H, $J = 8.0$ Hz, ArH). $^{13}\text{CNMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 166.1, 134.8, 134.0, 133.6, 129.2, 128.2, 125.5, 94.3. ESIMS: m/z 420.8 $[\text{M}-\text{H}^-]$, 422.7, 424.7.

MOF synthesis (A, B, C, and D).

$\text{Zn}(\mathbf{1a})_2(\text{BIPY})$ (A). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (7.5 mg, 25 μmol), **1a** (7.0 mg, 26 μmol), and BIPY (4.0 mg, 26 μmol) were combined in a 8-mL scintillation vial. DMF (5 mL) and deionized water (0.5 mL) were then added. The vial was capped and placed in a sonicating bath until all solid was uniformly dispersed (~ 5 min). The reaction vial then was placed in an aluminum block and heated at 60 °C for 1 day. Colorless crystals (5.5 mg, 45%) of the product were collected by filtration and washed with DMF (~ 4 x 5 mL). EA: Calculated for evacuated **A** ($\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_2\text{Zn}$): (% C, 64.14; H, 3.52; N, 5.75. Found: C, 63.88; H, 3.21; N, 5.87.

$\text{Zn}_2(\mathbf{1b})_2(\text{BIPY})$ (B). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mg, 10 μmol), **1b** (3 mg, 10 μmol), and BIPY (1.6 mg, 10 μmol) were combined in a 8-mL scintillation vial. DMF (1 mL) and deionized water (0.1 mL) were then added. The vial was capped and placed in a sonicating bath until all solid was uniformly dispersed (~ 5 min). The vial was placed in an aluminum block and heated at 80 °C for 1 day. Colorless crystals (5.1 mg, 58%) of the product were collected by filtration and washed with DMF (~ 4 x 5 mL). EA: Calculated for evacuated **B** ($\text{C}_{46}\text{H}_{32}\text{O}_8\text{N}_2\text{Zn}_2$): (% C, 63.24; H, 3.92; N, 3.21. Found: C, 62.85; H, 3.58; N, 3.34.

$\text{Zn}_2(\mathbf{1c})_2(\text{BIPY})$ (C). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mg, 10 μmol), **1c** (1.6 mg, 5 μmol) and BIPY (1.6 mg, 10 μmol) were combined in a 8-mL scintillation vial. DMF (1 mL) and deionized water (0.1 mL) were then added. The vial was capped and placed in a sonicating bath until all solid was uniformly dispersed (~ 5 min). The vial was placed in an aluminum block and heated at 80 °C for 1 day. Colorless crystals (1.4 mg, 31%) of the product were collected by filtration and washed with DMF (~ 4 x 5 mL). EA: Calculated for evacuated **C** ($\text{C}_{46}\text{H}_{32}\text{O}_{12}\text{N}_2\text{Zn}_2$): (% C, 58.93; H, 3.66; N, 2.99. Found: C, 59.02; H, 3.45; N, 3.07.

$\text{Zn}_2(\mathbf{1d})_2(\text{BIPY})$ (D). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mg, 10 μmol), **1d** (2.1 mg, 5 μmol) and BIPY (1.6 mg, 10 μmol) were combined in a 8-mL scintillation vial. DMF (0.5 mL) and deionized water (0.05 mL) were then added. The vial was capped and placed in a sonicating bath until all solid was uniformly dispersed (~ 5 min). The vial was placed in an aluminum block and heated at 60 °C for 1 day. Colorless crystals (1.3 mg, 46%) of the product were collected by filtration and washed with DMF (~ 4 x 5 mL). EA: Calculated (%) for evacuated **D** ($\text{C}_{42}\text{H}_{20}\text{Br}_4\text{O}_8\text{N}_2\text{Zn}_2$): (% C, 44.52; H, 1.96; N, 2.47. Found: C, 44.55; H, 2.11; N, 2.69.

In the aforementioned small-scale MOF syntheses, deionized water (10 vol%) was found to be the best co-solvent for growing single-crystal samples. However, the scale-up syntheses were carried out at 80 °C with no added water (all other reagents and solvent were scaled up properly in the same ratios as for the case of single-crystal samples). Hence, the overall concentration of substrates is greater in bulk syntheses.

Crystal Characterization

Single-crystal X-ray structure determination. Single crystals were mounted on a Bruker SMART1000 CCD diffractometer equipped with a graphite-monochromated MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation source in a cold nitrogen stream at 153(2) K. The DMF solvent molecules can be reasonably modeled in **A** using SHELXTL. For **B-D**, contributions from disordered solvent molecules were removed by the SQUEEZE routine (PLATON), and the outputs from the SQUEEZE calculations are attached to each CIF file. All crystallographic data were corrected for Lorentz and polarization effects (SAINT), as well as face-index absorption corrections. The structures were solved by direct methods and refined by the full-matrix least-squares method on F2 with the appropriate software implemented in the SHELXTL program package. For structures **A**, **B**, and **D**, the non-hydrogen atoms were refined anisotropically; hydrogen atoms were added at their geometrically ideal positions.

The current single-crystal diffraction data for **C** are inadequate for modeling all the disorder in the ligands; however, we are confident that this structure is a two-fold interpenetrating, pillared-paddlewheel framework (See Notes and References section in the main text for unit cell data). For the interested readers, the P4P and RAW data files for **C** were also submitted as parts of this ESI package. CIF files for **A**, **B**, and **D** are available as part of this SI, as a separate file.

Powder X-ray diffraction (PXRD). Powder X-ray diffraction patterns (Figure S1) were recorded on a Rigaku XDS 2000 diffractometer using nickel-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a range of $5^\circ < 2\theta < 40^\circ$ in 0.1° steps with a 1-s counting time per step. Simulations were made based on the single-crystal data using the Mercury software.

“As-synthesized” samples of **A-D** were collected from the bottom of the reaction vial as a thick suspension in DMF and spread on a fritted glass slide immediately before PXRD measurements. Given the high boiling point of DMF, the crystals never dry out during the PXRD measurement.

The evacuated samples were prepared by drying the as-synthesized samples in a vacuum oven at 100°C (~25 inches of Hg) overnight. The resulting powder samples were then mounted on clear cellophane tape and PXRD data were collected immediately after mounting.

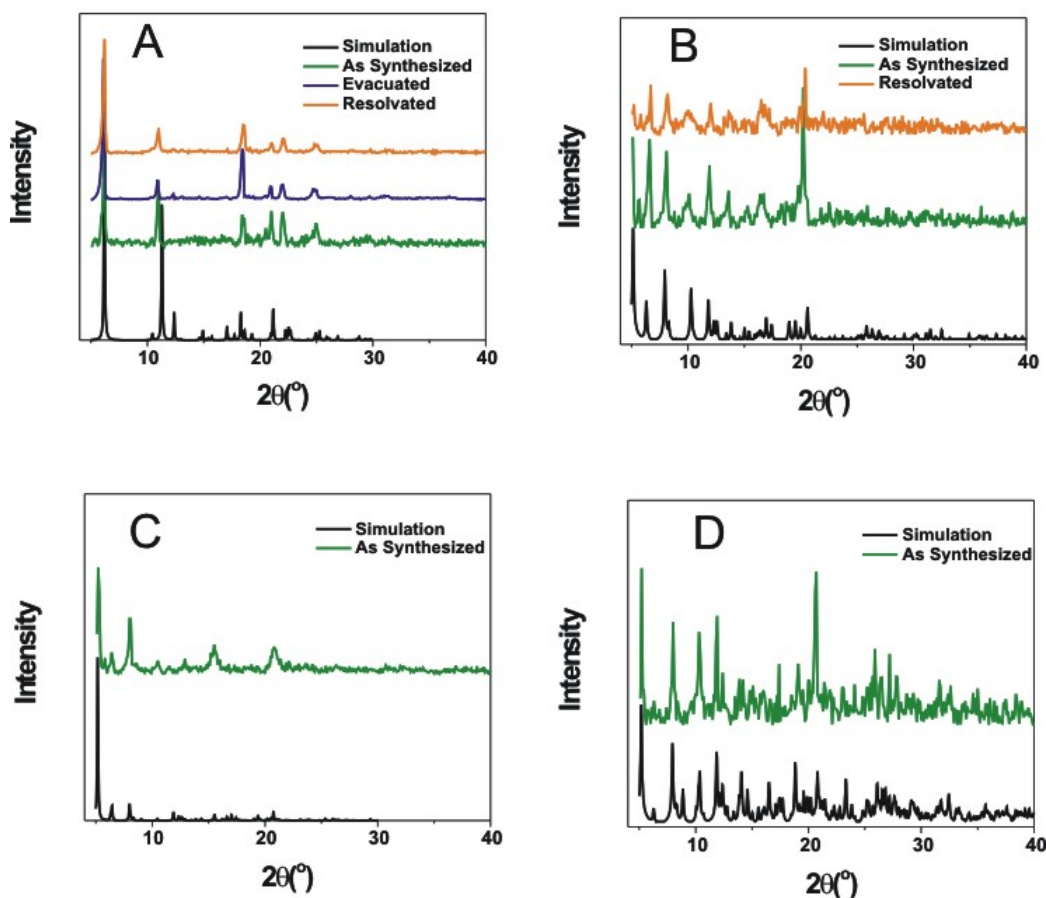


Figure S1. Powder X-ray Diffraction patterns for MOFs A-D.

Thermogravimetric analysis. Thermal gravimetric analysis (Figure S2) was performed on a Mettler Toledo TGA/SDTA851 interfaced with a PC using Star software. Samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. The data were shown in Figure S2.

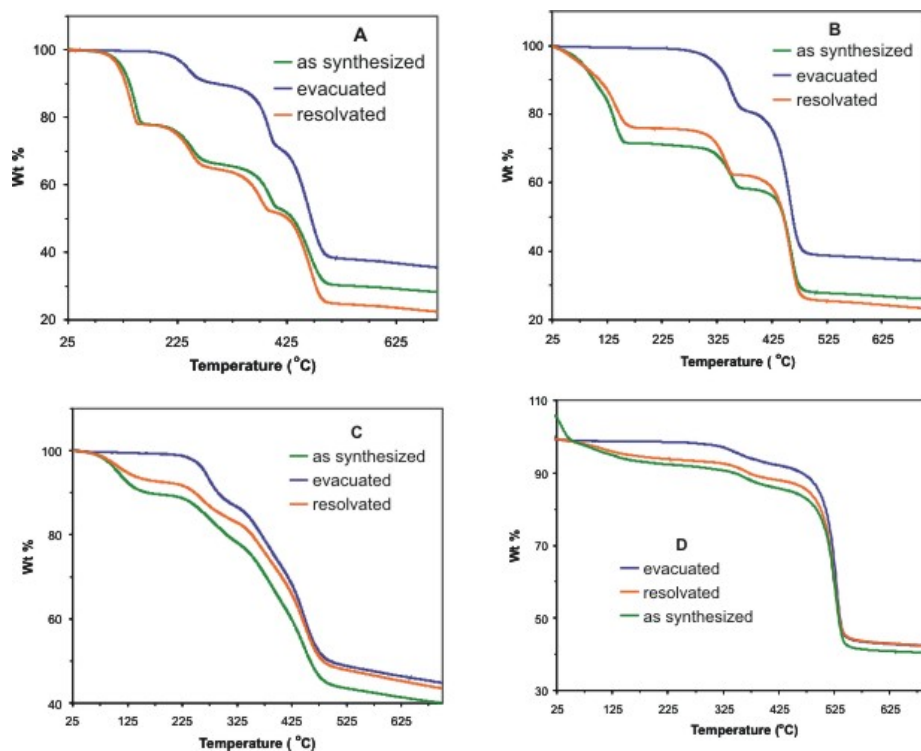


Figure S2. TGA curves for MOFs A-D.

N₂, CO₂, H₂ and Ar uptake and desorption. Gas adsorption/desorption isotherms were measured volumetrically at 77 K for N₂ and H₂, and at 273 K for CO₂ in the range $8.0 \times 10^{-6} \leq P/P_0 \leq 1.0$ using an Autosorb 1 instrument (Quantachrome Instruments) equipped with the ASWin software package. Ultra-high purity N₂ (99.999%), H₂ (99.999%), Ar (99.999%), and CO₂ (99.999%) were purchased from Airgas Inc. and used as received. All samples were outgassed at 100 °C at the outgas port of the Autosorb 1. For nitrogen, specific surface areas were calculated by applying Brunauer-Emmet-Teller (BET) theory over the linear region of the isotherm ($0.001 \leq P/P_0 \leq 0.3$). For CO₂, non-local density functional theory (NLDFT) was used for $0.005 \leq P/P_0 \leq 1.0$.

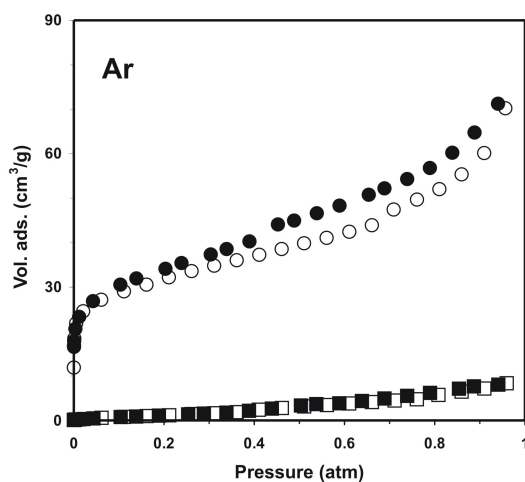


Figure S3. Ar adsorption (open), and desorption (closed) isotherms for A (□) and B (○).

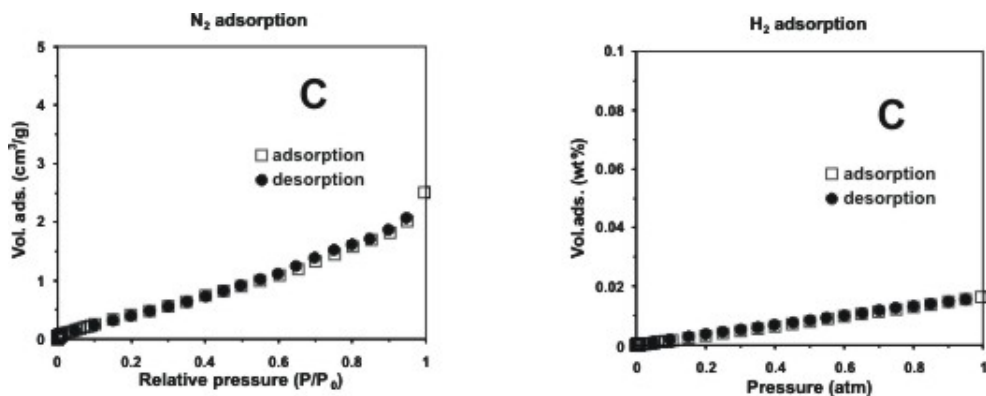


Figure S4. N₂ and H₂ adsorption isotherms for MOF C.

References

1. M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199-3202.