Electronic Supplementary Information (ESI)

Gas and Liquid Phase Adsorption in Isostructural Cu_3[biaryltricarboxylate]$_2$ Microporous Coordination Polymers

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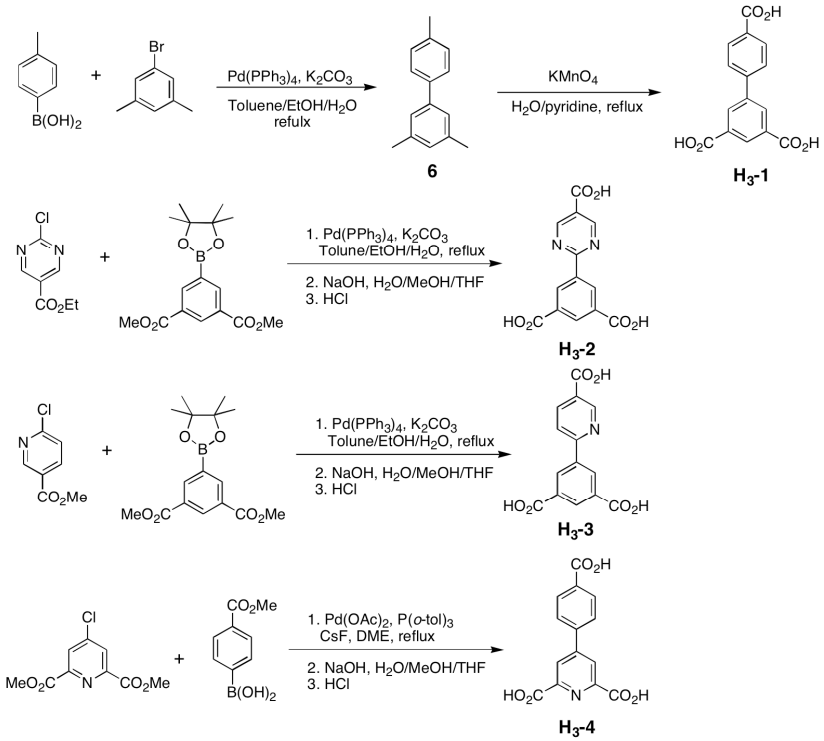
Contents

I. Synthesis

p-Tolylboronic acid, 1-bromo-3,5-dimethylbenzene, methyl-6-chloropyridine-3-carboxylate, and $Pd(OAc)_2$ were purchased from Sigma-Aldrich and used as received. $Pd(PPh_3)_4$ and $P(o\text{-tol})_3$ were purchased from Strem Chemicals and Acros, respectively and used as received. Ethyl-2-chloro-5-pyrimidinecarboxylate,[1] dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzenedicarboxylate,[2] and methyl-4-chloro-2,6-pyridinedicarboxylate[3] were synthesized according to published procedures. Elemental analysis was performed after weighing the sample in ambient conditions at Atlantic Microlab, Inc. (Norcross, GA, USA).

Scheme S1. Synthesis of Linkers



3,4',5-Trimethyl-1,1'-biphenyl (**6**). *p*-Tolylboronic acid (4.23 g, 31.1 mmol) and 1-bromo-3,5-dimethylbenzene (4.8 g, 25.9 mmol) were placed in a 250 mL round-bottom flask. 2 M K_2CO_3 (26 mL), EtOH (26 mL) and toluene (52 mL) were added and the suspension was degassed for 15 min by sparging with N_2. $Pd(PPh_4)_2$ (0.750 g, 0.649 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel using hexanes as eluent to afford a white solid (4.56 g, 88.1 % yield based on 1-bromo-3,4-dimethylbenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, *J* = 7.6 Hz), 7.23 (d, 2H, J = 8.0 Hz), 7.20 (s, 2H), 6.98 (s. 1H), 2.40 (s, 3H), and 2.38 (s. 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.8, 138.4, 137.0, 130.0, 128.8, 127.2, 125.1, 21.6 and 21.3 ppm.

Biphenyl-3,4',5-tricarboxylic acid (**H_3-1**). $KMnO_4$ (10.9 g, 69.0 mmol) was added to a suspension of **6** (4.50 g, 22.9 mmol) in H_2O (100 mL) and pyridine (50 mL), and the mixture was refluxed for 3 d. During that period, additional $KMnO_4$ (10.9 g, 69.0 mmol) was added every 12 h (total amount of $KMnO_4$, 77 g). After cooling to room temperature, the mixture was filtered over a plug of celite and washed with water. The filtrate was evaporated and the residue was dissolved in water. The insoluble solid was filtered off and the filtrate was acidified with 4 M HCl to pH ~2. The white solid was filtered and dried (5.63 g, 85.9% yield based on **6**). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.49 (s, 1H), 8.42 (s. 2H), 8.06 (d, *J* = 8.4 Hz, 2H), and 7.88 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.0, 166.4, 142.4, 140.0, 132.3, 131.5, 130.5, 130.2,

129.5, and 127.2 ppm; HRMS (EI) calcd. for $C_{15}H_{10}O_6$ (m/e): 286.0477; found: 286.0485.

5-[2-(4-carboxypyrimidinyl)]isophthalic acid (**H_3-2**). Ethyl-2-chloro-5-pyrimidinecarboxylate (1.00 g, 5.36 mmol) and dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzenedicarboxylate (2.00 g, 6.25 mmol) were placed in a 100 mL round-bottom flask. 2 M K_2CO_3 (4 mL), EtOH (4 mL) and toluene (12 mL) were added and the suspension was degassed for 15 min by sparging with N_2. $Pd(PPh_4)_2$ (0.310 g, 0.268 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel using 1% acetone in CH_2Cl_2 as eluent. The ester was hydrolyzed in 5 M KOH (5 mL) and THF/MeOH (1:1, 10 mL) at room temperature for 24 h. The solvent was evaporated and the residue was dissolved in water. The insoluble solid was filtered off and the filtrate was acidified (pH ~2). The white solid was filtered and dried (0.690 g, 44.7 % yield based on ethyl-2-chloro-5-pyrimidinecarboxylate). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.29 (s, 2H), 9.17 (d, J = 1.2 Hz, 2H), and 8.61 (d, J = 1.5 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 164.8, 164.1, 158.7, 137.2, 132.8, 132.6, 132.2, and 132.3 ppm; HRMS (EI) calcd. for $C_{13}H_8N_2O_6$ (m/e): 288.0382; found: 286.0378.

5-[2-(4-carboxypyridinyl)]isophthalic acid, hydrochloric acid (**H_3-3**). Methyl-4-chloro-2,6-pyridinedicarboxylate (1.00 g, 5.83 mmol) and dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzenedicarboxylate (1.87 g, 5.83 mmol) were placed in a 100 mL round-bottom flask. 2 M K_2CO_3 (6 mL), EtOH (6 mL) and toluene

(20 mL) were added and the suspension was degassed for 15 min by sparging with N_2. $Pd(PPh_4)_2$ (0.340 g, 0.294 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel using 5% acetone in CH_2Cl_2 as eluent. The ester was hydrolyzed in 5 M KOH (5 mL) and THF/MeOH (1:1, 10 mL) at room temperature for 24 h. The solvent was evaporated and the residue was dissolved in water. The insoluble solid was filtered off and the filtrate was acidified (pH ~2). The white solid was filtered and dried (0.602 g, 32.0 % yield based on methyl 4-chloro-2,6-pyridinedicarboxylate). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (d, J = 2.0 Hz, 1H), 8.88 (d, J = 1.6 Hz, 2H), 8.55 (t, J = 1.6 Hz, 1H), 8.37 (dd, J = 8.0, 2.0 Hz, 1H), and 8.23 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 166.2, 157.3, 150.6, 138.5, 138.5, 132.4, 131.4, 131.0, 126.2, and 120.4 ppm; HRMS (EI) calcd. for $C_{14}H_9NO_6$ (m/e): 287.0430; found: 286.0437.

5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid, hydrochloric acid (**H_3-4**). In a 25 mL round bottom flask were placed dimethyl-4-chloro-2,6-pyridinedicarboxylate (0.500 g, 2.18 mmol), 4-carboxyphenylboronic acid (0.433 g, 2.62 mmol), P(*o*-tol)$_3$ (33.0 mg, 0.108 mmol), $Pd(OAc)_2$ (24.7 mg, 0.109 mmol) and CsF (0.828 g, 5.45 mmol). The mixture was degassed for 15 min by sparging with N_2 and refluxed for 24 h after adding N_2-purged DME (12 mL). After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel using 2% acetone in CH_2Cl_2 as eluent. The ester was hydrolyzed in 5 M KOH (5 mL) and

THF/MeOH (1:1, 10 mL) at room temperature for 24 h. The solvent was evaporated and the residue was dissolved in water. The insoluble solid was filtered off and the filtrate was acidified (pH ~2). The white solid was filtered and dried (0.353 g, 56.4 % yield based on dimethyl-4-chloro-2,6-pyridinedicarboxylate). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.50 (s, 2H) and 8.07 (q, AB system, J = 8.6 Hz, 4H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 165.6, 149.7, 148.8, 139.9, 132.0, 130.3, 127.6, and 124.6ppm; HRMS (EI) calcd. for $C_{14}H_9NO_6$ (m/e): 287.0430; found: 286.0437.

General Procedure for the MCP synthesis. Linker (~20 mg) and $Cu(NO_3)_2{\cdot}2.5H_2O$ (33.0 mg, 0.142 mmol) were dissolved in DMF/dioxane/water (4:1:1, 10 mL) mixture in a 20 mL vial and heated at 75 °C for 8-12 h. The mother liquor was removed and replaced twice with fresh DMF and then with acetone, which was replaced with fresh solvent three times over a period of three days. The crystals were dried under vacuum at room temperature for 20 h and further evacuated at 100 °C overnight.

UMCM-150. The general procedure with **1** (20.0 mg, 0.0699 mmol) afforded purple UMCM-150 (20.1 mg, 75.4% yield). Anal. calcd for $C_{30}H_{18}O_{14}Cu_3$(Cu_3**1**$_2{\cdot}2H_2O$): C, 45.43; H, 2.29; found C, 45.43; H, 2.11.

UMCM-150(N)$_2$. A drop of 1 M HCl (aq) was added in the reaction mixture including **2** (20.2 mg, 0.0701 mmol). The general procedure afforded purple UMCM-150(N)$_2$ (19.8 mg, 73.6% yield). Anal. cacld for $C_{26}H_{16}N_4O_{15}Cu_3$ (Cu_3**2**$_2{\cdot}3H_2O$): C, 38.31; H, 1.98; N, 6.87; found C, 38.54; H, 1.78; N, 6.77.

UMCM-150(N)$_1$. A drop of 1 M HCl (aq) was added in the reaction mixture including **3** (20.0 mg, 0.0696 mmol). The general procedure afforded purple UMCM-

150(N)$_1$ (15.3 mg, 57.5% yield). Anal. calcd for $C_{28}H_{16}N_2O_{14}Cu_3$ (Cu_3**3**$_2$·2H_2O): C, 42.30; H, 2.03; N, 3.52; found C, 42.08; H, 2.15; N, 3.60.

II. X-ray Crystallography

Crystal Structure Determination. Single crystals suitable for X-ray structure determination were selected under a microscope and mounted in MiTiGen micro-mounts or on Nylon loops with Paratone N hydrocarbon oil and placed in a stream of cold nitrogen delivered from an Oxford Cryosystems Cryostream Plus cooler for low temperature data collection. Intensity data were collected on a three circle (quarter χ–arm) Rigaku R-Axis Spider diffractometer (460 mm × 256 mm curved imaging plate detector with graphite monochromated Cu Kα radiation (λ = 1.54187 Å)). Initial ω scans of each sample were performed to determine preliminary unit cell parameters and to allow the selection of image widths for data collection. For all cases oscillation images were collected using widths of 2.0° in ω. Data were collected using the d*TREK package in the CrystalClear software suite[4] to obtain ω scans for χ at 0° and 54°. Using the FS_PROCESS[5] package in CrystalClear, the raw intensity data were then reduced to F^2 values with corrections for Lorentz, and polarization effects. Decay of the crystals during data collection was negligible. An empirical absorption correction was applied as implemented by FS_PROCESS. The structures were solved within the CrystalStructure[6] package by direct methods and refined against all data.[7] Hydrogen atoms were placed at calculated positions (C-H = 0.95 Å) using a riding model with isotropic displacement parameters scaled by the U_{eq} of the attached carbon atom. Hydrogen atoms on coordinated water molecules could not be located in the difference Fourier maps and thus

were not included in the final model used for refinement. Thermal parameters for all non-hydrogen atoms were refined anisotropically. In structures with voids, attempts to locate and model the highly disordered solvent molecules in the voids were unsuccessful. Therefore the SQUEEZE routine of PLATON[8] was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities.

Table S1. Crystallographic Data and Structural Refinement Summary for.

Compound	UMCM-150(N)$_2$·3H$_2$O	UMCM-150(N)$_1$·2H$_2$O
Chemical formula	$C_{26}H_{16}N_4O_{15}Cu_3$	$C_{28}H_{16}N_2O_{14}Cu_3$
MW	815.06	795.07
Temperature, K	95(2)	95(2)
Space group	*P*6$_3$/mmc (#194)	*P*6$_3$/mmc (#194)
a, Å	18.4456(3)	18.2056(3)
b, Å	18.4456(3)	18.2056(3)
c, Å	39.5369(7)	40.6655(7)
α, deg	90	90
β, deg	90	90
γ, deg	120	120
V, Å^3	11649.8(5)	11672.6(4)
Z	6	6
λ, Å (CuK$_\alpha$)	1.54187	1.54187
ρ_{calcd}, g/cm^3	0.697	0.679
μ, mm^{-1}	1.237	1.210
$R_1[I > 2\sigma(I)]$[a]	0.0786[c]	0.0615[c]
$\omega R_2[I > 2\sigma(I)]$[b]	0.2868[c]	0.2020[c]
goodness-of-fit on F^2	0.99[c]	1.10[c]

[a] $R_1 = \Sigma\, ||F_o| - |F_c|| / \Sigma |F_o|$

[b] $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2 / \Sigma\omega(F_o^2)^2]^{1/2}$

[c] After SQUEEZE routine applied in PLATON

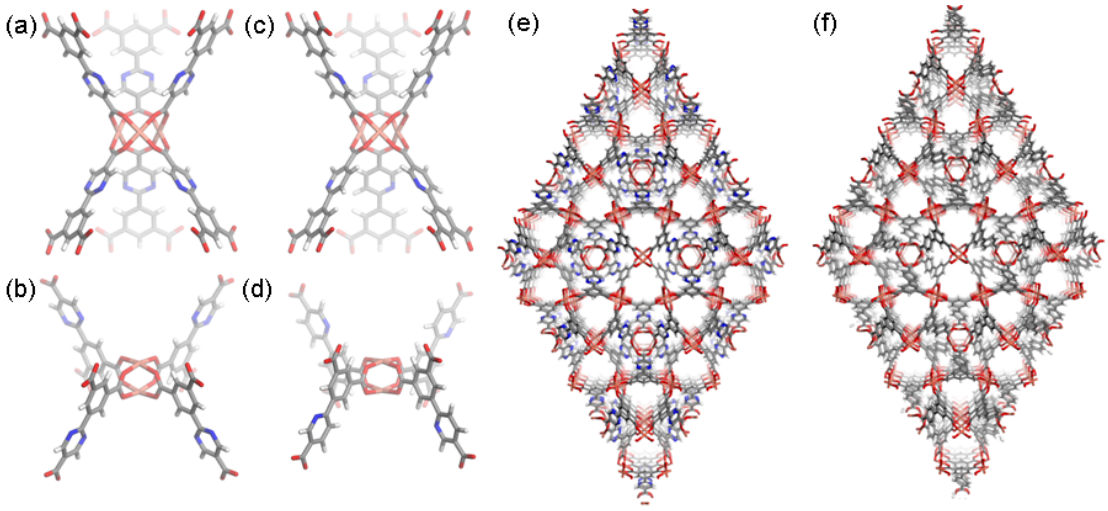


Figure S1. (a) Trinuclear metal clusters and (b) peddle wheel clusters of UMCM-150(N)$_2$. (c) Trinuclear metal clusters and (d) peddle wheel clusters of UMCM-150(N)$_1$. Packing structures along the [001] direction of (e) UMCM-150(N)$_2$ and (f) UMCM-150 for comparison. Guest molecules are omitted for clarity.

III. Low Pressure H_2 and CO_2 Gas Sorption Properties

Ultra-high purity He (99.999%), N_2 (99.999%), H_2 (99.999%), and CO_2 (99.999%) were purchased from Cryogenic Gases and used as received. N_2, H_2, and CO_2 gas sorption was measured volumetrically with an Autosorb-1C outfitted with the micropore option by Quantachrome Instruments (Boynton Beach, Florida, USA). Isosteric heats of adsorption were calculated as previously described[9]

Table S2. Surface areas of UMCM-150 analogs and their gas adsorption properties.

MCP	Linker	Surface area (m^2/g)[a]	H_2 uptake (mg/g)[b]	CO_2 uptake (mg/g)[c]
UMCM-150	**1**	2910	21.7	114
UMCM-150$(N)_2$	**2**	2980	21.6	120
UMCM-150$(N)_1$	**3**	3020	22.8	127

[a] BET surface area; [b] obtained at 77 K and 760 Torr; [c] at 298 K and 760 Torr.

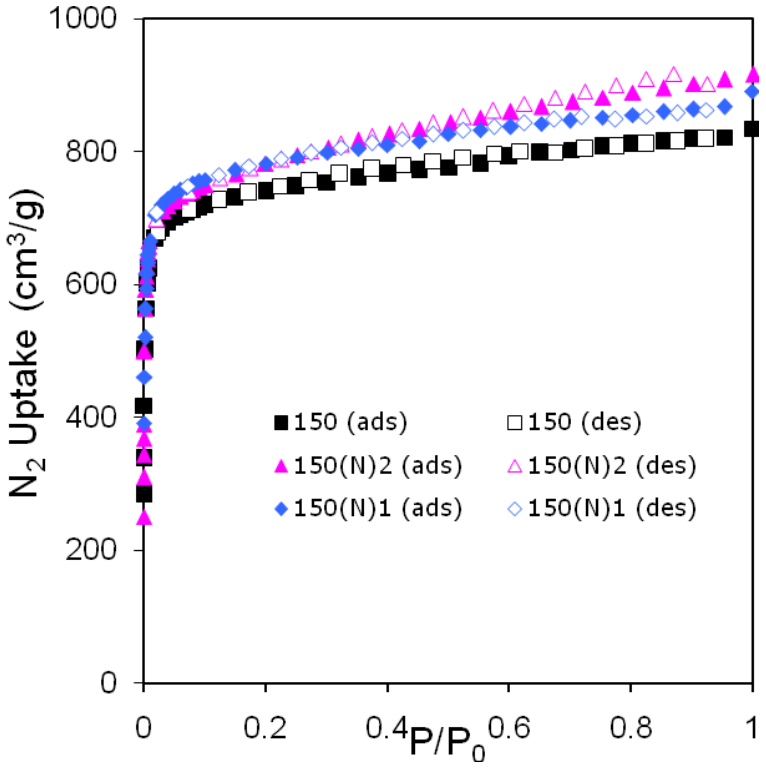


Figure S2. N_2 isotherms of UMCM-150 (black squares), UMCM-150$(N)_2$ (red triangles), and UMCM-150$(N)_1$ (blue diamonds). Solid symbols represent adsorption points and open symbols represent desorption points.

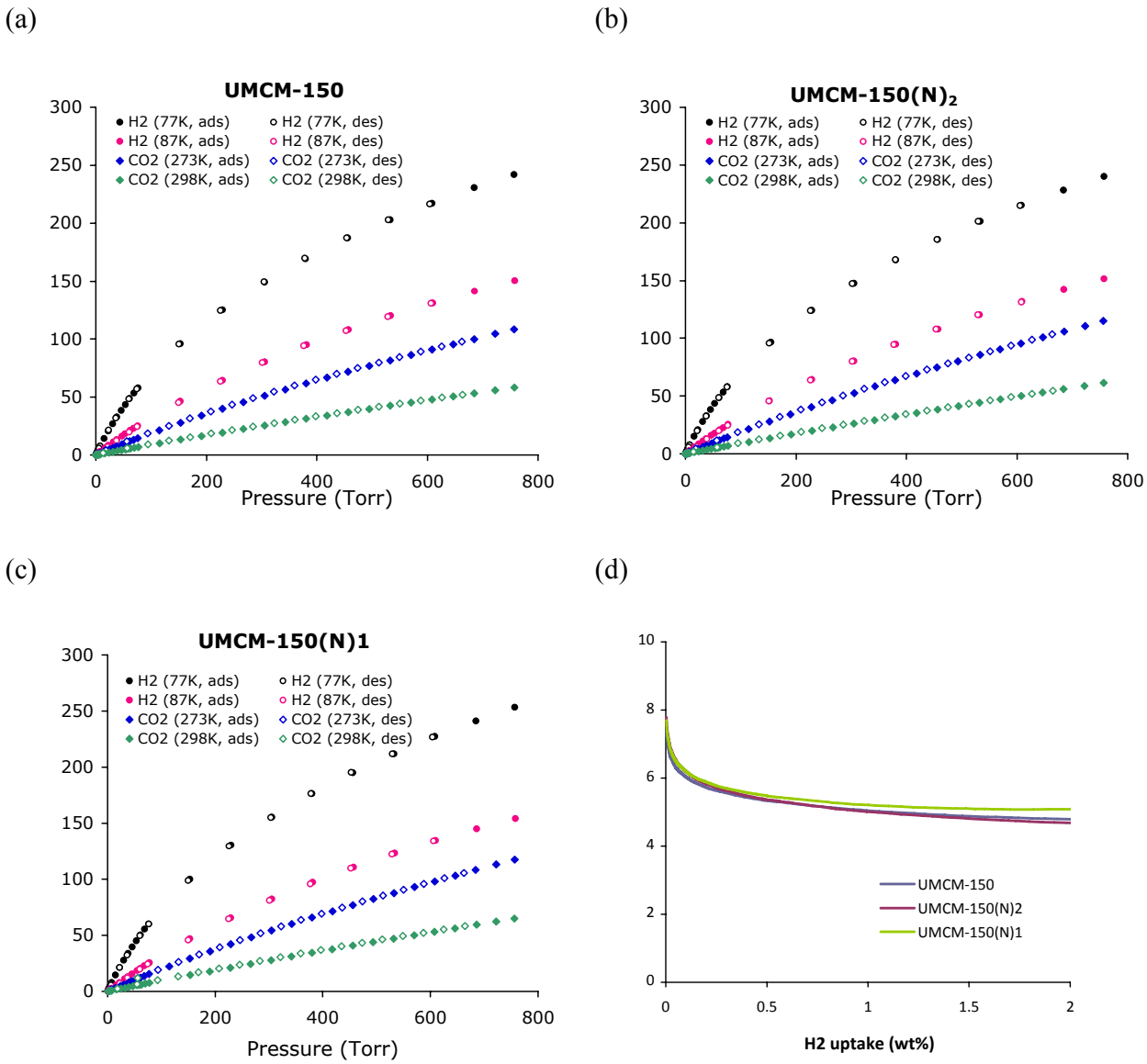


Figure S3. H_2 and CO_2 isotherms of (a) UMCM-150, (b) UMCM-150$(N)_2$, and (c) UMCM-150$(N)_1$ (c). Solid symbols represent adsorption points and open symbols represent desorption points. (d) Heat of adsorption of H_2 as a function of gravimetric uptake.

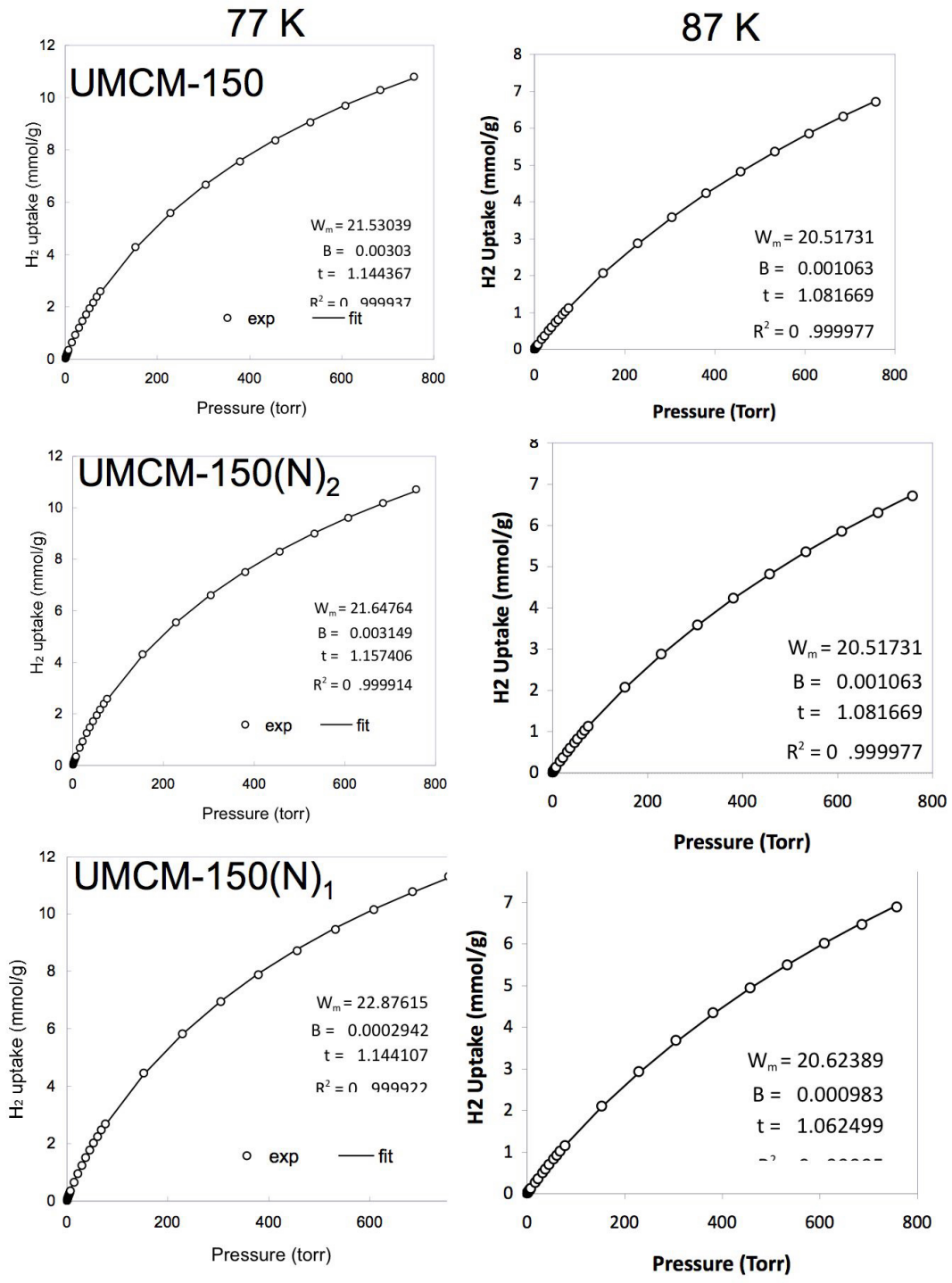
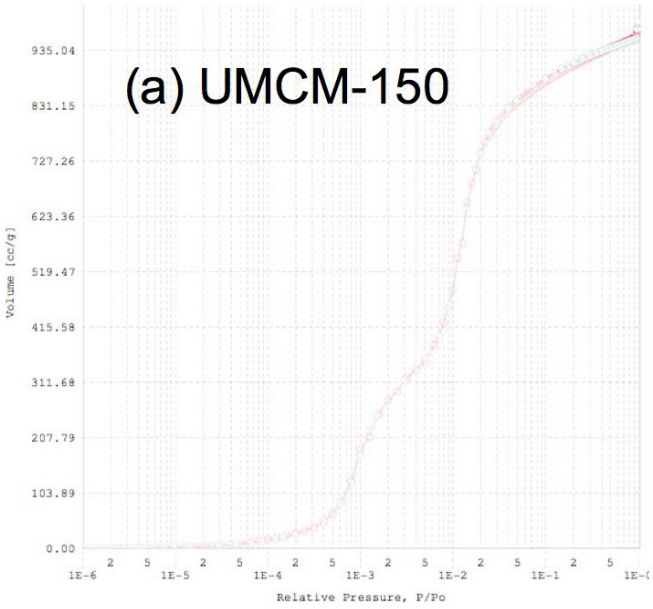
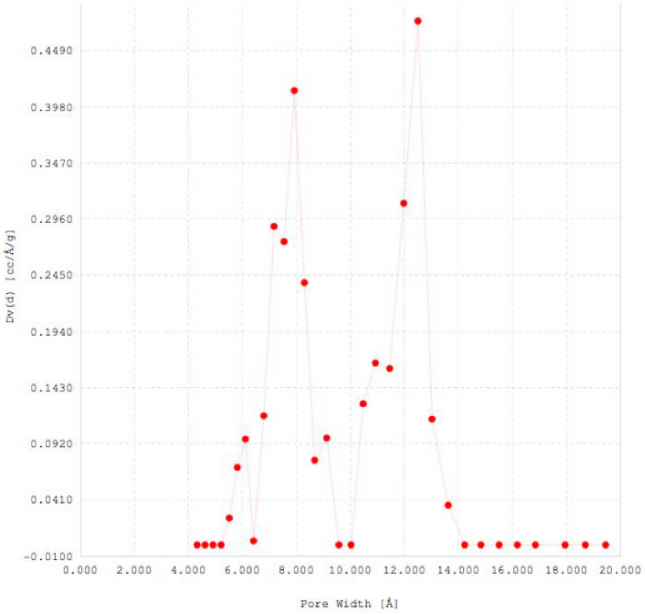
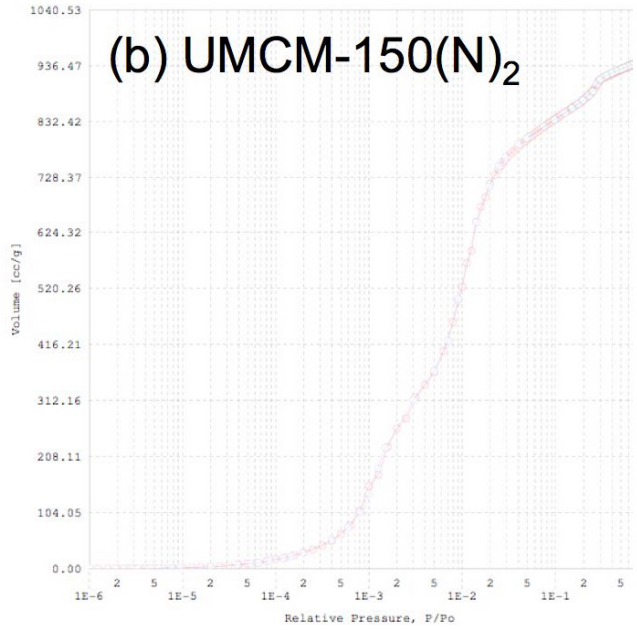
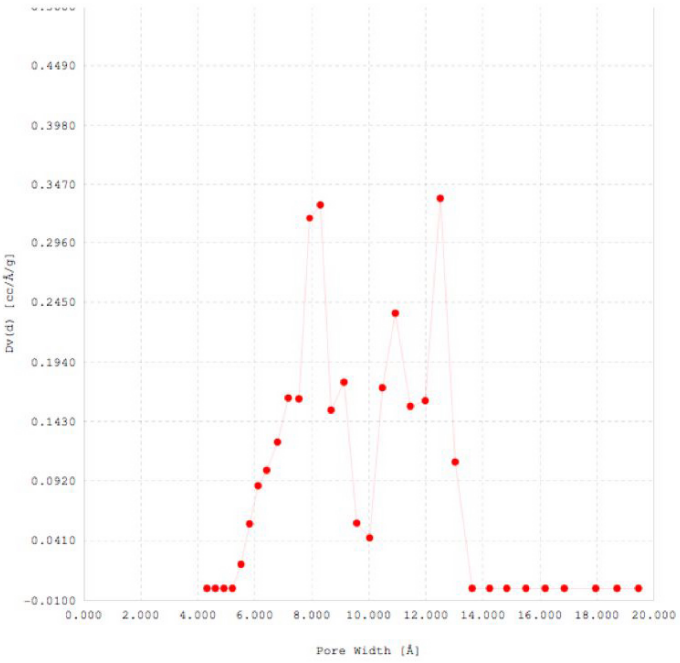


Figure S4. H2 gas adsorption branch at 77 (left column) and 87 K (right column). The solid line corresponds to a Langmuir-Freundlich fit to the experimental data.


(a) UMCM-150
935.04
831.15
727.26
623.36
519.47
415.58
311.68
207.79
103.89
0.00
Volume [cc/g]
1E-6
1E-5
1E-4
1E-3
1E-2
1E-1
Relative Pressure, P/Po


0.4490
0.3980
0.3470
0.2960
0.2450
0.1940
0.1430
0.0920
0.0410
-0.0100
Dv(d) [cc/Å/g]
0.000
2.000
4.000
6.000
8.000
10.000
12.000
14.000
16.000
18.000
20.000
Pore Width [Å]


(b) UMCM-150(N)2
1040.53
936.47
832.42
728.37
624.32
520.26
416.21
312.16
208.11
104.05
0.00
Volume [cc/g]
1E-6
1E-5
1E-4
1E-3
1E-2
1E-1
Relative Pressure, P/Po


0.4490
0.3980
0.3470
0.2960
0.2450
0.1940
0.1430
0.0920
0.0410
-0.0100
Dv(d) [cc/Å/g]
0.000
2.000
4.000
6.000
8.000
10.000
12.000
14.000
16.000
18.000
20.000
Pore Width [Å]

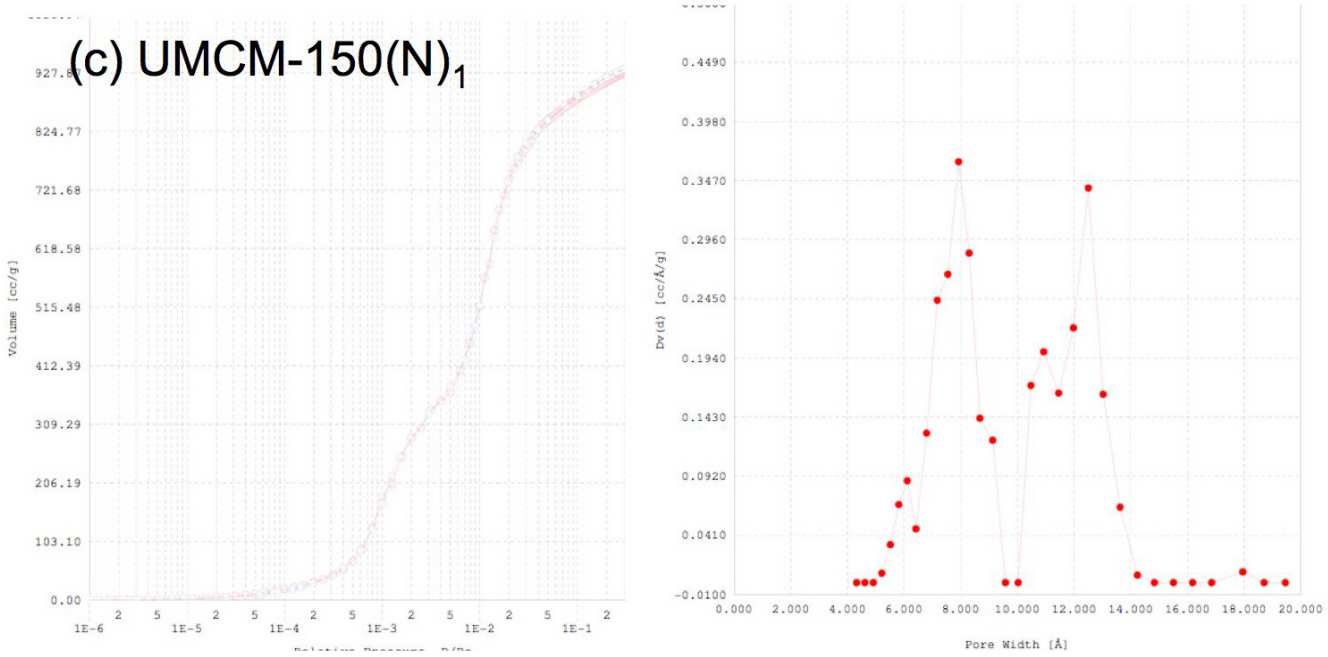


Figure S5. Calculated Ar isotherm (red curve) at 87 K for (a) UMCM-150, (b) UMCM-150(N)$_2$, and (c) UMCM-150(N)$_1$ using DFT/Monte-Carlo method overlaid on top of the experimental isotherm (left column). Pore size distribution (right column) from Ar adsorption at 87 K

IV. High pressure H_2 sorption measurements

High pressure volumetric measurements were performed at General Motors over the pressure range 0-70 bar using an automated Sievert's apparatus (PCT-Pro 2000 from Hy-Energy LLC). The sample holder was loaded with 224 mg of Be-BDC sample under an argon atmosphere in a glove box. The sample was degassed at room temperature for 12 h. All measurements were made with ultra high purity grade (99.999%) H_2 and He. Measurements were carried out at 77 K by submerging the sample holder in a liquid nitrogen bath, the level of which was maintained constant throughout each experiment. The volume of the sample holder was determined using helium at 298 K and H_2 at 298 K and 77 K. H_2 was used to determine the dead space volume correction for a non-porous inert insert of a known geometrical volume (typically steel or aluminum); this correction accounts for the change in effective sample volume observed when cooling the sample holder from room temperature to 77 K. Also, helium was used to determine the volume occupied by a sample in the sample holder at 298 K because of its negligibly small adsorption on solid surfaces. Our volumetric analysis can be viewed as a precise application of the real gas law taking into account deviation from non-ideal behavior found at high pressures and/or low temperatures. The non-ideal gas behavior is taken into account by determining the H_2 compressibility factor, Z, from National Institute of Standards and Technology (NIST) data.[10]

V. Equilibrium adsorption of organosulfur compounds.

The experiments were performed as previously described.[11]

VI. References

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