

Supporting Information

A porous coordination copolymer with over 5000 m²/g BET surface area

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I. Synthetic procedure for UMCM-2

$\text{H}_2\text{T}^2\text{DC}^1$ (0.0740 g, 0.325 mmol) and H_3BTB^2 (0.139 g, 0.317 mmol) were dissolved in 30 mL of *N,N*-diethylformamide and the solution was clarified by filtration. $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.500 g, 1.91 mmol) was added to the solution. The mixture was sonicated for 15 min and heated to 85 °C. After 3 days, crystals of a single phase were obtained. After cooling to room temperature the product was isolated by decanting the mother liquor and washing with DMF (3 × 30 mL). The resulting solid was then immersed in 30 mL CH_2Cl_2 for 2 days, during which time the CH_2Cl_2 was replaced three times. The yield of the reaction, determined from the weight of the solvent-free material, is 35% based on H_3BTB . Anal. Calcd for $\text{C}_{44}\text{H}_{24}\text{O}_{13}\text{S}_2\text{Zn}_4$: C, 48.7; H, 2.00. Found: C, 48.9; H, 1.73.

II. TGA of UMCM-2

Measurements were performed on a TA Q50 TGA apparatus.

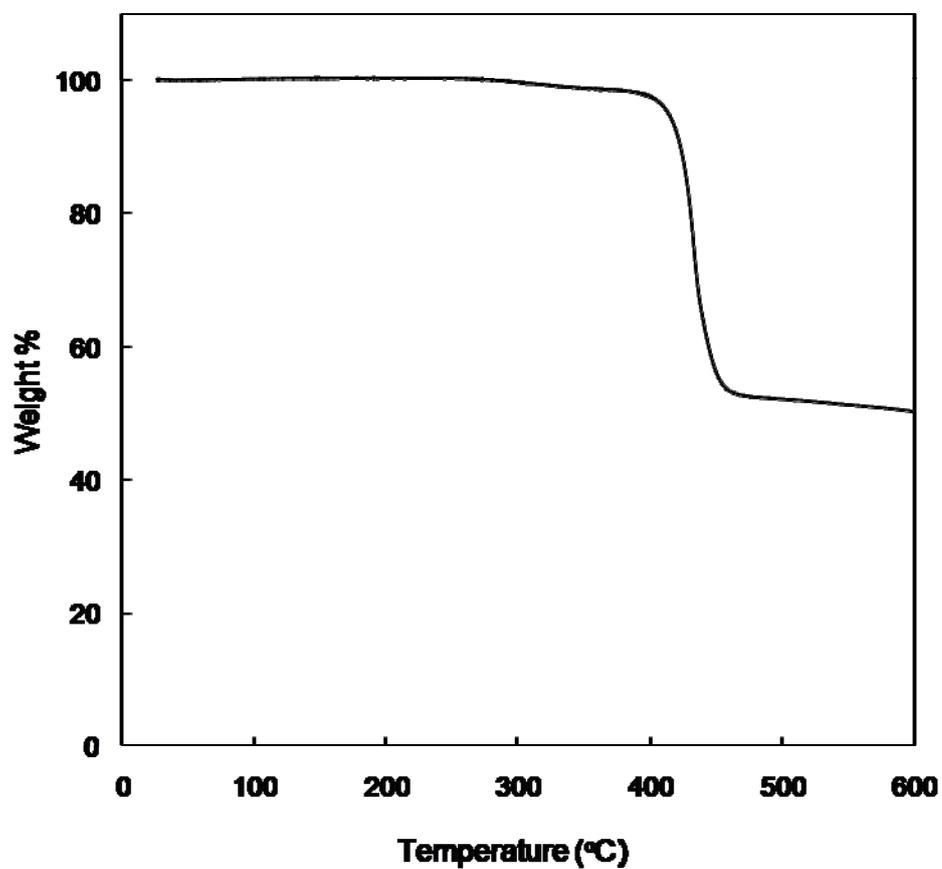


Figure S1. TGA trace of UMCM-2. Conditions: temperature ramp from 25 °C to 600 °C at 2 °C/min under flow of N₂ gas.

III. X-ray crystallography of UMCM-2

Crystals of UMCM-2 exchanged in CH_2Cl_2 were coated in paratone oil. A clear colorless platelet ($0.11 \times 0.09 \times 0.04 \text{ mm}^3$) was mounted on a MitiGen cryoloop and cooled under a nitrogen gas stream at 95(2) K. X-ray diffraction data was collected on a Rigaku R-Axis Spider diffractometer (460 mm \times 256 mm curved imaging plate detector, graphite monochromated Cu $K\alpha$ radiation at 2 kW power). A total of 273 oscillation images were collected using widths of 1.5° in ω . Data were collected using the d*TREK package in the CrystalClear software suite (v. 1.4, Rigaku 2007) to obtain overlapping ϕ and ω scans. Using the FS_PROCESS package in CrystalClear, the raw intensity data were then reduced to F^2 values with corrections for Lorentz, and polarization effects. Decay of the crystal during data collection was negligible. An empirical absorption correction was applied as implemented by FS_PROCESS. Based on the analysis of variance for the reflections used in refinement, it was determined that the structure was a merohedral twin. Application of the twin law for hexagonal crystal systems³ facilitated refinement of the structure. The structure was solved by direct methods and refined against all data using the CrystalStructure (v. 3.8.2) software package in the hexagonal space group $P6_3/m$ (#176) $Z = 6$ using direct methods.⁴ Due to severe disorder in the phenyl ring defined by carbon atoms C63-C68, these atoms were restrained to lie coplanar with the plane defined by O15-C71-O16. Hydrogen atoms were placed at calculated positions (C-H = 0.95 Å) using a riding model with isotropic thermal parameters 1.2 times that of the attached carbon atom. Thermal parameters for all non-hydrogen atoms were refined anisotropically. Attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Therefore the SQUEEZE routine of PLATON⁵ was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities.

Table 1. Crystal data and structure refinement for UMCM-2.

Empirical formula	$C_{132}H_{66}O_{39}S_8Zn_{12}$	
Formula weight	3317.35	
Temperature	95(2) K	
Wavelength	1.54180	
Crystal System	Hexagonal	
Space Group	$P6_3/m$	
Unit Cell Dimensions	$a = 42.1589(8) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 42.1589(8) \text{ \AA}$	$\beta = 90^\circ$
	$c = 52.5682(10) \text{ \AA}$	$\gamma = 120^\circ$
Volume	$80916(3) \text{ \AA}^3$	
Z	6	
Density (calculated)	0.401 g/cm^3	
Absorption coefficient	0.957 mm^{-1}	
F(000)	9756	
Crystal Size	$0.11 \times 0.090 \times 0.040 \text{ mm}^3$	
Theta range for data collection	6.50 to 50.4	
Index ranges	$-33 \leq h \leq 41, -42 \leq k \leq 41, -47 \leq l \leq 52$	
Reflections collected	329007	
Independent reflections	28533 [R(int) = 0.116]	
Completeness to theta = 66.58	98.7 %	
Absorption correction	Empirical from equivalents	
Max. and min. transmission	0.9627 and 0.9020	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	28533 / 4 / 872	
GOF on F^2	0.979 (1.08 before SQUEEZE)	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0773 (0.1068 before SQUEEZE), wR2 = 0.1899 (0.2888 before SQUEEZE)	
R indices (all data)	R1 = 0.1320 (0.1571 before SQUEEZE), wR2 = 0.2236 (0.3202 before SQUEEZE)	
Largest diff. peak and hole	0.520 and $-0.417 \text{ e}^-/\text{\AA}^3$	

IV. Gas sorption measurements

1. N₂ surface area

N₂ adsorption/desorption isotherms were measured volumetrically at 77 K in the range $1.00 \times 10^{-5} \leq P/P_0 \leq 1.00$ with an Autosorb-1C outfitted with the micropore option by Quantachrome Instruments (Boynton Beach, Florida USA), running version 1.2 of the ASWin software package. Ultra-high purity He (99.999%, for void volume determination) and N₂ (99.999%) were purchased from Cryogenic Gasses and used as received. UMCM-2 exchanged with CH₂Cl₂ was charged into a sample cell and dried under vacuum (< 0.1 millitorr) at room temperature. The resulting mass of dried material in the cell was ~10 mg

2. Pore size distribution from Ar sorption at 87 K

Argon sorption experiments were performed at 87 K in the range $1.00 \times 10^{-4} \leq P/P_0 \leq 1.00$ with ultra-high purity Ar (99.999%) purchased from Cryogenic Gasses. Pore size distributions were calculated using the Non-linear Density Functional Theory (NLDFT) zeolite/silica equilibrium transition kernel for Ar adsorption at 87 K based on a cylindrical pore model as implemented in version 1.2 of the ASWin software package.

3. H₂ sorption isotherms

For H₂ isotherms, 89 mg of activated material was used. Isothermic heats of adsorption were calculated by first fitting the adsorption branches of isotherms collected at 77 K and 87 K to the Langmuir-Freundlich equation.⁶ Application of a modified Clausius-Clapeyron equation using these fits then yielded the enthalpy of adsorption as a function of gas uptake.³

$$\frac{W}{W_m} = \frac{BP^{1/n}}{1 + BP^{1/n}}$$

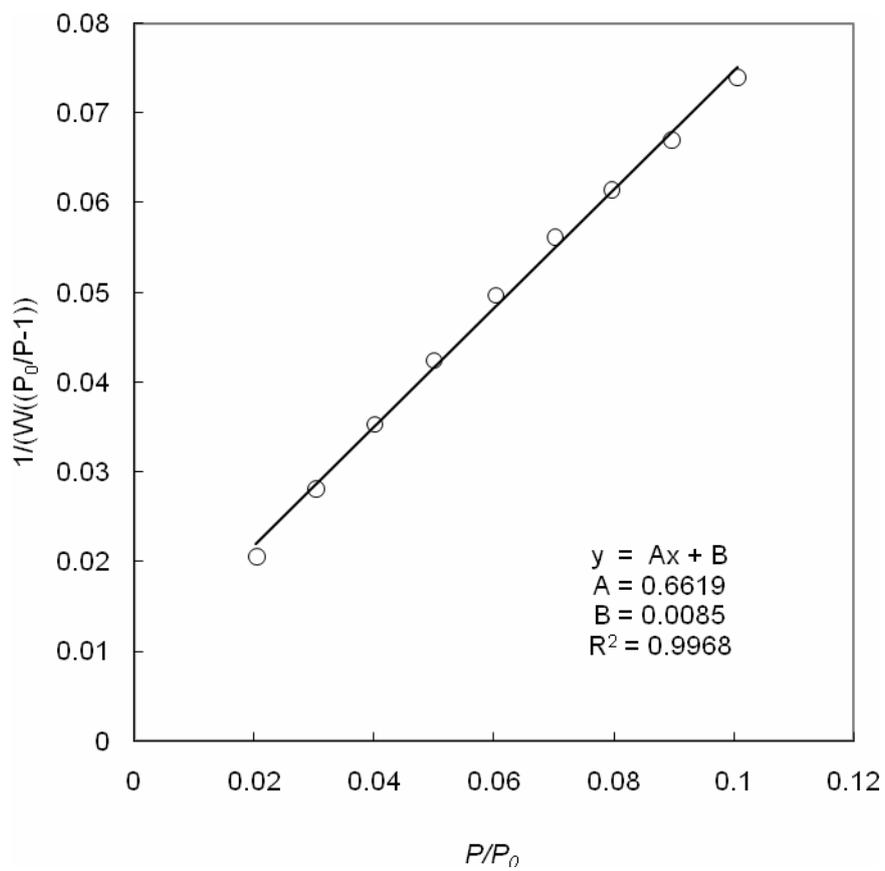


Figure S3. BET fit for the N_2 adsorption isotherm of UMCM-2.

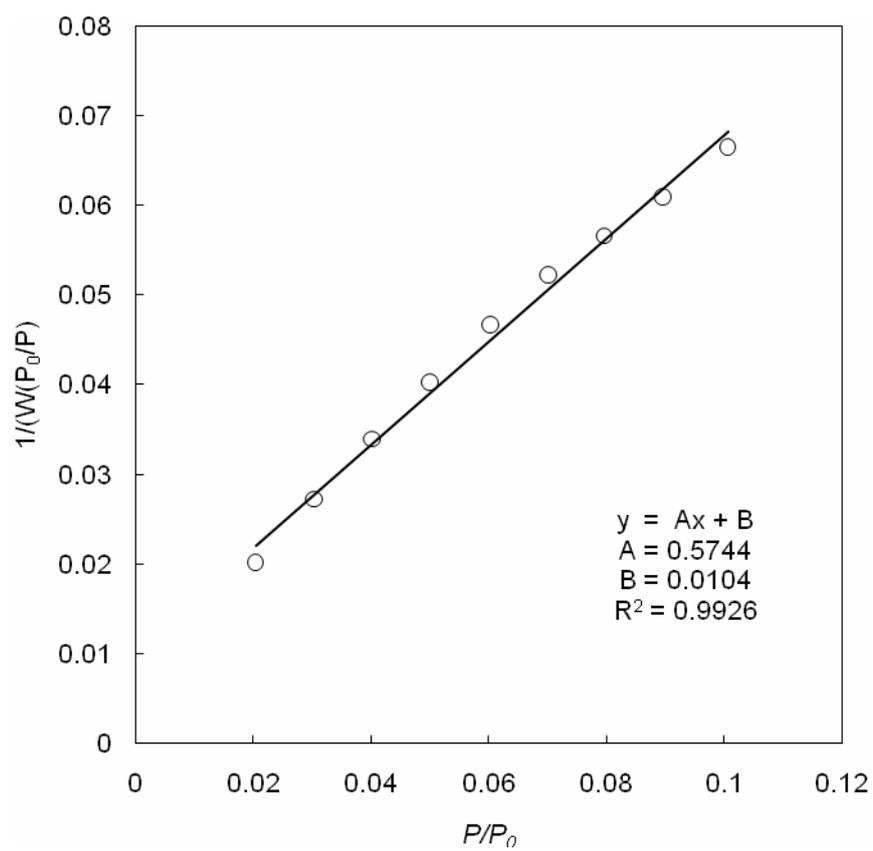


Figure S4. Langmuir fit for the N_2 adsorption isotherm of UMCM-2.

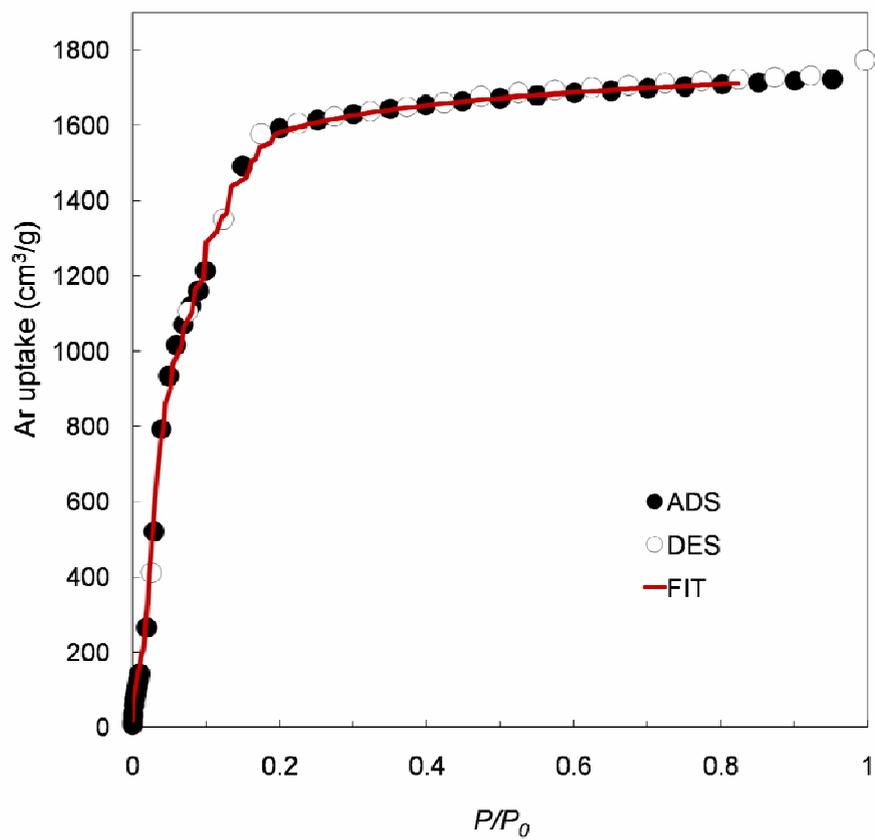


Figure S5. Ar adsorption/desorption isotherm at 87 K for UCMCM-2 and the corresponding NLDFT fit base on a cylindrical pore model.

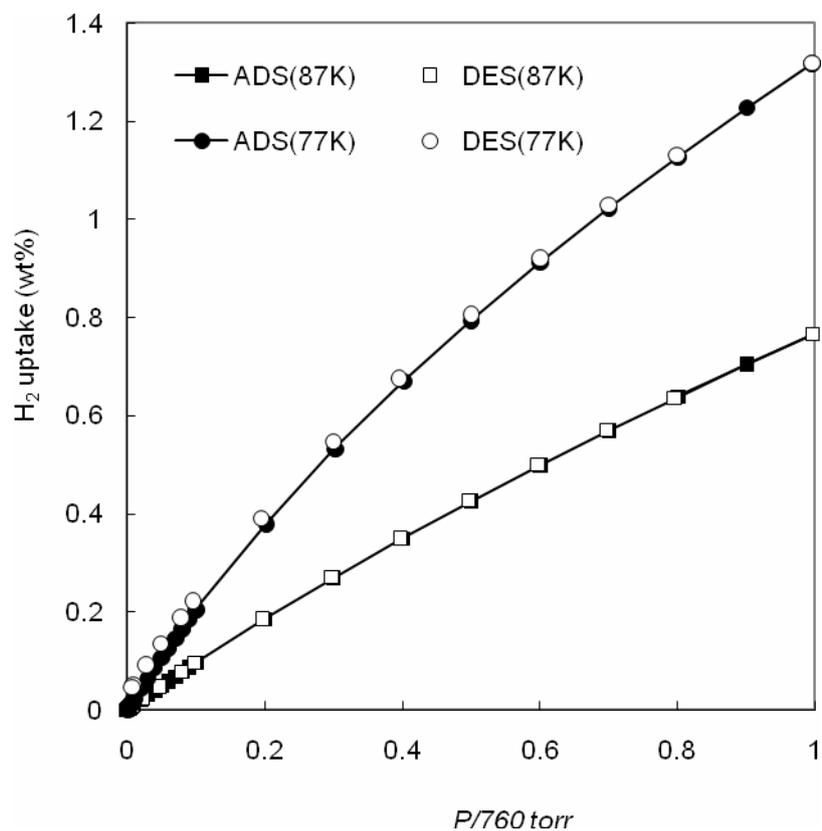


Figure S6. Hydrogen gas sorption isotherms for UCMCM-2 at 77 K and 87 K in the pressure range $0.4 \text{ torr} < P < 760 \text{ torr}$ (filled markers represent adsorption points; open markers represent desorption).

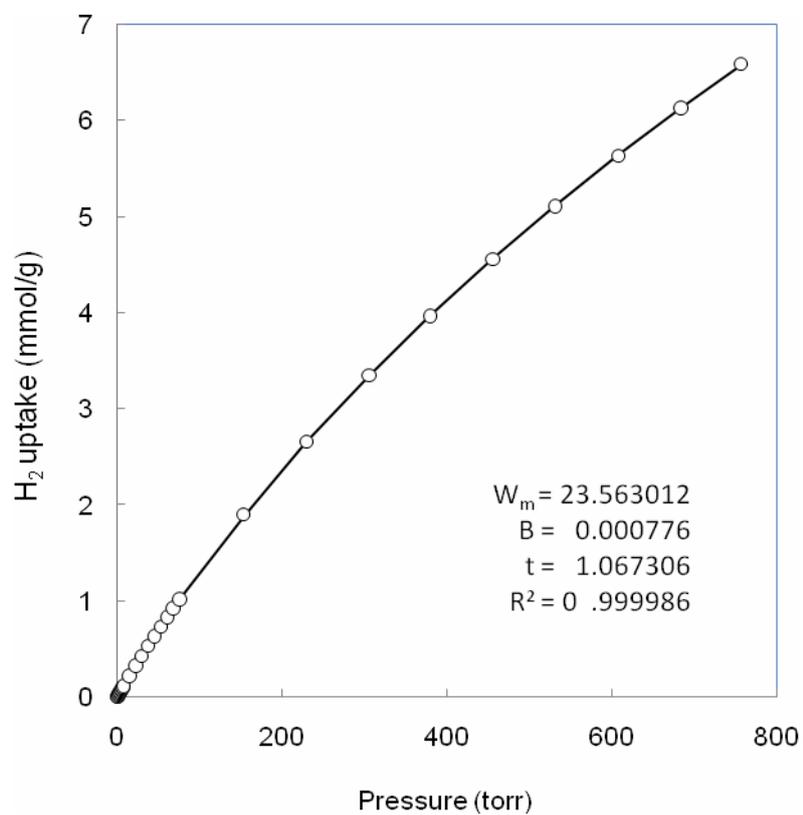


Figure S7. Hydrogen gas adsorption branch for UMCM-2 at 77 K. The solid line corresponds to a Langmuir-Freundlich fit to the experimental data.

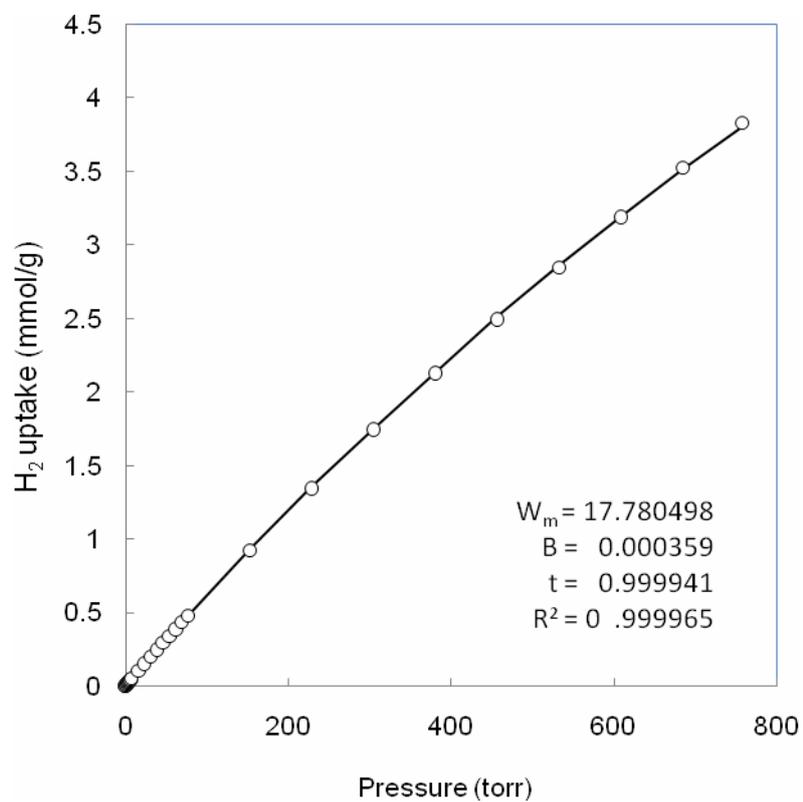


Figure S8. Hydrogen gas adsorption branch for UCMC-2 at 87 K. The solid line corresponds to a Langmuir-Freundlich fit to the experimental data.

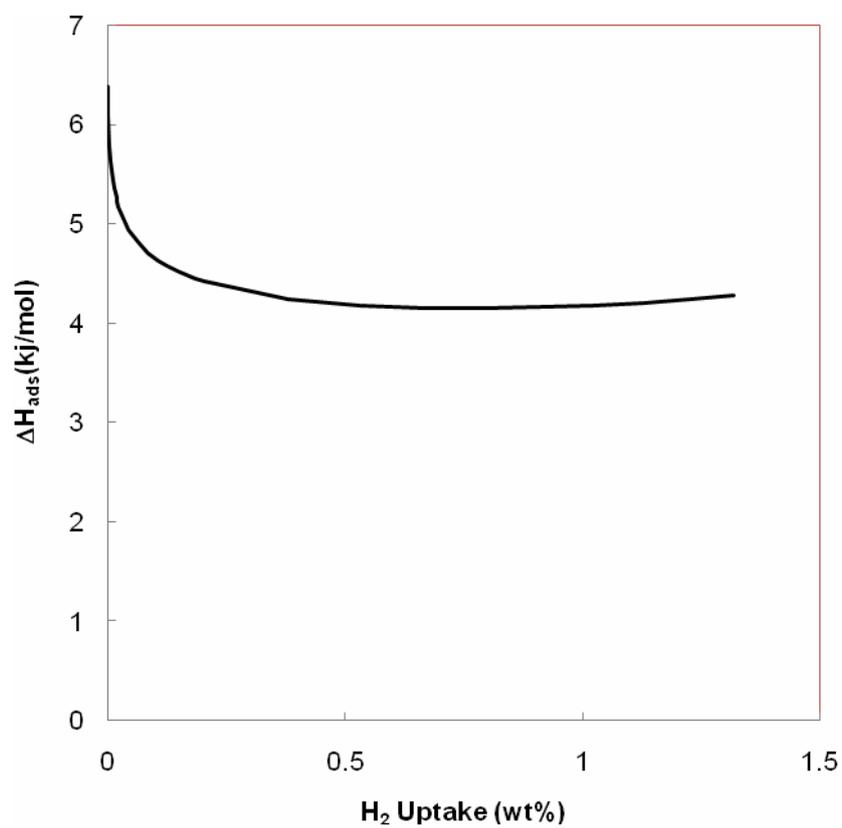


Figure S9. Heat of adsorption of H_2 for UMCM-2 as a function of gravimetric uptake.

High pressure H₂ gas sorption measurements. Equilibrium H₂ adsorption/desorption isotherms were measured using the static volumetric method as previously described. Activated UMCM-2 (0.682 g) was loaded into a 4.5 mL stainless steel cell inside an inert atmosphere (N₂) glove box. Prior to H₂ sorption the void volume of the cell was determined by using He gas at 23 °C. H₂ isotherms were measured at 77 K from 0 to 70 bar on the adsorption side and from 60 to 2 bar on the desorption side.

Table S1. H₂ Sorption Data for UMCM-2 at 77 K.

Pressure (bar)	Vol. at STP(cm ³ /g)	Excess H ₂ Adsorbed ^a (gravimetric basis,mg/g)	Excess H ₂ Adsorbed ^b (volumetric basis, g/L)
0.31	60.37	5.43	2.17
1.51	190.51	17.14	6.85
1.93	224.67	20.21	8.08
3.31	314.56	28.29	11.32
3.85	342.07	30.77	12.31
4.66	380.23	34.20	13.68
6.50	451.41	40.60	16.24
8.64	514.36	46.26	18.51
11.22	571.98	51.45	20.58
14.52	627.07	56.40	22.56
19.40	682.32	61.37	24.55
25.42	724.17	65.13	26.05
34.43	755.85	67.98	27.19
46.08	763.41	68.66	27.47
58.34	750.21	67.48	26.99
69.60	725.68	65.27	26.11
72.28	719.31	64.70	25.88
64.45	739.02	66.47	26.59
51.73	760.64	68.41	27.37
38.82	764.78	68.79	27.51
26.75	734.09	66.03	26.41
19.11	682.27	61.37	24.55
14.20	625.26	56.24	22.50
10.53	561.25	50.48	20.19
7.62	489.15	44.00	17.60

^amg H₂ per g adsorbent. ^bBased on empty crystal density of 0.4 g/cm³ which reflects the maximum theoretical excess H₂ adsorption a single crystal with a volume of 1 L could adsorb.

V. Thermal stability studies of UMCM-2

The following experiments were performed in order to verify the thermal stability of UMCM-2.

1. Powder X-Ray Diffraction. A 0.5 mg of dry sample was heated at a constant rate of 5 °C/min from 25 °C to 300 °C and cooled at a constant rate 10 °C/min to 30 °C under N₂ flow. The resulting UMCM-2 sample was then coated on a Nylon loop using mineral oil and mounted on a Rigaku R-Axis Spider diffractometer. Images were collected in transmission mode with χ set at 45°, ϕ rotating at 10°/min, and ω oscillating between 10° and 100° to minimize the effects of preferred orientation. Integration of the resulting image was performed in the AreaMax (2.0) software package with a step size of 0.1° in 2θ .

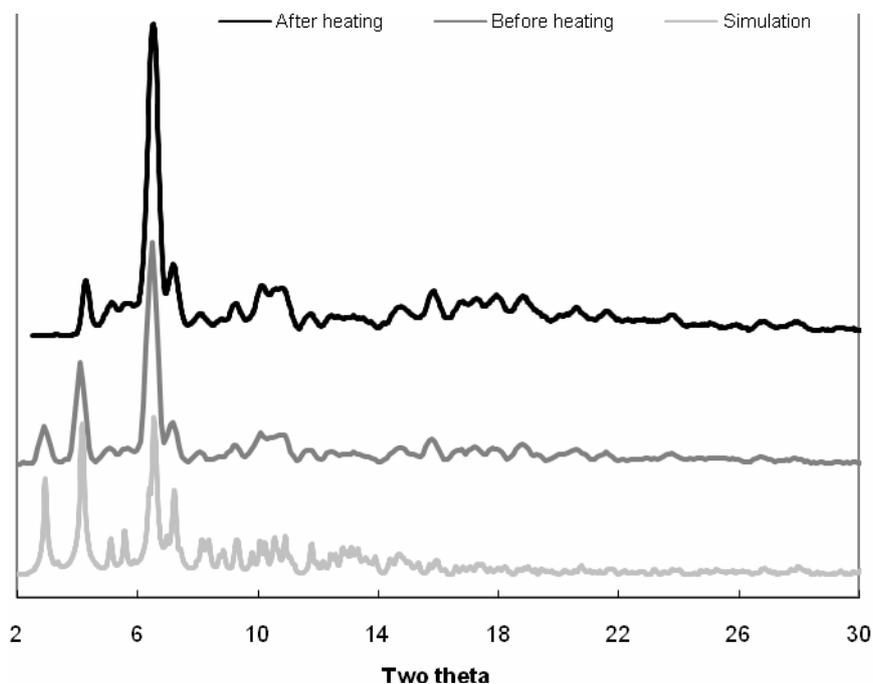


Figure S10. Powder XRD pattern of UMCM-2 before and after heating at 300 °C.

2. N₂ sorption isotherms. A sample of UMCM-2 dried under vacuum (10 mg) was heated at a constant rate of 5 °C/min from 25 °C to 300 °C then held at 300 °C for 3 hr. The sample was then cooled to room temperature and an N₂ isotherm was collected. After the measurement, the same sample was reheated to 300 °C and held at 300 °C for another 3 hr. After cooling, a N₂ isotherm was recollected. The described process above was repeated two more times.

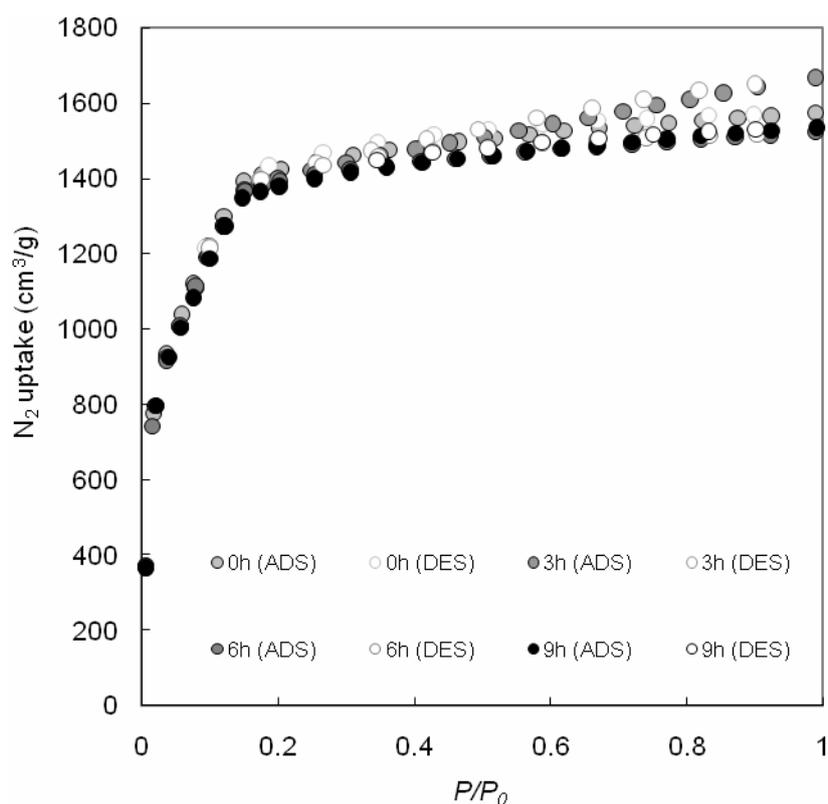


Figure S11. N₂ sorption isotherm of UMCM-2 after multiple heating and cooling cycles at 300 °C.

VI. Disclaimer

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