Electronic Supplementary Information

Exceptional surface area from coordination copolymers derived from two linear linkers of differing lengths

Kyoungmoo Koh, Jacob D. Van Oosterhout, Saikat Roy, Antek G. Wong-Foy, Adam J. Matzger* *Department of Chemistry, Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109-1055, USA*

Contents

*Author to whom correspondence may be addressed: matzger@umich.edu

I. Prediction of possible structures by tiling different vertex-edge combinations derived from a single octahedron

Model framework structures were created by tiling the repeating units derived from all possible arrangements of short and long linear linkers around an octahedron. The coordination modes and their structures were optimized using the Forcite Plus module in Materials Studio 5.5 from Accelrys. Note: the figure below depicts the actual structures used in the calculations as an assembly of octahedra and lines for clarity.

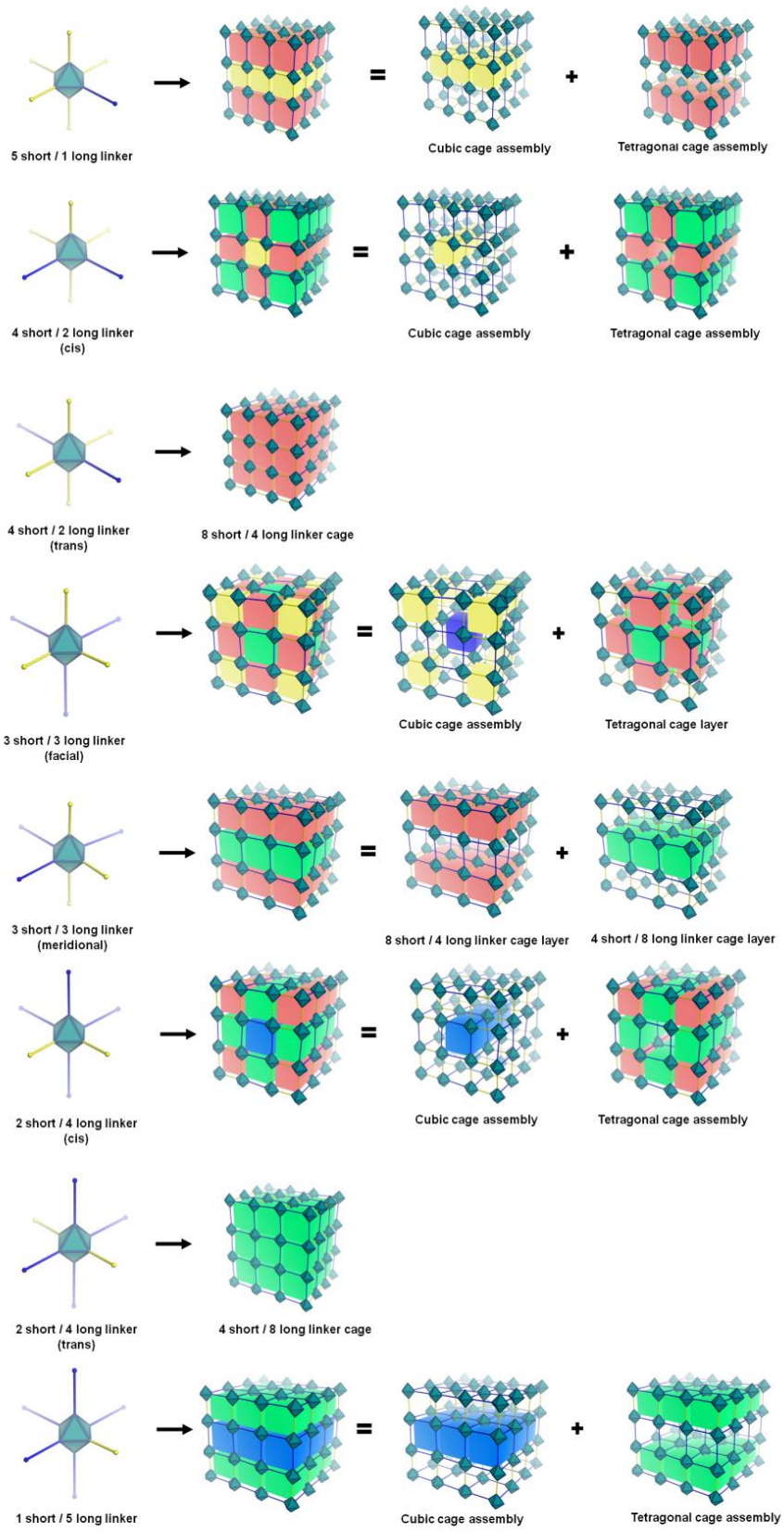

Figure S1. Structures derived from various coordination modes.

II. Structural modeling and X-ray diffraction analyses

Powder X-ray diffraction was performed on a Rigaku R-Axis Spider diffractometer equipped with an image plate detector and Cu Kα radiation operating in transmission mode. The sample was set at 45° in χ, rotated in φ and oscillated in ω to minimize preferred orientation.

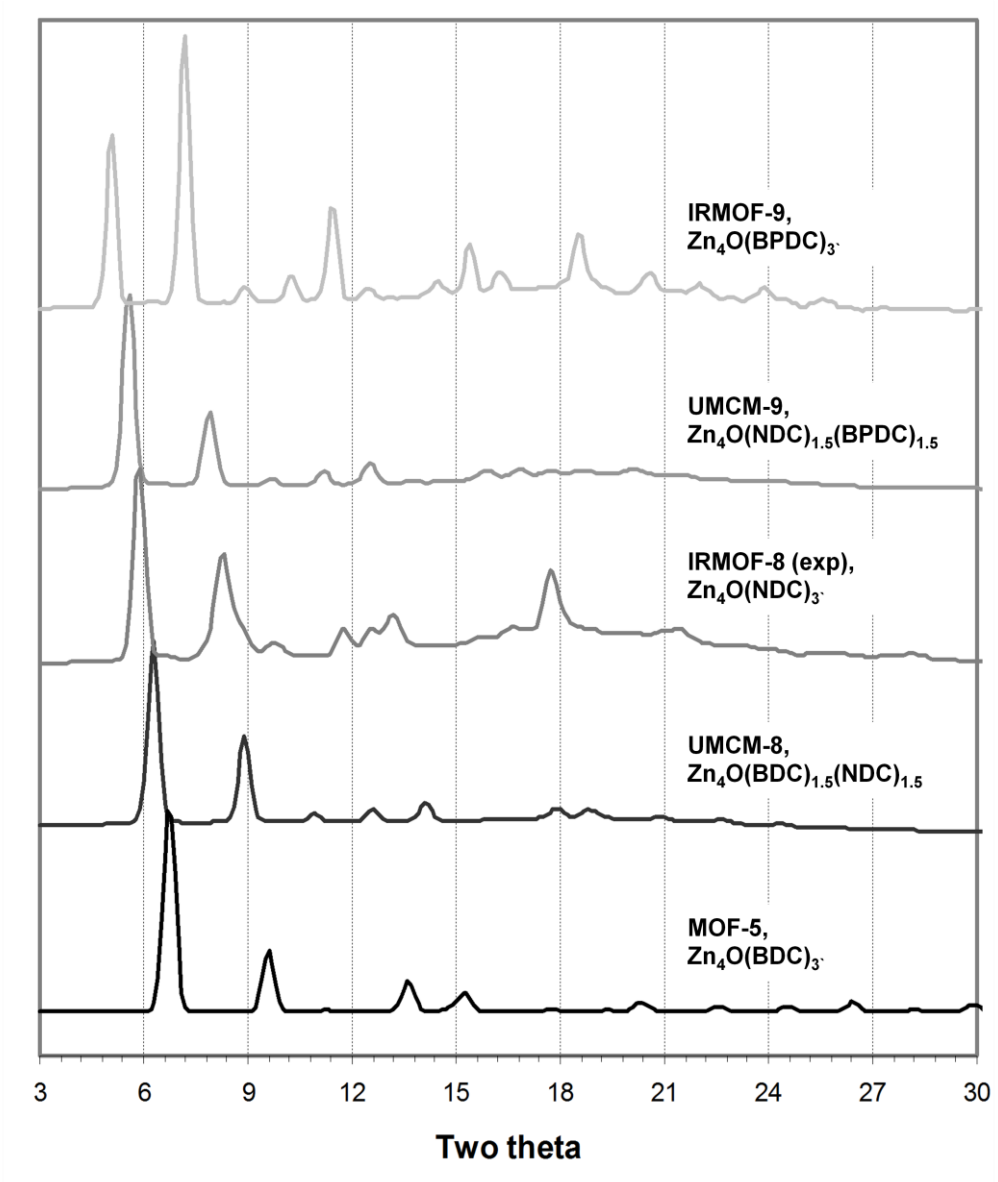

Figure S2. PXRD patterns of IRMOF-9, UMCM-9, IRMOF-8, UMCM-8, and MOF-5 (From top to bottom).

All models were constructed in the cubic crystal system (space group 195) using Materials Studio 5.5 from Accelrys. A geometry optimization was performed for the assembly of building units, applying the Forcite module to obtain the cell parameters. The simulated powder patterns were generated from the model structures and refined against the experimental data using a full pattern Pawley refinement. Based on the results of the refinements, the structures of the products were confirmed.

Table S1. Pawley refinement results of UMCM-8 and UMCM-9

Sample name	Rwp	Rwp (w/o bck)	Rp
UMCM-8	3.68 %	3.56 %	7.11 %
UMCM-9	2.92 %	2.73 %	7.45 %

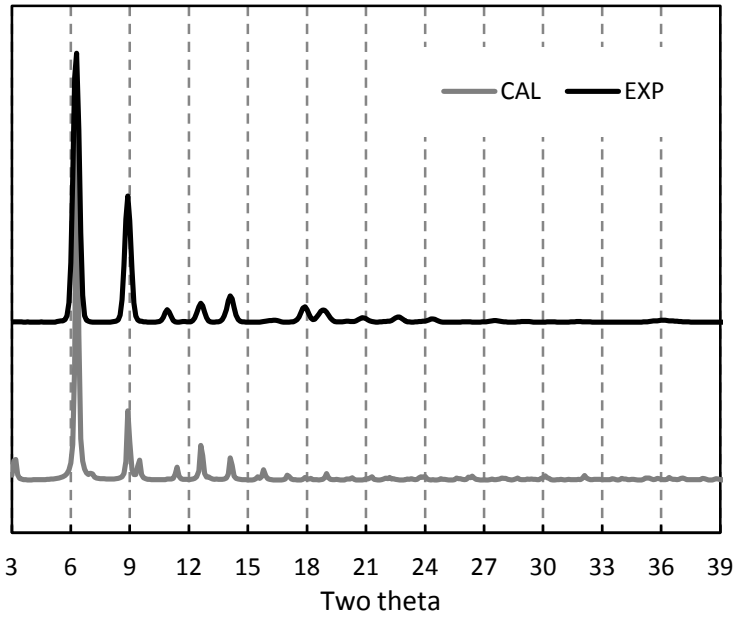

Figure S3. Powder XRD pattern of bulk UMCM-8 (black) and simulated pattern (grey).

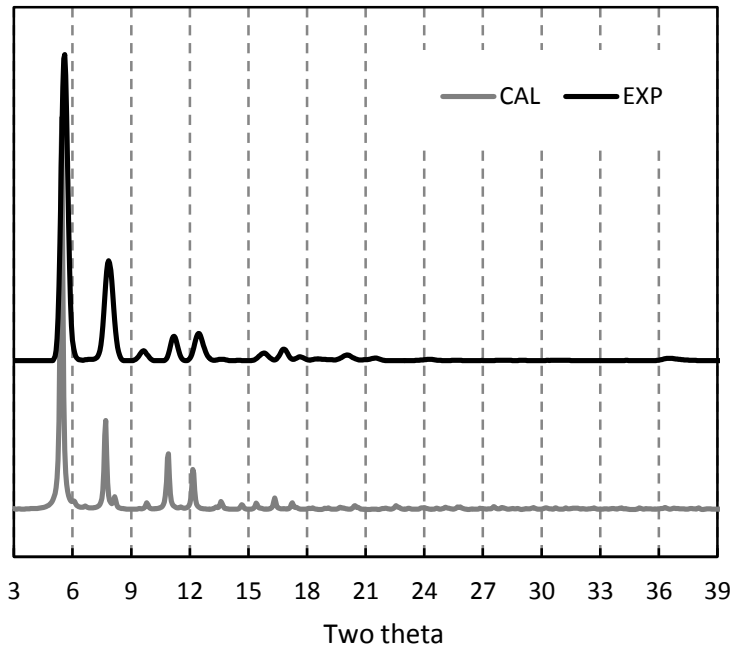

Figure S4. Powder XRD pattern of bulk UMCM-9 (black) and simulated pattern (grey).

Table S2. Refined unit cell parameters and fractional atomic coordinates for UMCM-8

Name	UMCM-8						
Space group : *P23*, *a* (Å)= 28.0							
Atom name	*x*	*y*	*z*	Atom name	*x*	*y*	*z*
Zn1	0.18899	0.18899	0.18899	H34	0.76823	0.83598	0.57389
Zn2	0.18921	0.26414	0.26793	H35	0.78162	0.67295	0.50501
O3	0.20001	0.12473	0.19913	H36	0.77843	0.68361	0.59186
O4	0.19696	0.32837	0.25746	H37	0.71384	0.9533	0.82494
O5	0.20126	0.2527	0.33202	H38	0.71504	1.0409	0.82652
O6	0.12517	0.25282	0.25836	H39	0.82534	1.0420	0.71968
C7	0.22348	0.35288	0.22953	H40	0.82446	0.95446	0.71722
C8	0.22937	0.10234	0.22601	H41	0.70667	0.57729	0.21948
O9	0.25917	0.87104	0.20226	H42	0.85816	0.59518	0.23924
O10	0.25895	0.79604	0.1283	H43	0.86921	0.5084	0.23777
O11	0.33462	0.79703	0.20355	O44	0.77247	0.77247	0.22753
O12	0.33292	0.74435	0.26268				
C13	0.23143	0.8943	0.2302				
Zn14	0.27000	0.80681	0.19236				
Zn15	0.26931	0.73069	0.26931				
C16	0.35642	0.77141	0.23449				
C17	0.77363	0.76066	0.58989				
C18	0.77138	0.80047	0.55882				
C19	0.77132	0.79435	0.50829				
C20	0.77579	0.74815	0.48829				
C21	0.7786	0.70877	0.51933				
C22	0.77675	0.71492	0.56919				
C23	0.76904	0.9456	0.77087				
C24	0.73853	0.97178	0.8016				
C25	0.73914	1.02228	0.80267				
C26	0.77041	1.04857	0.7734				
C27	0.80093	1.0229	0.74282				
C28	0.80024	0.97242	0.74145				
O29	0.23111	0.76889	0.23111				
C30	0.74211	0.56224	0.22338				
C31	0.78158	0.59334	0.22914				
C32	0.82707	0.57258	0.23484				
C33	0.83348	0.52272	0.23389				

Table S3. Refined unit cell parameters and fractional atomic coordinates for UMCM-9

Name	UMCM-9						
Space group : *P23*, *a* (Å)= 32.5							
Atom name	*x*	*y*	*z*	Atom name	*x*	*y*	*z*
Zn1	0.19958	0.19207	0.26375	C34	1.06549	1.28158	0.76455
O2	0.21217	0.13746	0.25301	C35	1.08396	1.24245	0.76367
O3	0.20039	0.32047	0.207	C36	1.05781	1.20765	0.76399
O4	0.25206	0.24871	0.31211	H37	0.26132	0.11866	0.24618
O5	0.14231	0.19589	0.25535	H38	0.26255	0.87287	0.21315
C6	0.22668	0.33687	0.23114	H39	0.40212	1.30918	0.77594
C7	0.23333	0.1195	0.22506	H40	0.47979	1.30573	0.77511
O8	0.21499	0.84953	0.21602	H41	0.47342	1.17344	0.74767
O9	0.26364	0.7311	0.15005	H42	0.39569	1.17739	0.74621
O10	0.32365	0.77886	0.25645	H43	0.53866	1.30084	0.7407
O11	0.32935	0.72755	0.21453	H44	0.61633	1.29668	0.74456
C12	0.23943	0.86991	0.23936	H45	0.60686	1.17053	0.79246
Zn13	0.27232	0.72432	0.20677	H46	0.52945	1.17388	0.78642
C14	0.34719	0.75449	0.23677	H47	0.9394	1.28868	0.77051
C15	0.39352	1.24333	0.76112	H48	1.00194	1.14563	0.76158
C16	0.41762	1.27845	0.76917	H49	0.92446	1.15451	0.76162
C17	0.46105	1.27669	0.76911	H50	1.00882	1.31857	0.76783
C18	0.48208	1.23954	0.76172	H51	1.0862	1.30987	0.76364
C19	0.45793	1.20431	0.75379	H52	1.07156	1.17538	0.76342
C20	0.41441	1.20622	0.75319	Zn53	0.20631	0.79369	0.20631
C21	0.52858	1.2374	0.76343	O54	0.23965	0.76035	0.23965
C22	0.55348	1.27115	0.75208	O55	0.77061	0.77061	0.22939
C23	0.59695	1.26916	0.75445	Zn56	0.26265	0.73735	0.73735
C24	0.61697	1.23356	0.76892				
C25	0.59209	1.19998	0.78041				
C26	0.54879	1.20172	0.77742				
C27	0.92679	1.22176	0.7663				
C28	0.95305	1.25645	0.76807				
C29	0.9965	1.25187	0.76685				
C30	1.01435	1.21223	0.76503				
C31	0.98832	1.17791	0.76328				
C32	0.94525	1.18269	0.76359				
C33	1.02247	1.28628	0.76651				

III. ^{1}H NMR spectrum of decomposed UMCM-8 and 9

The composition of linkers in MCPs was determined by ^{1}H NMR spectroscopy after the fully dried products were digested in 1 M NaOH in D_2O solution.

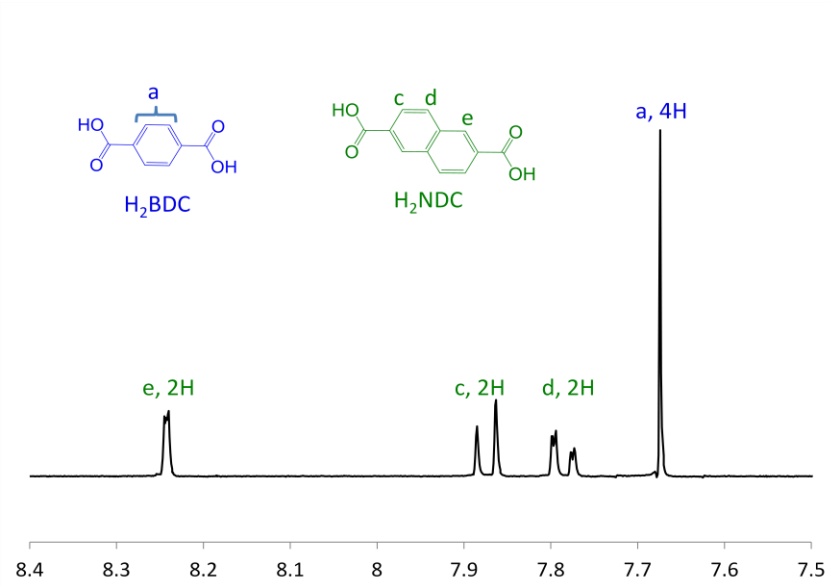

Figure S5. ^{1}H spectrum of UMCM-8 after digesting in 4 wt% NaOD solution. From integration, the empirical formula is calculated as $Zn_4O(BDC)_{1.35}(NDC)_{1.65}$.

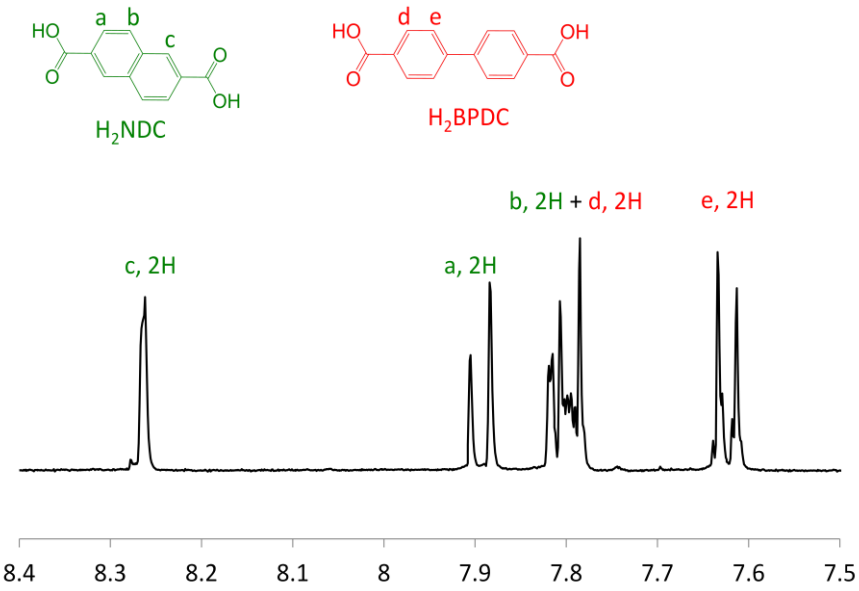

Figure S6. ^{1}H spectrum of UMCM-9 after digesting in 4 wt% NaOD solution. From integration, the empirical formula calculated as $Zn_4O(NDC)_{1.32}(BPDC)_{1.68}$.

IV. Gas sorption measurements

1. N_2 sorption measurement

N_2 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 N_2 (99.999%) were purchased from Cryogenic Gasses and used as received. Samples were stored in CH_2Cl_2. UMCM-8 was dried under vacuum (< 0.1 millitorr) at room temperature, and the solvent in UMCM-9 was removed by flowing supercritical CO_2. The resulting mass of dried material in the cell was ~30 mg.

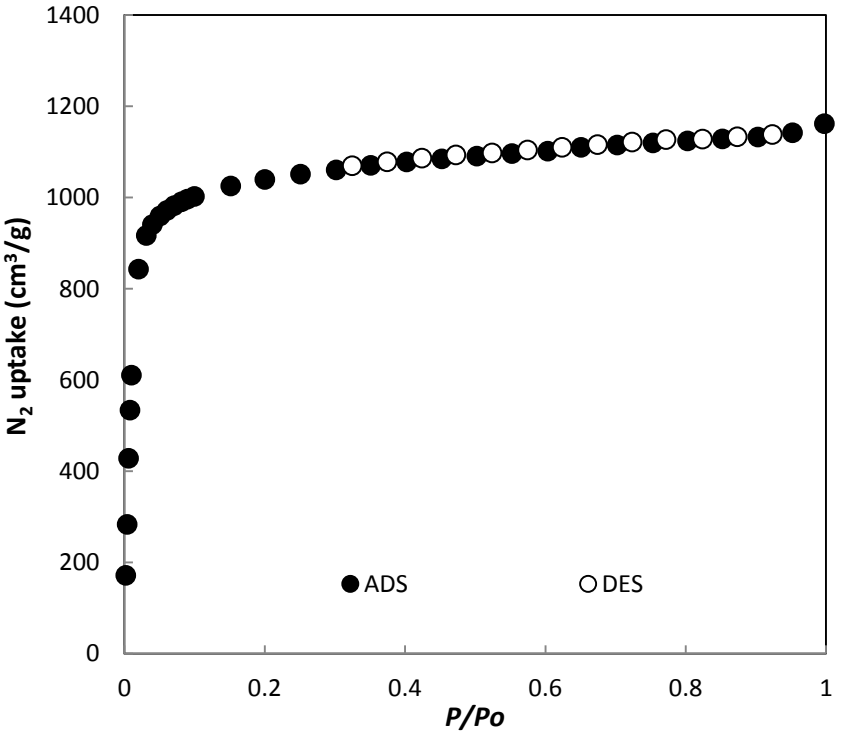

Figure S7. N_2 sorption isotherm at 77 K for UMCM-8.

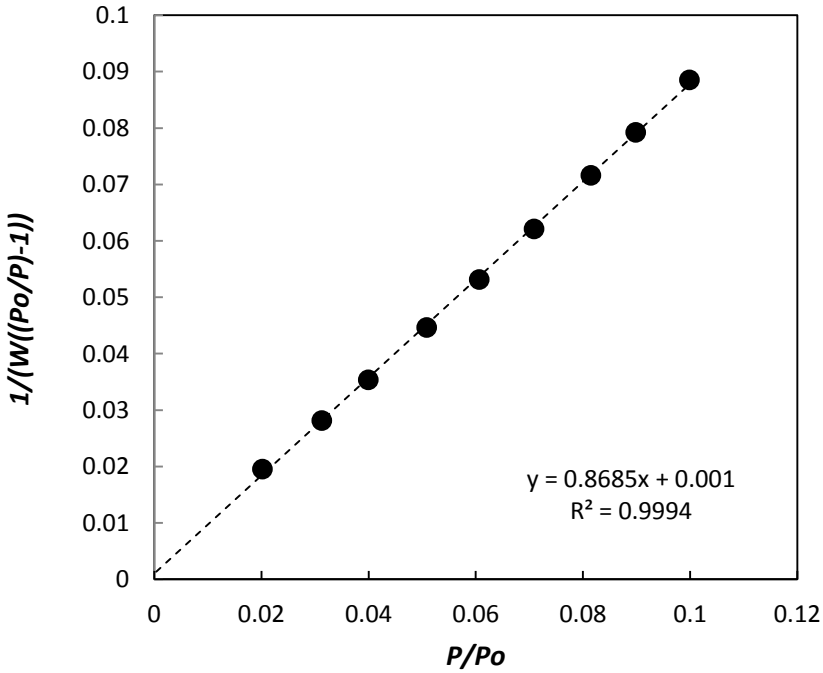

Figure S8. BET fit for the N_2 adsorption isotherm of UMCM-8 (BET SA = 4005 m^2/g). The relative pressure range ($0.02 \leq P/P_o \leq 0.1$) for calculating the surface area satisfies the criteria for applying BET theory.[1]

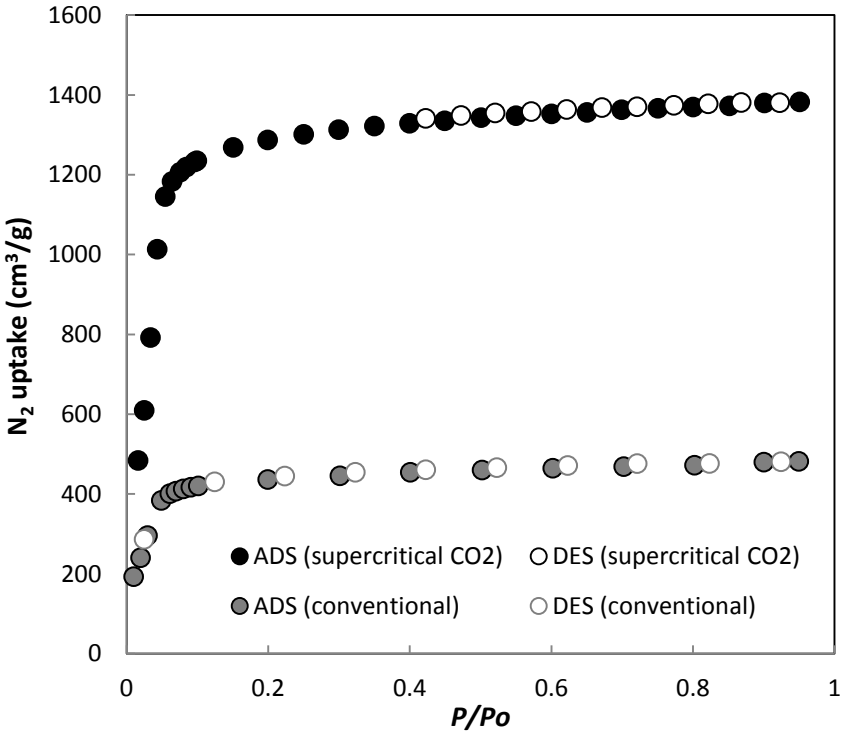

Figure S9. N_2 sorption isotherm at 77 K for UMCM-9 activated by conventional evacuation (grey) and with a supercritical CO_2 flow system (black).

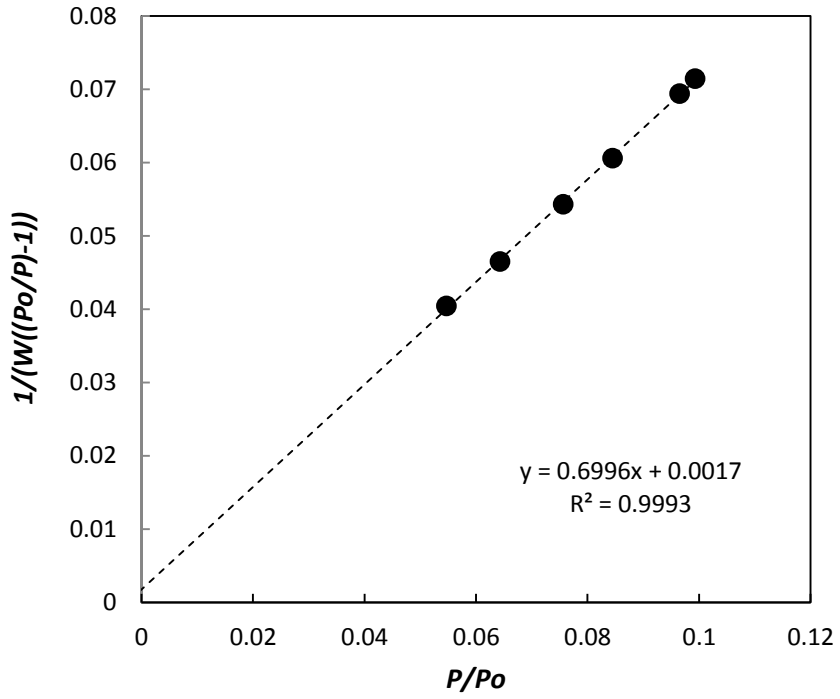

Figure S10. BET fit for the N_2 adsorption isotherm of UMCM-9 (BET SA = 4969 m^2/g). The relative pressure range ($0.05 \leq P/P_o \leq 0.1$) for calculating the surface area satisfies the criteria for applying BET theory.[1]

V. Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

---

1. Walton, K. S. & Snurr, R. Q., Applicability of the BET method for determining surface areas of microporous metal−organic frameworks, *J. Am. Chem. Soc.* **129**, 8552 (2007).