Submitted to *J. Am. Chem. Soc.*

Supporting information

Coordination Copolymerization mediated by $Zn_4O(CO_2R)_6$ Metal Clusters: a balancing act between statistics and geometry

Kyoungmoo Koh, Antek G. Wong-Foy, and Adam J. Matzger*

Department of Chemistry, Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109-1055, USA

Contents

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

I. Thermal gravimetric analysis (TGA)

Measurements were performed on a TA Q50 TGA apparatus. Temperature was ramped from 25 °C to 600 °C at 2 °C/min under flow of N_2 gas.

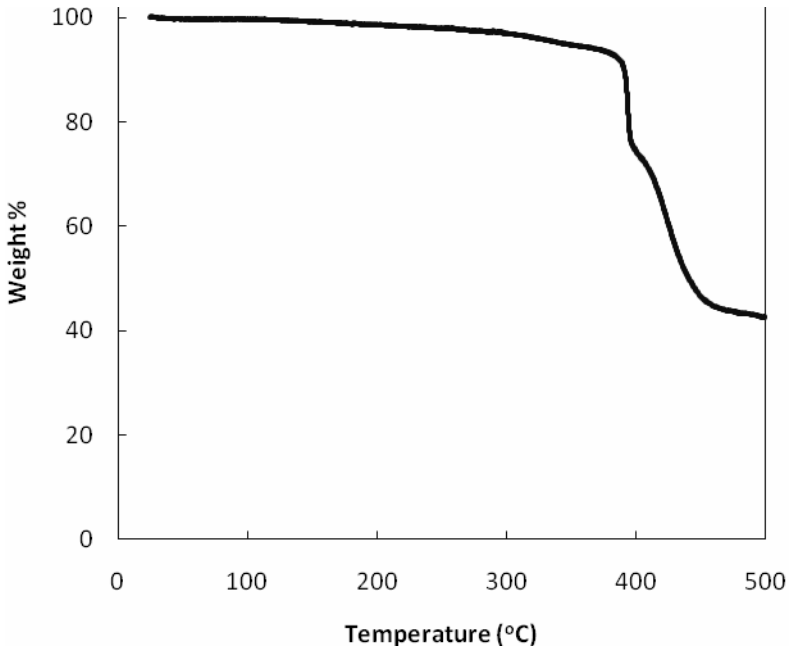

Figure S1. TGA trace of UMCM-3.

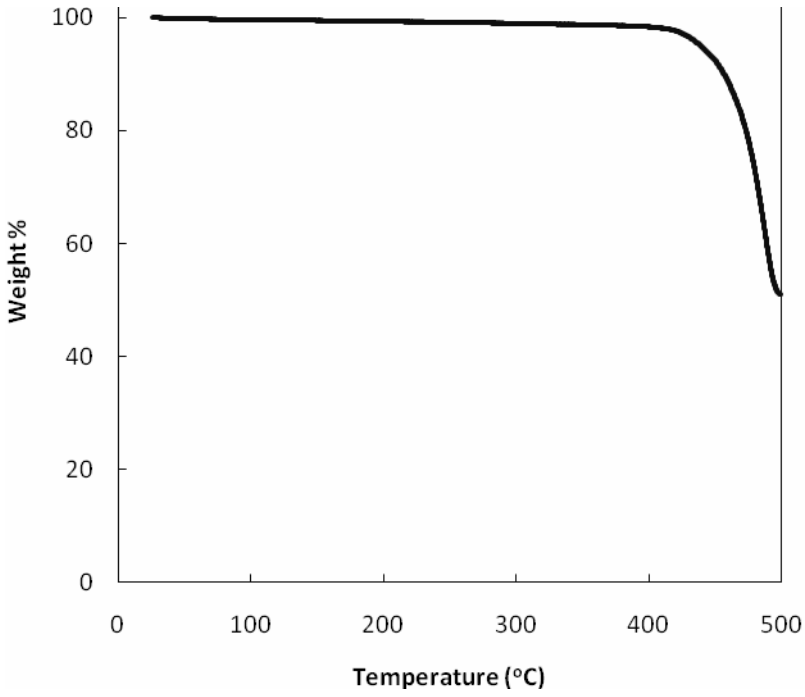

Figure S2. TGA trace of UMCM-4.

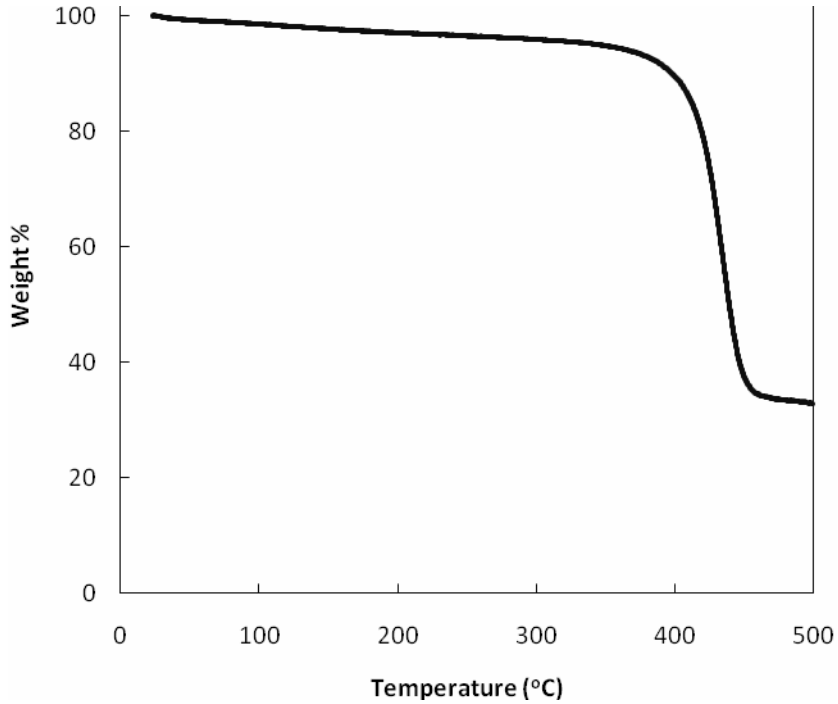

Figure S3. TGA trace of UMCM-5.

II. X-ray crystallography of UMCM-3 and 4

X-ray structure determination

X-ray diffraction data were collected for UMCM-3 and UMCM-4 on a Rigaku-Axis Spider diffractometer equipped with graphite monochromated CuKα radiation (λ = 1.54180 Å). Crystals of UMCM-3 and UMCM-4 were immersed in CH_2Cl_2 for one day followed by immersion in light mineral oil until data could be collected. Suitable crystals were mounted on MitiGen cryoloops using Paratone-N oil and cooled under a nitrogen gas stream at 95 K. Data were collected using the d*TREK package in the CrystalClear software suite (v. 2.0, Rigaku 2009) 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 and empirical absorption corrections were applied as implemented by FS_PROCESS. Decay of the crystals during data collection was negligible. The structures were solved by direct methods and refined by full-matrix least-squares refinement against all data using SHELXL-97[1] in the CrystalStructure (v. 4.0) software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically except where noted. All hydrogen atoms were calculated at idealized positions (C-H = 0.93 Å) and refined using a riding model with isotropic thermal parameters 1.2 times that of the attached carbon atom. UMCM-3 was solved in the cubic space group $F\bar{4}3m$ (#216). Carbons C6, C7, C9, C10, C16, and C17 that contribute to the three benzene rings surrounding the central ring of the BTB linker were treated isotropically due to severe disorder. UMCM-4 was solved in the orthorhombic space group *Pnma* (#62). Attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Therefore the SQUEEZE[2] routine of PLATON was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities.

Table S1. Crystal data and structure refinement for UMCM-3 and UMCM-4

Compound	**UMCM-3**	**UMCM-4**
Empirical formula	'C99 H51 O32.50 S3 Zn10'	'C33 H16 N O13 Zn4'
Formula weight	2510.28	896.01
Temperature	95(2) K	95(2) K
Wavelength	1.54180	1.54180
Crystal System	cubic	orthorhombic
Space Group	*F-43m* (#216)	*Pnma* (#62)
Unit Cell Dimensions	a = 44.3453(8) Å b = 44.3453(8) Å c = 44.3453(8) Å α = 90º β = 90º γ = 90º	a = 25.0573(5) Å b = 25.4805(5) Å c = 32.9266(6) Å α = 90º β = 90º γ = 90º
Volume	87205(3) $Å^3$	21022.7(7) $Å^3$
Z	8	8
Density (calculated)	0.382 g/cm^3	0.566 g/cm^3
Absorption coefficient	0.886 mm^{-1}	1.228 mm^{-1}
F(000)	10024	3560
Crystal Size	0.131 × 0.018 × 0.070 mm^3	0.250 × 0.135 × 0.064 mm^3
Reflections collected/ unique	26757 / 6211	57266 / 11262
R(int)	0.0560	0.0809
Data Completeness	98.4 % (to theta = 71.59)	99.3 % (to theta = 50.47)
Absorption correction	Empirical from equivalents	Empirical from equivalents
Max. and min. transmission	1.0000 and 0.5051	0.782 and 0.439
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
restraints/parameters	2/147	0/460
GOF on F^2	0.839	0.847
Final R indices [I>2sigma(I)][a,b]	R1 = 0.0411 wR2 = 0.0893	R1 = 0.0549 wR2 = 0.1508
R indices (all data)[a,b]	R1 = 0.1032 wR2 = 0.1059	R1 = 0.1002 wR2 = 0.1678

[a)] $wR2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (mP)^2 + nP]$ and $P = [\max(F_o^2,0) + 2F_c^2)] / 3$ (m and n are constants); $\sigma = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

[b] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

III. PXRD data of UMCM-3, 4, 5

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

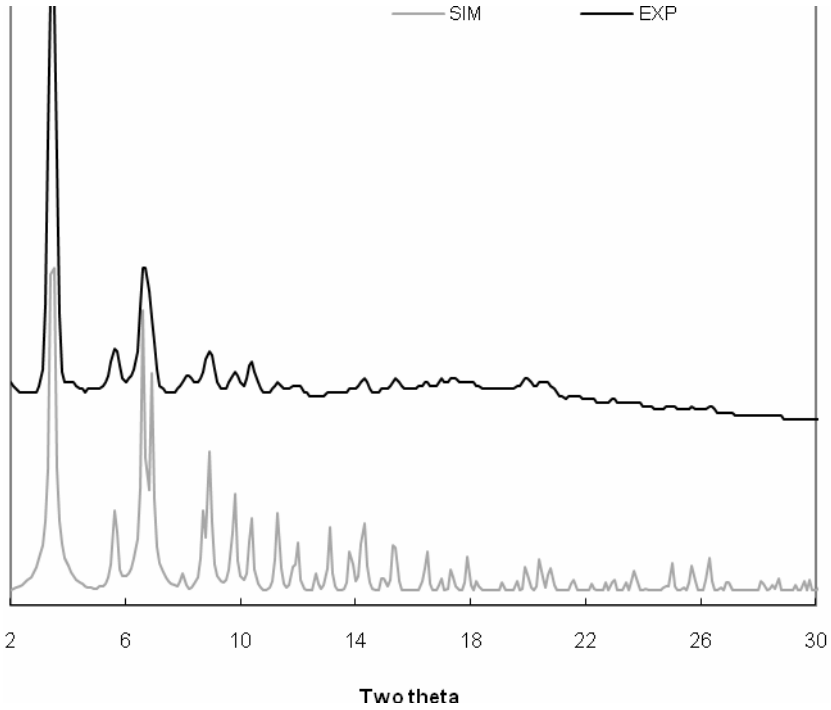

Figure S7. Powder XRD pattern of bulk UMCM-3 (black) and simulated pattern (grey).

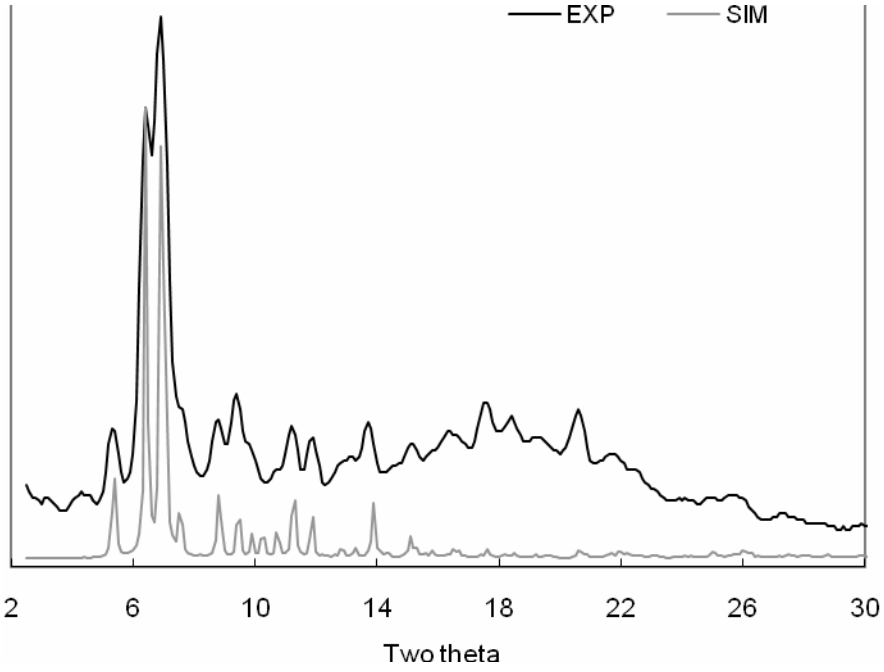

Figure S8. Powder XRD pattern of bulk UMCM-4 (black) and simulated pattern (grey).

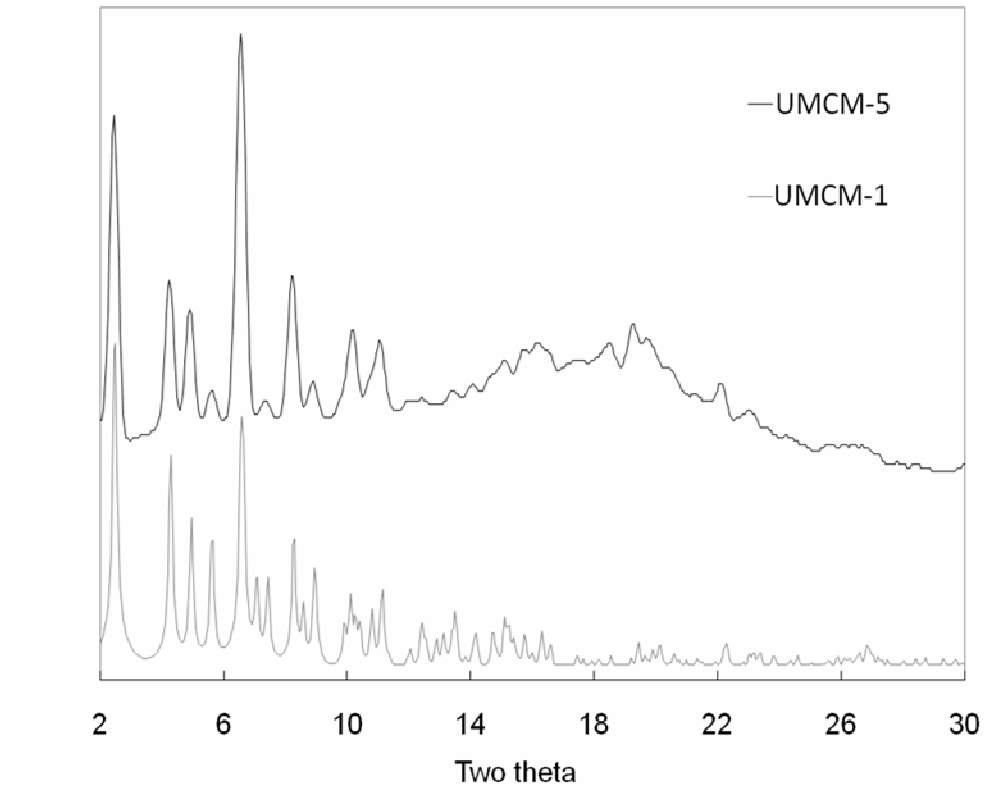

Figure S9. Powder XRD pattern of bulk UMCM-5 (black) and simulated UMCM-1 pattern (grey).

IV. Gas sorption measurements

1. N_2 surface area

N_2 adsorption/desorption isotherms were measured volumetrically at 77 K in the range 1.00 x $10^{-5} \leq P/P_0 \leq$ 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. The sample exchanged with CH_2Cl_2 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 x $10^{-4} \leq P/P_0 \leq$ 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.

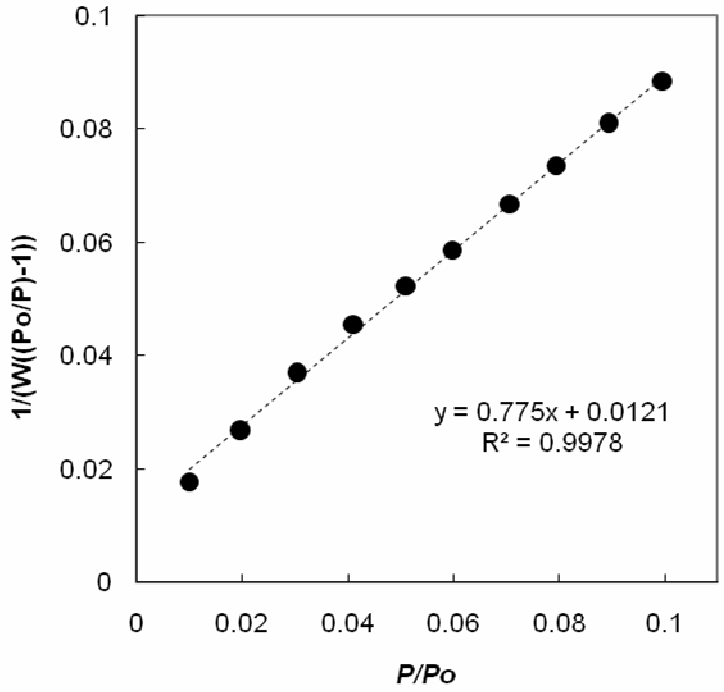

Figure S10. BET fit for the N_2 adsorption isotherm of UMCM-3 (BET SA = 4430 m^2/g).

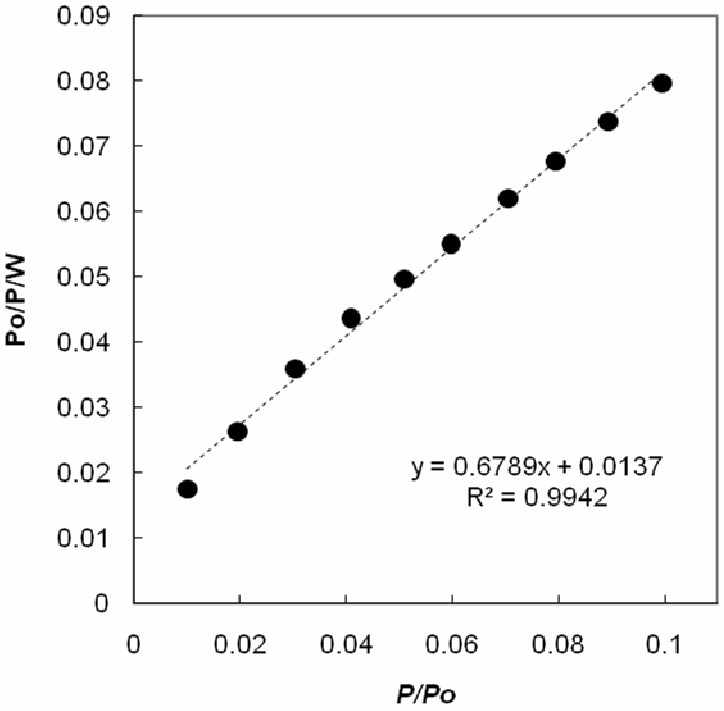

Figure S11. Langmuir fit for the N_2 adsorption isotherm of UMCM-3. (Lagmuir SA = 5130 m^2/g).

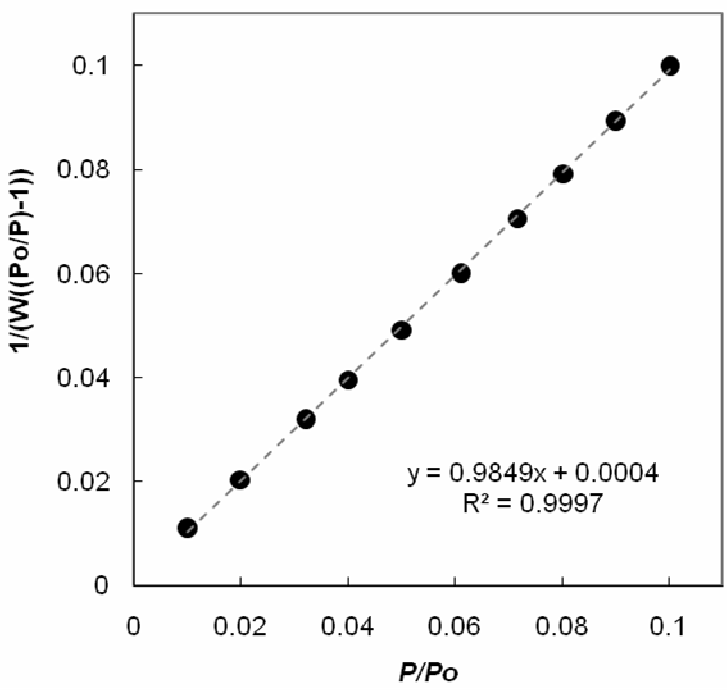

Figure S12. BET fit for the N_2 adsorption isotherm of UMCM-4. (BET SA = 3530 m^2/g).

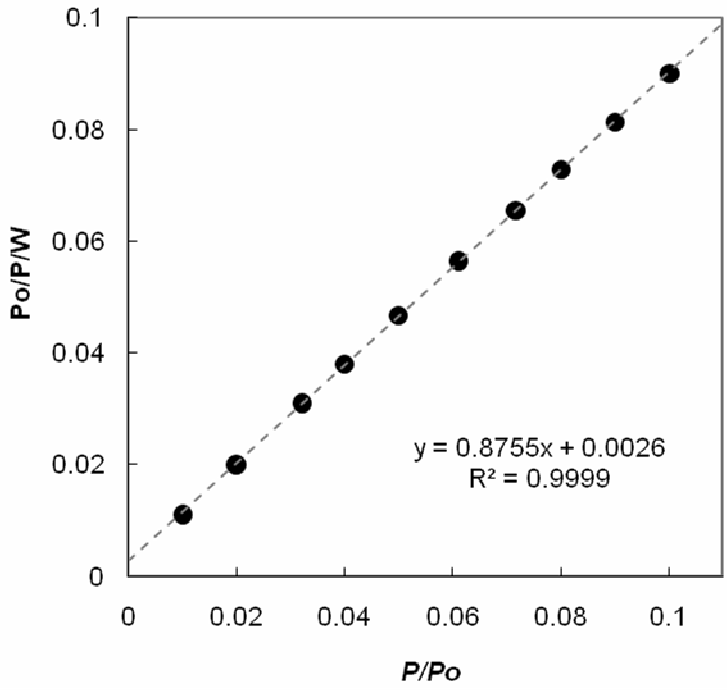

Figure S13. Langmuir fit for the N_2 adsorption isotherm of UMCM-4. (Lagmuir SA = 3980 m^2/g).

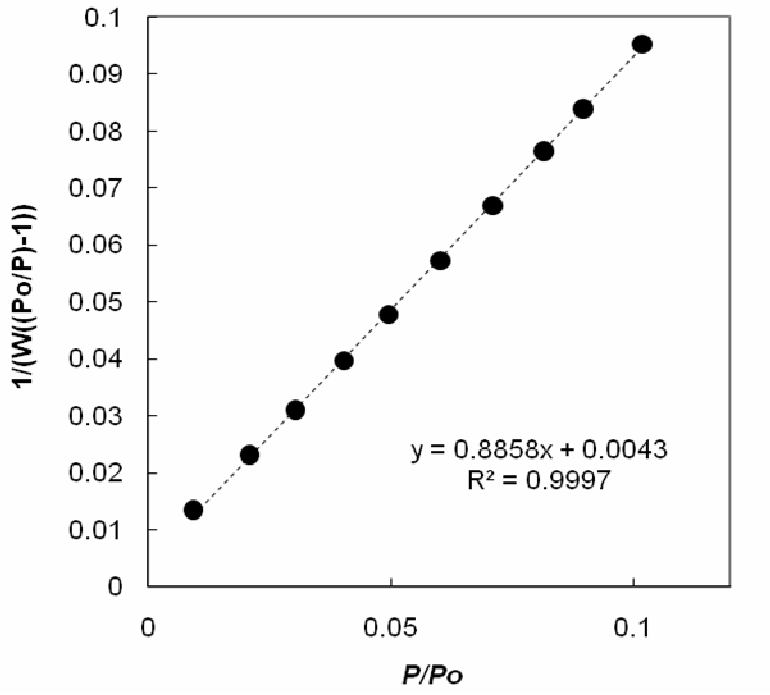

Figure S14. BET fit for the N_2 adsorption isotherm of UMCM-5 (BET SA = 3910 m^2/g).

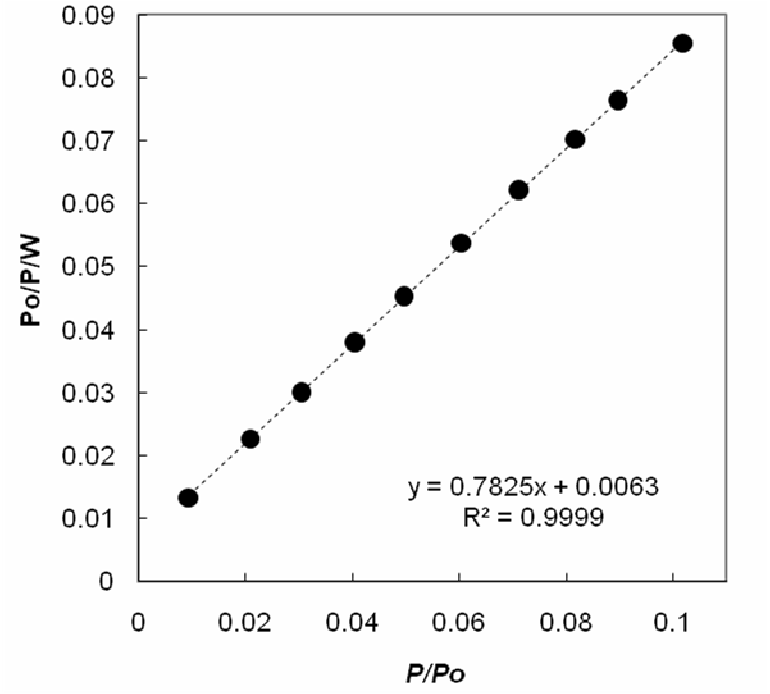

Figure S15. Langmuir fit for the N_2 adsorption isotherm of UMCM-5 (Lagmuir SA = 4450 m^2/g).

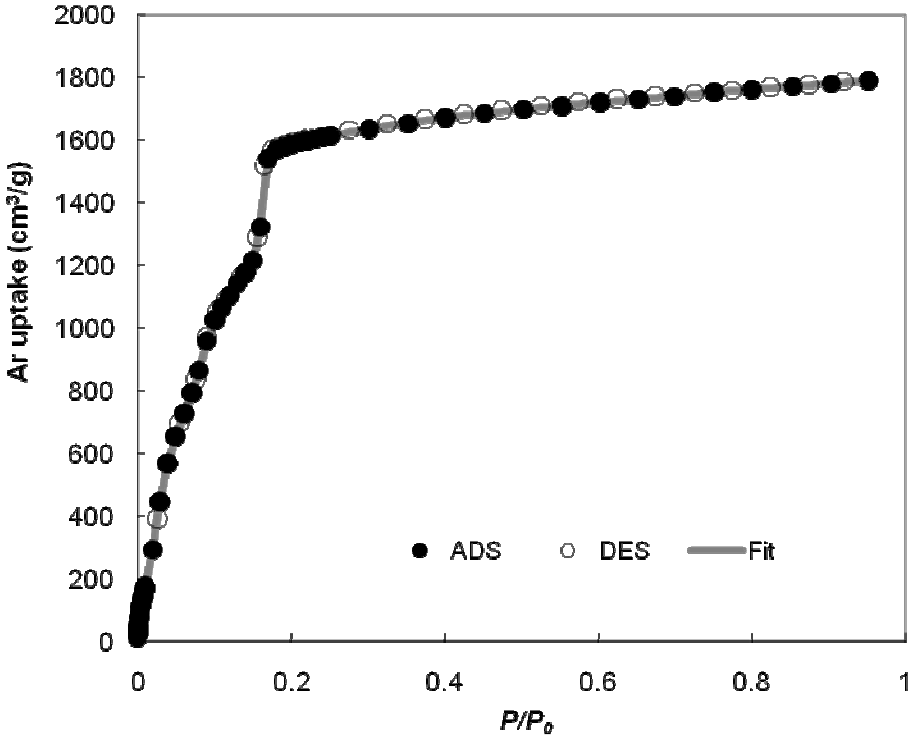

Figure S16. Ar adsorption/desorption isotherm at 87 K for UMCM-3 and the corresponding NLDFT fit base on a cylindrical pore model.

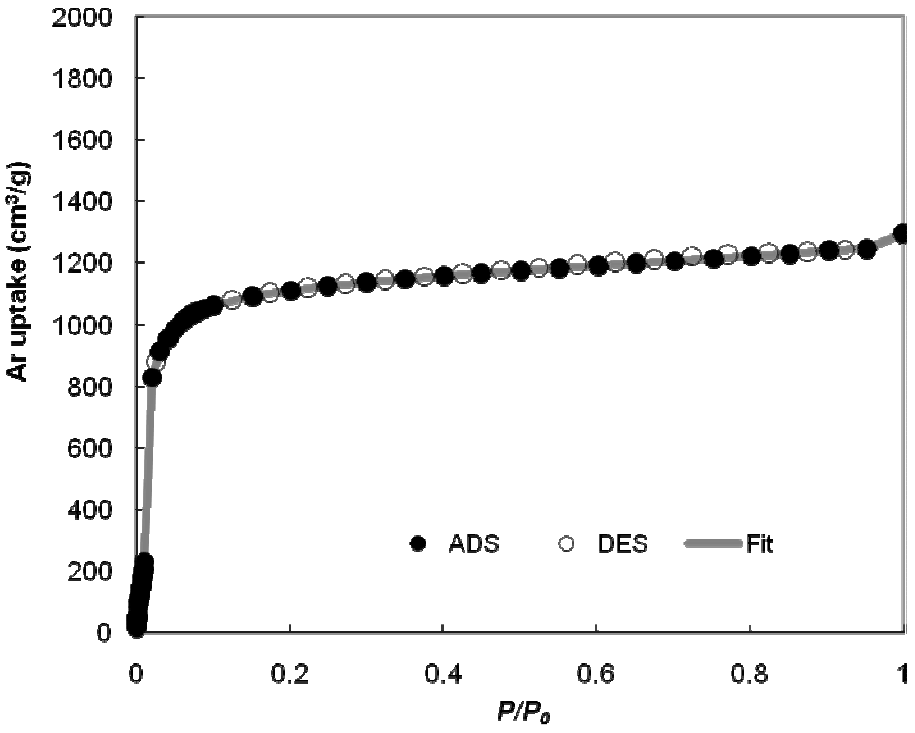

Figure S17. Ar adsorption/desorption isotherm at 87 K for UMCM-4 and the corresponding NLDFT fit base on a cylindrical pore model.

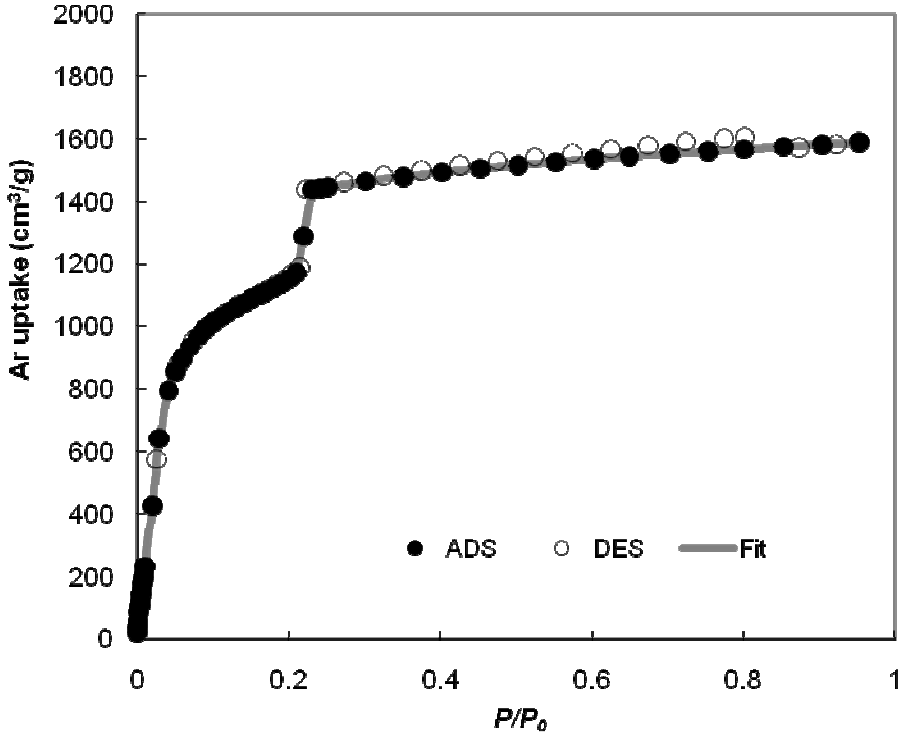

Figure S18. Ar adsorption/desorption isotherm at 87 K for UMCM-5 and the corresponding NLDFT fit base on a cylindrical pore model.

V. Quantification and characterization of PHT in UMCM-1.

A 1.0 M NaOH solution (1.37 g) was added to 1.20 mg of the PHT/UMCM-1 inclusion complex to decompose the UMCM-1 framework. The polymer was extracted with 0.97 g of chlorobenzene. The resulting chlorobenzene solution was washed with H_2O (2 × 1 mL) and the amount of PHT was quantified by UV-Vis spectroscopy and determined to be 40.6 mg/g. The chlorobenzene solvent was removed under vacuum and the polymer obtained was dissolved in tetrahydrofuran (THF) and characterized by a gel permeation chromatographic (GPC) analysis on a Waters system equipped with three columns (Waters, styragel HT) and a UV detector. THF was used as an eluent at a flow rate of 1 mL/min. Polystyrene standards were used to calibrate the GPC system. The results are shown in Table S1.

Table S2. Molecular weight (M_n) and polydispersity index (PDI) for PHT

	M_n	PDI
PHT	21700	2.18
PHT in UMCM-1	17500	1.75

VI. Microscope images of Nile red and Reichardt's dye incorporated in UMCM-1

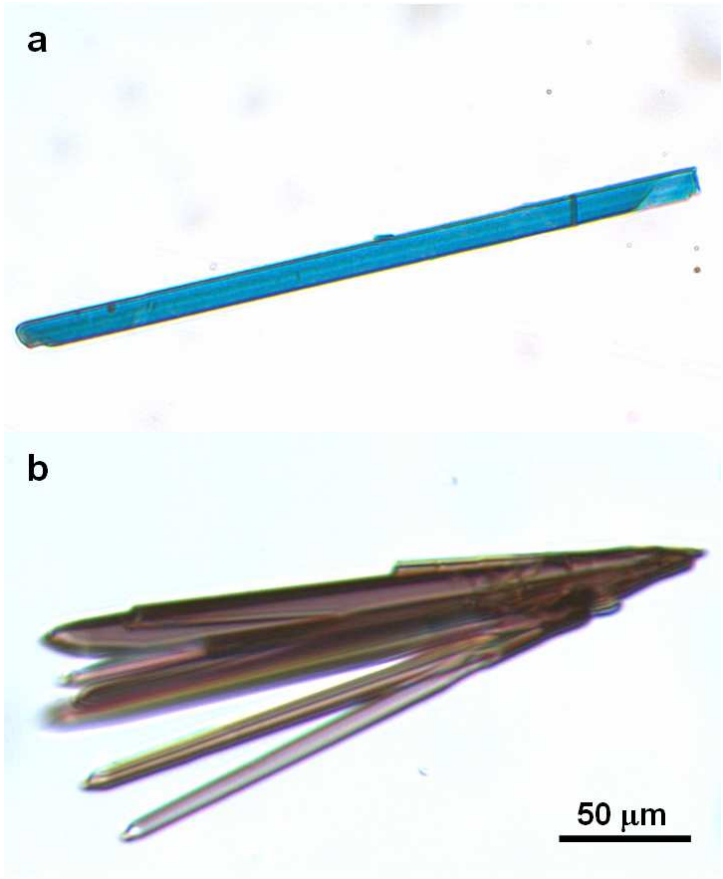

Figure S19. Microscope images of Nile red (a) and Reichardt's dye (b) incorporated UMCM-1 (CH_2Cl_2).

---

[1] a)G. M. Sheldrick, *SHELXS '97 and SHELXL '97.* (University of Göttingen, Germany, **997**). b) Sheldrick, G.M., *Acta Cryst. A64,* **2008**, 112-122.

[2] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, (Utrecht University, Utrecht, The Netherlands, **2005**).