

Supporting Information

The role of modulator in controlling layer spacings in a tritopic linker based zirconium 2D-microporous coordination polymer

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1.

Reagents. Zirconium tetrachloride (Acros, 98%), concentrated HCl (Fisher Scientific, ACS reagent grade), benzoic acid (Acros, 99.5%), biphenyl-4-carboxylic acid (Alfa Aesar, 98%) and dimethylformamide (DMF, Fisher Scientific, ACS reagent grade) were used as-received without further purification.

Powder X-ray diffraction. The powder X-ray data of UMCM-309a for Rietveld refinement were collected on Rigaku R-Axis Spider diffractometer with an image plate detector and Cu-K α radiation operating at 40 kV and 44 mA in transmission mode. The sample was loaded into a 0.4 mm diameter capillary. The capillary was rotated on the goniometer in ϕ and oscillated in ω to minimize preferred orientation with χ fixed at 45°. Another image of a blank capillary was acquired in the same manner and subtracted from the sample image. The powder pattern then was obtained by integration of the two-dimensional image in AreaMax 2.0 software with an integration step of 0.01°.

All other PXRD data were collected with a Bruker D8 advance diffractometer equipped with a 60 mm sealed Göbel mirror and a LynxEye linear position sensitive detector. The Cu-K α X-ray source was operated at 40 kV and 40 mA. Samples were ground and evenly dispersed on a low-background quartz plate.

Gas sorption measurements. Gas sorption experiments were carried out at 77K using a NOVA 4200 by Quantachrome Instruments (Boynton Beach, Florida, USA) or an Autosorb-1C Quantachrome Instruments (Boynton Beach, Florida, USA). Ultra-high purity N₂ (99.999%) and Ar (99.999%) was purchased from Cryogenic Gasses and used as received. Pore size distributions were calculated using the Non-linear Density Functional Theory (NLDFT) zeolite/silica equilibrium kernel on a cylindrical pore model for Ar adsorption at 87 K using ASWin software package (version 1.2).

Thermogravimetric analysis. TGA data were acquired using a TA instrument Q50. Samples were heated and analyzed in a platinum pan under a nitrogen atmosphere. Temperature was ramped up to 600 °C at a rate of 10 °C/min.

NMR analysis. NMR data were obtained using a 500 MHz Varian Inova NMR spectrometer. A relaxation time of 25 s was applied to ensure full relaxation and accurate integration.

Scanning Electron Microscopy. Activated UMCM-309a (~2-3 mg) was transferred to conductive carbon tape on a sample holder with no coating performed. A Zeiss 1455VP instrument was used for acquiring images at 10 kV with a 5 mm working distance under vacuum.

2. General synthetic procedures for UMCM-309a, UMCM-309b and UMCM-309c.

UMCM-309a. ZrCl_4 (0.0863 g, 0.370 mmol) and H_3BTB (0.1095 g, 0.250 mmol) were dissolved in 10 mL of *N,N*-dimethylformamide (DMF) in a 20 mL vial. Concentrated HCl (10.75 mL, 100 equiv.) was added to the solution. The mixture was sonicated for 10 minutes. The solution was transferred to a Parr 45 mL acid digestion vessel, sealed and heated to 120 °C. After 2 days, white microcrystalline powder was obtained. The powder was collected by centrifugation and washed with clean DMF (3×20 mL). The powder was then immersed in 10 mL acetone for 3 days, during which time the acetone was replaced three times each day. After exchange with acetone, the sample was evacuated at 120 °C under dynamic vacuum for 12 h prior to sorption analysis. The yield of the reaction, determined from the weight of the solvent-free material, is 17.3% based on H_3BTB . Anal. Calcd for $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{BTB})_2(\text{OH})_6(\text{H}_2\text{O})_3] \cdot 0.5(\text{BTB})$ which is equivalent to $\text{Zr}_6\text{O}_{29}\text{C}_{54}\text{H}_{46} \cdot 0.5(\text{C}_{27}\text{H}_{15}\text{O}_6)$: Zr, 28.45%; C, 42.13%; H, 2.81%. Found: Zr, 28.70%; C, 42.09%; H, 2.75%.

UMCM-309b and UMCM-309c. ZrCl_4 (0.0345 g, 0.148 mmol), H_3BTB (0.0438 g, 0.100 mmol) and modulators (100 equiv. benzoic acid or biphenyl-4-carboxylic acid) were dissolved in 4 mL of DMF in a 20 mL vial. The mixture was sonicated for 10 mins. The solution was then heated at 120 °C. After two days, white microcrystalline powder was obtained and subjected to the same washing procedure for UMCM-309a.

3. Model structure building, geometry optimized and refinement procedures.

A unit cell was created in Material Studio 7.0 using PXRD indexing results. A Zr_6 cluster and BTB linker were placed in the unit cell according to the connectivity of the kgd-a network. The unit cell was subjected to geometry optimization with a UFF forcefield and convergence conditions from coarse to ultra-fine were applied sequentially using default parameters. A Pawley refinement was applied to the model against the powder pattern sequentially with specimen displacement, background, lattice parameters, peak profile, and peak asymmetry. The convergence quality was applied starting from coarse to ultra-fine to give the final unit cell parameters.

Table S1. Refined unit cell parameter and fractional atomic coordinates for UCMCM-309a. Atomic coordinates were derived from geometry optimization with fractional coordinates computed from optimized cell parameters.

Name	UMCM-309a		
Space group: P- $\bar{3}$ (Space group #147)			
a=b=19.54 Å c=7.01 Å			
Atom name	x	y	z
O1	0.84841	0.77791	0.04287
C1	0.71915	0.53731	0.971
H1	0.66703	0.50433	0.05301
C2	0.75974	0.6174	0.99108
H2	0.73717	0.64374	0.08644
O2	0.94071	0.78659	0.84398
C3	0.81579	0.54542	0.75171
H3	0.83831	0.51877	0.65727
C4	0.85653	0.62565	0.77202
H4	0.90983	0.65861	0.69426
Zr1	0.90747	0.89026	0.15775
C5	0.82944	0.66256	0.89375
C6	0.74697	0.5001	0.8526
C7	0.87508	0.74699	0.9269
C8	0.70571	0.41433	0.84054
C9	0.74716	0.3748	0.84074
H5	0.80943	0.40721	0.84416
O3	0.90351	0.88588	0.86446

O4	0.90063	0.79216	0.29614
O5	0.85466	0.87126	0.41838
H6	0.94339	0.78348	0.25817
H7	0.81954	0.8159	0.45408
H8	0.89525	0.89097	0.5214
O6	0	0	0.28129

4.

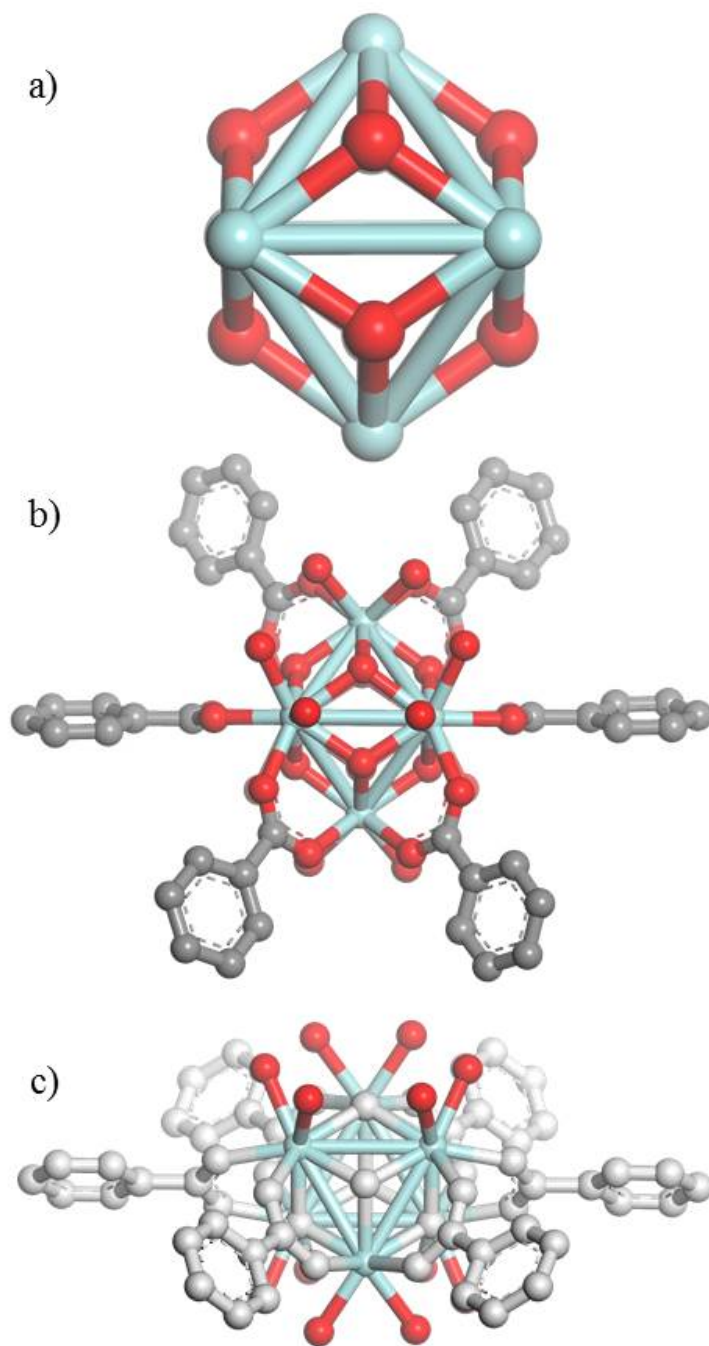


Figure S1. a) Octahedral core of the Zr₆ cluster. Four of the μ₃-O on the face of the octahedral are hydroxyl b) A Zr₆ cluster with 6 coordinate (hexagonal planar) arrangement of ligands. c) A Zr₆ cluster with 6 coordinate (hexagonal planar) arrangement of ligands highlighting terminal oxygen demonstrating coordination environment for Zr centers in UMCM-309a.

The coordination environment for Zr centers here is exactly the same as in PCN-224 and Zr/BTB (*J. Am. Chem. Soc.* **2013**, 135, 17105–17110; *Inorg. Chem.* **2014**, 53, 7086–7088). Each zirconium is eight coordinated to two μ_3 -O, two μ_3 -OH, two carboxylate oxygen, one –OH and one –H₂O to maintain a neutral cluster. Hydrogen atoms are omitted for clarity in the figure.

5.

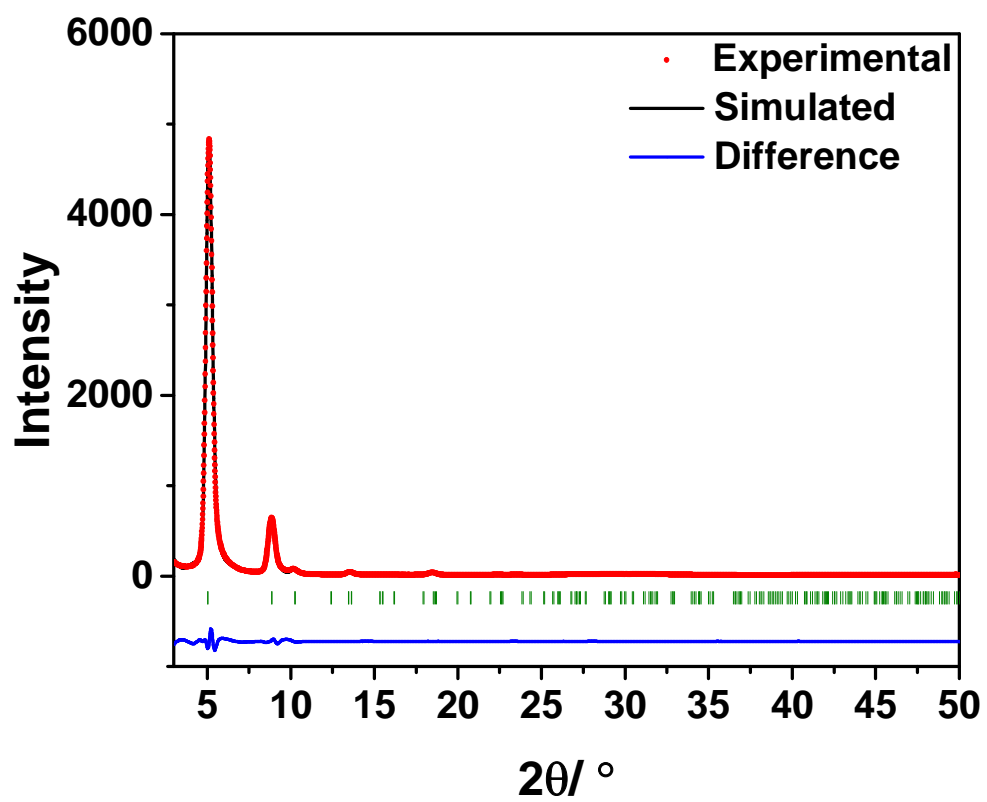


Figure S2. Results of Pawley refinement for UMCM-309a.

6.

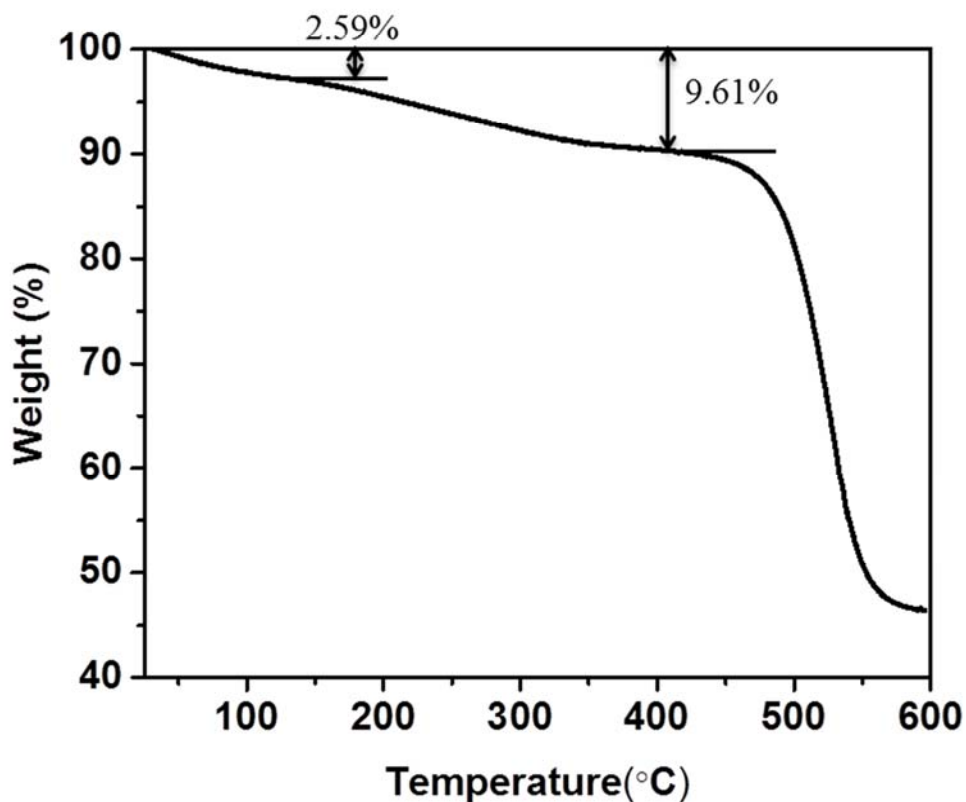


Figure S3. TGA trace of UMCM-309a. Conditions: temperature ramp from 25 °C to 600 °C at 10 °C/min under flow of N₂ gas.

The TGA data shows a steady weight loss up to 400 °C of 9.61%. Theoretically, the maximum number of water molecules that can condense and leave from Zr₆ cluster in our model is 11 (calculated weight loss of 10.01%). Since UMCM-309a is activated at 120 °C in vacuum before being subjected to elemental analysis, it is prone to partial dehydration. The weight loss up to 120 °C is 2.59% and corresponds to 3 water molecules loss per Zr₆ cluster (calculated weight loss 2.73%). Taken that into account, the formula proposed is [Zr₆(μ₃-O)₄(μ₃-OH)₄(BTB)₂(OH)₆(H₂O)₃]•0.5(BTB). The calculated EA is Zr, 28.45%; C, 42.13%; H, 2.81% and matches well with the observed ICP/EA (Zr, 28.70%; C, 42.09%; H, 2.75%).

7.

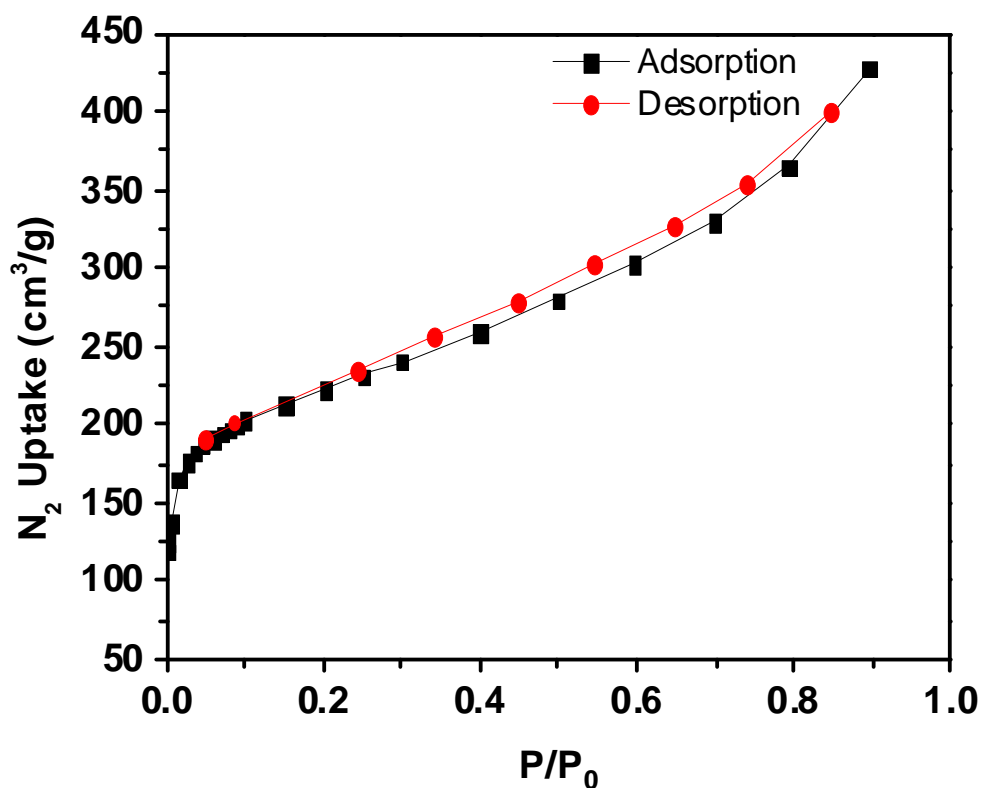


Figure S4. N₂ isotherm at 77 K for UMCM-309a

The deviation from typical type I behavior is presumably due to the presence of defects in the crystals. This effect has also been observed in UiO-66 N₂ isotherm when large amount of acetic acid used as modulator (*J. Am. Chem. Soc.* **2013**, *135*, 10525–10532). Pore size distribution analysis of UMCM-309a shows that pore size around 50 Å is present besides the pore size around 8 Å matching the model (Figure S5). SEM data of UMCM-309a supports that we obtained a pure phase material and is consistent with a sheet morphology (Figure S6).

8.

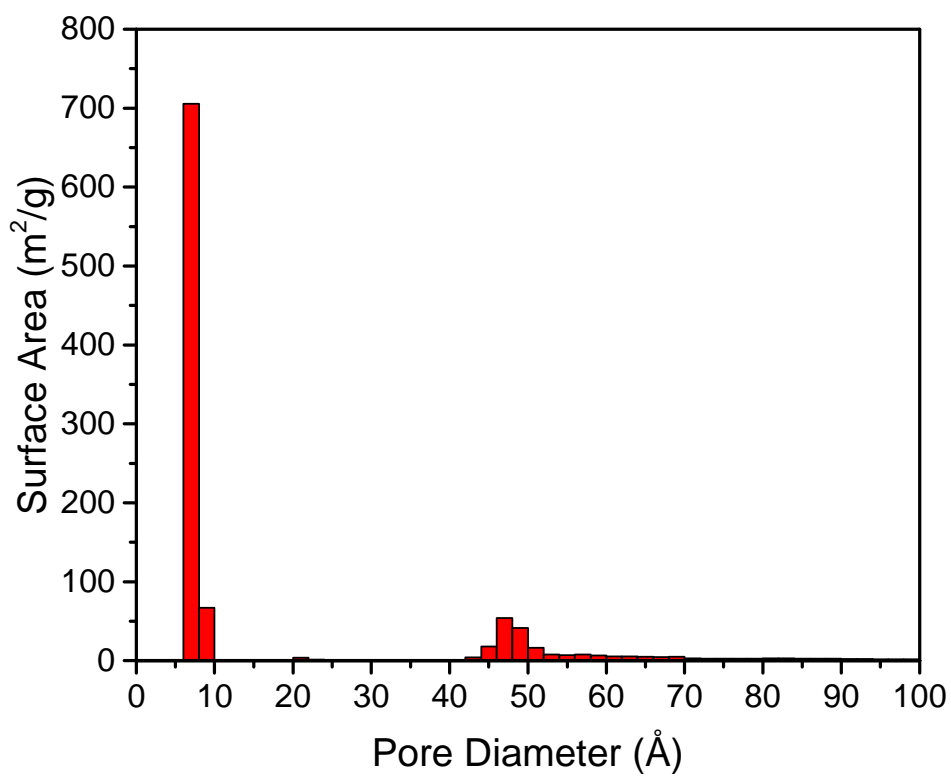


Figure S5. Pore size distribution calculated from Ar sorption isotherm at 87K for UMCM-309a

9.

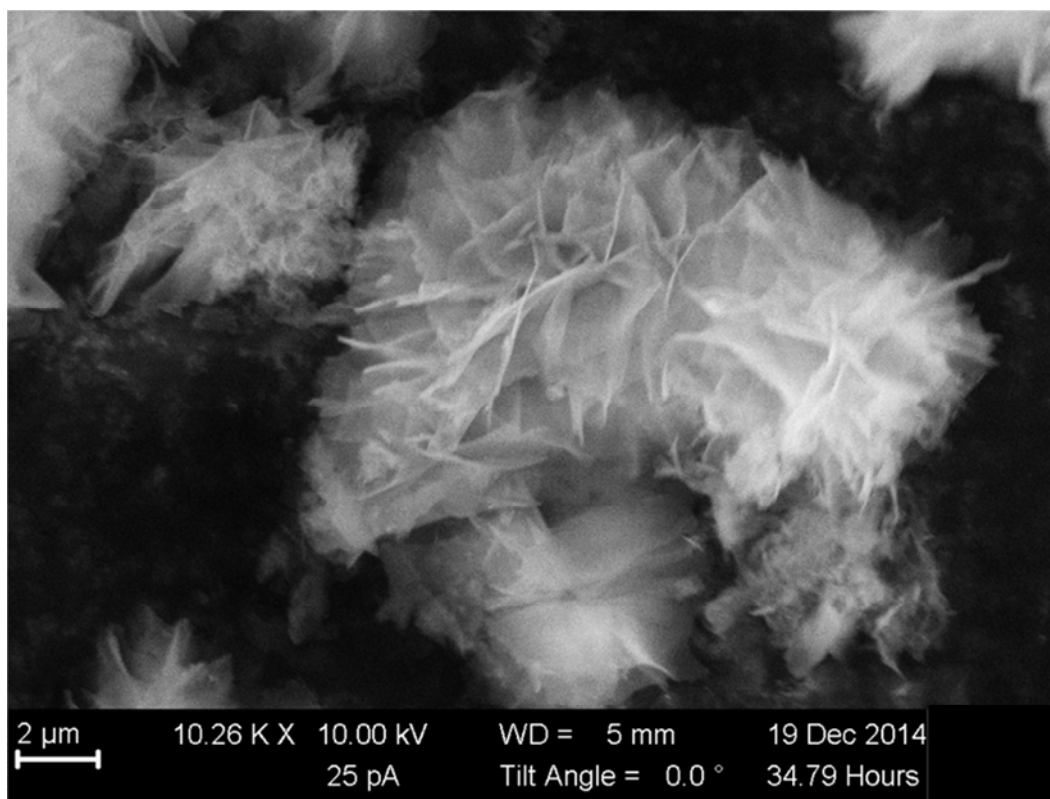


Figure S6. SEM image of UMCM-309a.

10.

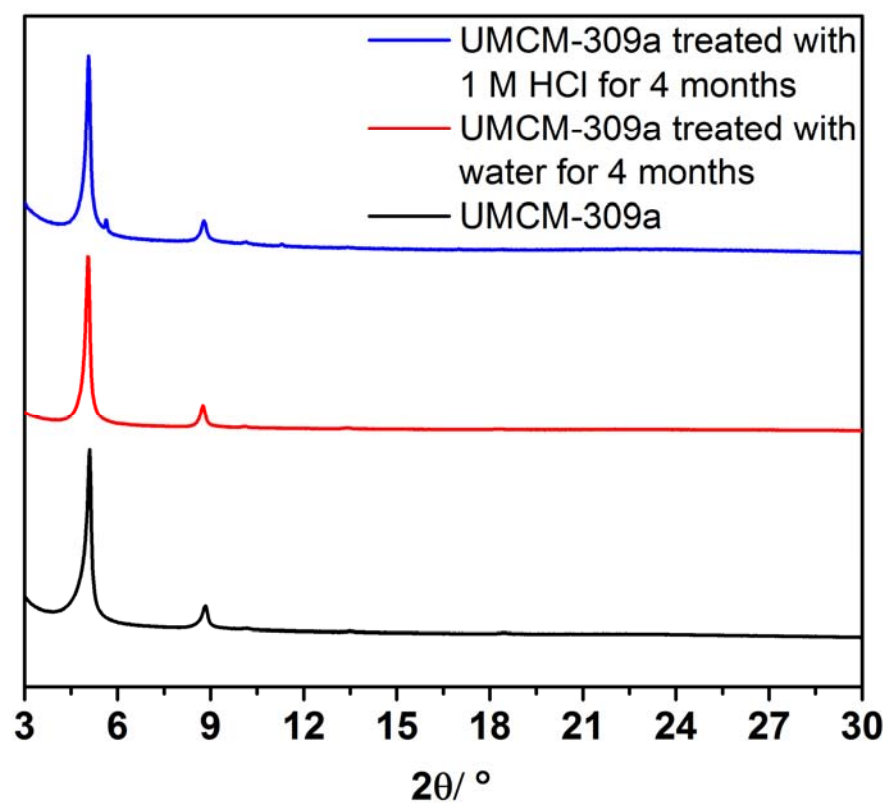


Figure S7. PXRD pattern of UMCM-309a and UMCM-309a treated with water and 1 M HCl for 4 months at room temperature.

11.

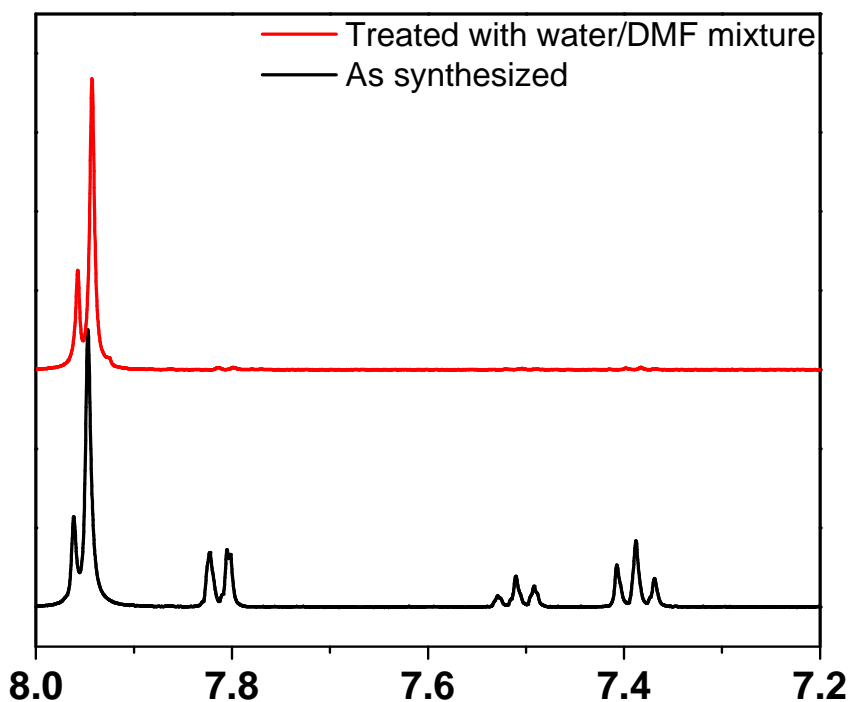


Figure S8. ^1H spectrum of digested UCMCM-309b before and after treatment with water/DMF at 120 °C for 3 days. Samples were digested with 10 wt% $\text{D}_2\text{SO}_4/\text{DMSO}-d_6$. From integration, the ratio between H_3BTB and benzoic acid was determined to be 2:4.84.

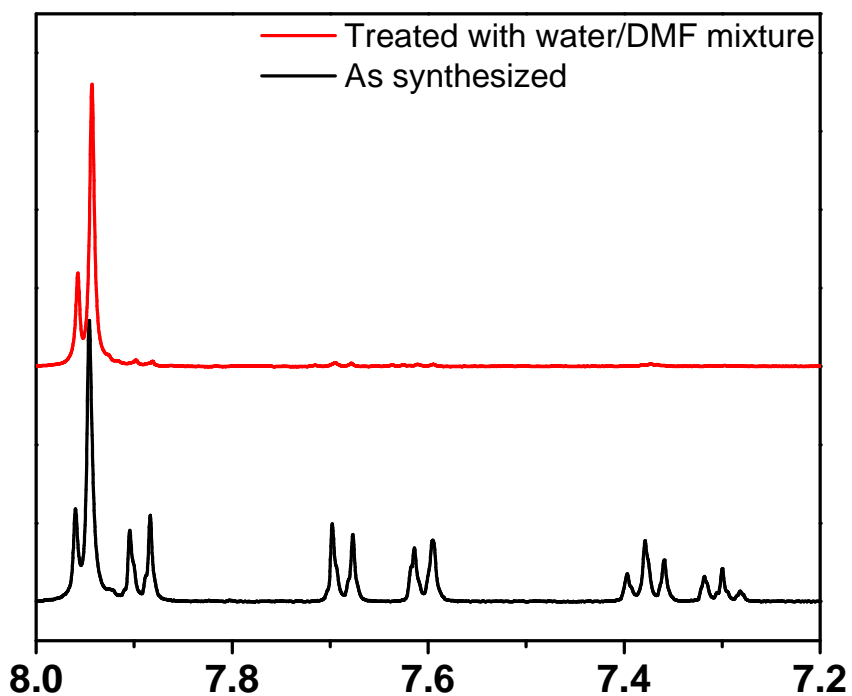


Figure S9. ^1H spectrum of digested UCMCM-309c before and after treatment with water/DMF at 120 °C for 3 days. Samples were digested with 10 wt% $\text{D}_2\text{SO}_4/\text{DMSO-d}_6$. From integration, the ratio between H_3BTB and biphenyl-4-carboxylic acid was determined to be 2:5.32.

12.

h	k	l	d(calculated)	d(experimental)
1	0	0	17.474	17.521
1	1	0	10.089	10.089
0	0	1	14.839	14.920
1	0	1	11.311	11.345
1	1	1	8.343	8.384
0	0	2	7.420	7.413
2	1	2	4.933	4.943

Table S2. Experimental and calculated peak positions of UMCM-309c based on a *c*-axis of 14.8 Å.

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \left(\frac{l^2}{c^2} \right)$$

Figure S10. Formula for calculating d-spacing in a hexagonal crystal system.

13.

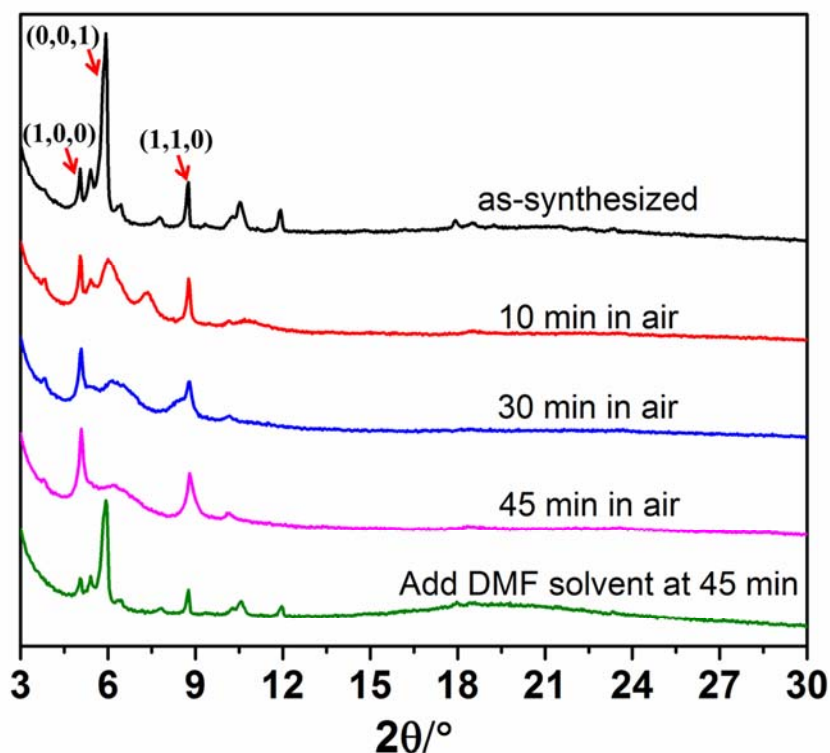


Figure S11. PXRD pattern of UMCM-309c as-synthesized and the pattern for UMCM-309c after 10 min, 30 min and 45 min in air. After 45 min in air, another PXRD pattern was obtained after adding DMF to the dried UMCM-309c.

Arrows show (1,0,0) and (1,1,0) peaks retained during structural change. This suggests that the layered structure is still intact whereas the (0,0,1) peak is broadened and shifted towards higher 2θ indicating the decrease of layer spacing. After adding solvent, the phase changes back to the as-synthesized UMCM-309c. This indicates that the structural change is reversible.

14.

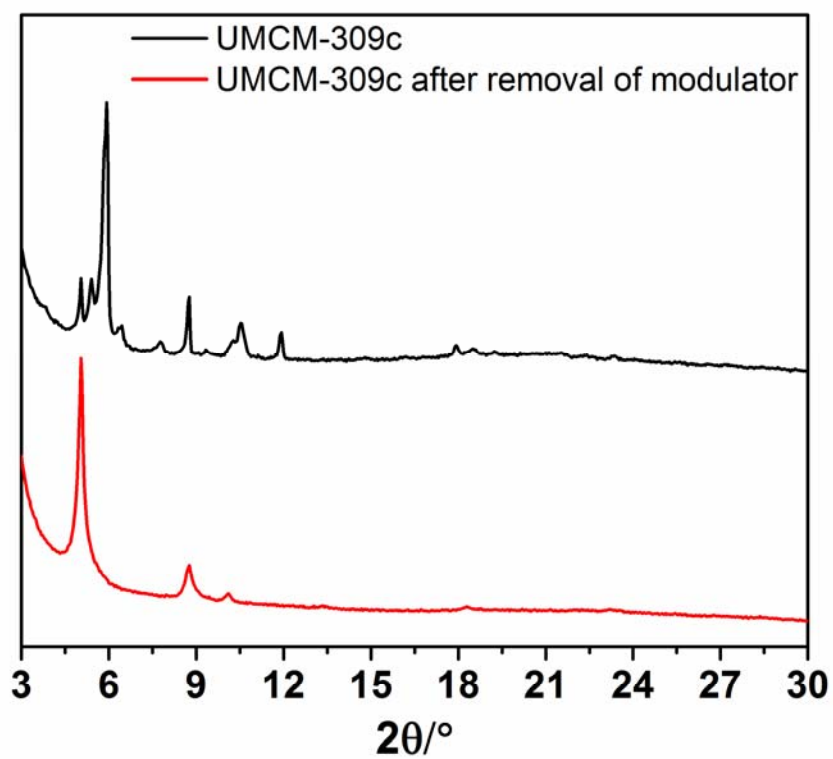


Figure S12. PXRD pattern of as-synthesized UMCM-309c and the pattern for UMCM-309c treated with water/DMF mixture at 120 °C for three days.

15.

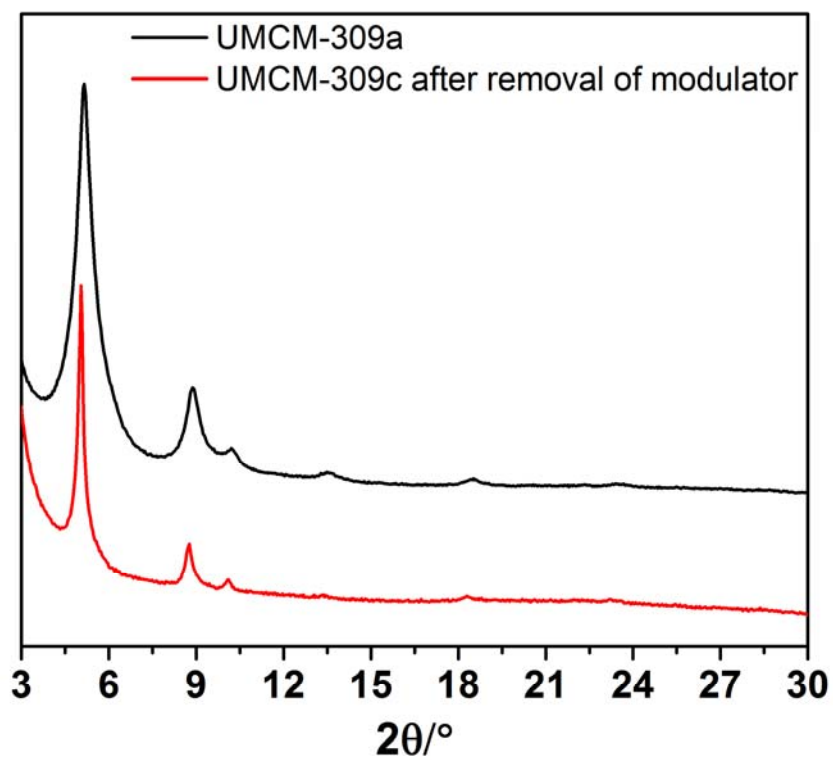


Figure S13. PXRD pattern of UMCM-309a and the pattern for UMCM-309c treated with water/DMF mixture at 120 °C for three days.

16.

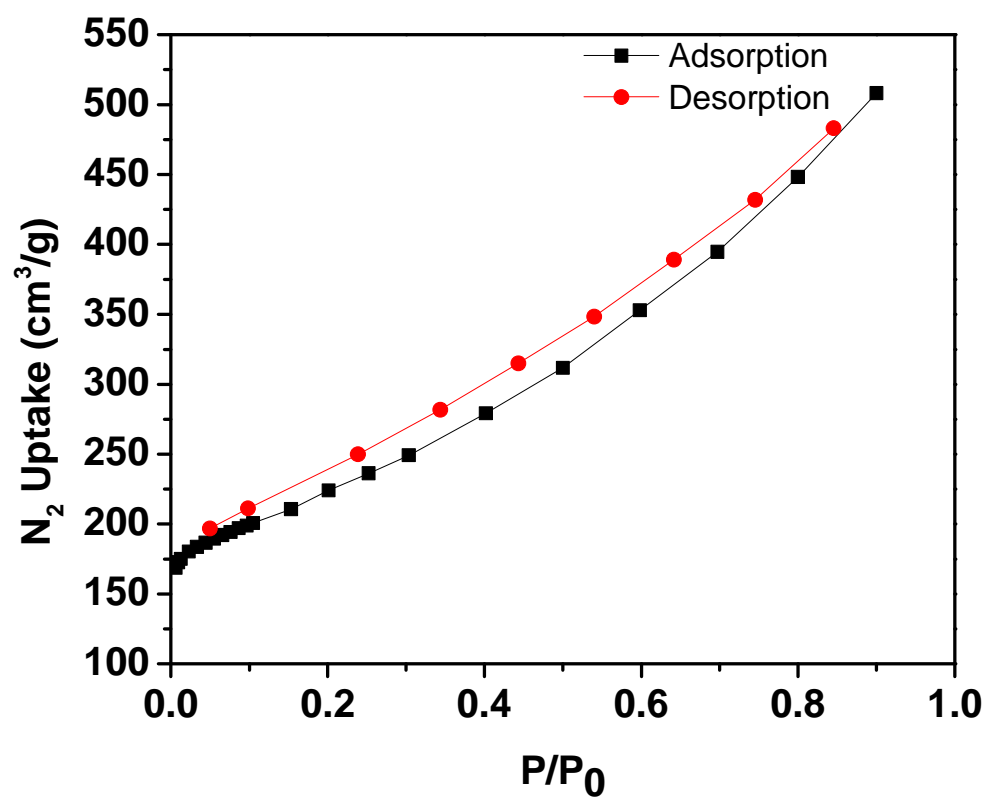


Figure S14. N₂ isotherm at 77 K for UMCM-309c treated with water/DMF mixture at 120 °C for three days.