Electronic Supplementary Information

A Non-regular Layer Arrangement of a Pillared-layer Coordination Polymer: Avoiding Interpenetration via Symmetry Breaking at Nodes

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Contents

1. Synthesis of UMCM-15 3
2. Morphology of UMCM-15 3
3. ^{1}H NMR spectroscopic data of digested UMCM-15 3
4. Structural modelling and X-ray diffraction analyses 4
5. Nile red dye diffusion experiments 5
6. Thermogravimetric analysis of UMCM-15 5
7. Gas sorption measurement 6

1. Synthesis of UMCM-15

H_2-BDC (166.0 mg, 0.9958 mmol), H_2-NDC (216.0 mg, 0.9991 mmol), 4,4'-bipy (156.0 mg, 0.9988 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (600.0 mg, 2.017 mmol) were dissolved in respectively 10.0 mL, 10.0 mL, 10.0 mL, and 20.0 mL of *N*,*N*-dimethylformamide. The individual solutions were sonicated for 30 min and mixed. The final solution was clarified by filtration through a glass wool plug. The reaction mixture was heated to 85 °C. After 1.5 days, needle-shaped crystals of a single phase were obtained. After cooling to room temperature, the product was isolated by decanting the mother liquor and washing with fresh DMF (3 × 50 mL).The yield of the reaction determined from the weight of the solvent-free material varies from 21.7 – 34.3% based on H_2-BDC. The mother liquor of the first reaction, when subjected to heating for 1 additional day, affords a combined yield of 38.6 – 53.9%.

The preparation of UMCM-15 was also conducted on smaller scale by dissolving all reactants in one vial to obtain a similar yield. The larger scale reactions were more variable in yield but afforded similar yields in optimal cases.

2. Morphology of UMCM-15

Optical images were taken with a Spot Insight Color camera fixed to a Leica DMIL microscope.

SEM image was collected on a Zeiss SEM instrument-1455 VP operating under 10 kV energy source in vacuum at a working distance of 5 mm. No coating was used for sample preparation.

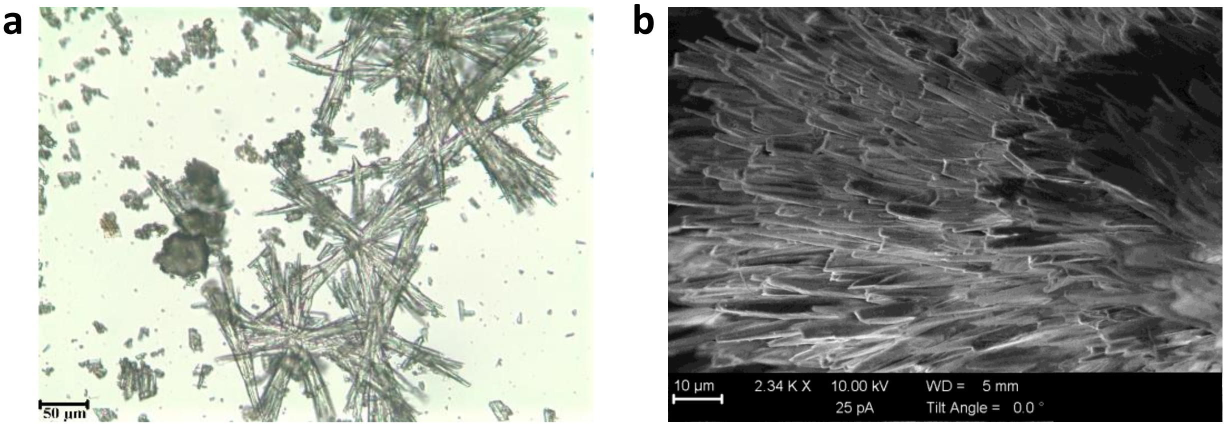

Figure S1. a) Optical micrograph and b) scanning electron micrograph of UMCM-15.

3. ^{1}H NMR spectroscopic data of digested UMCM-15

Solvent free material was digested in 35 wt% DCl in D_2O and diluted with DMSO-d_6 before performing ^{1}H NMR spectroscopic experiments.

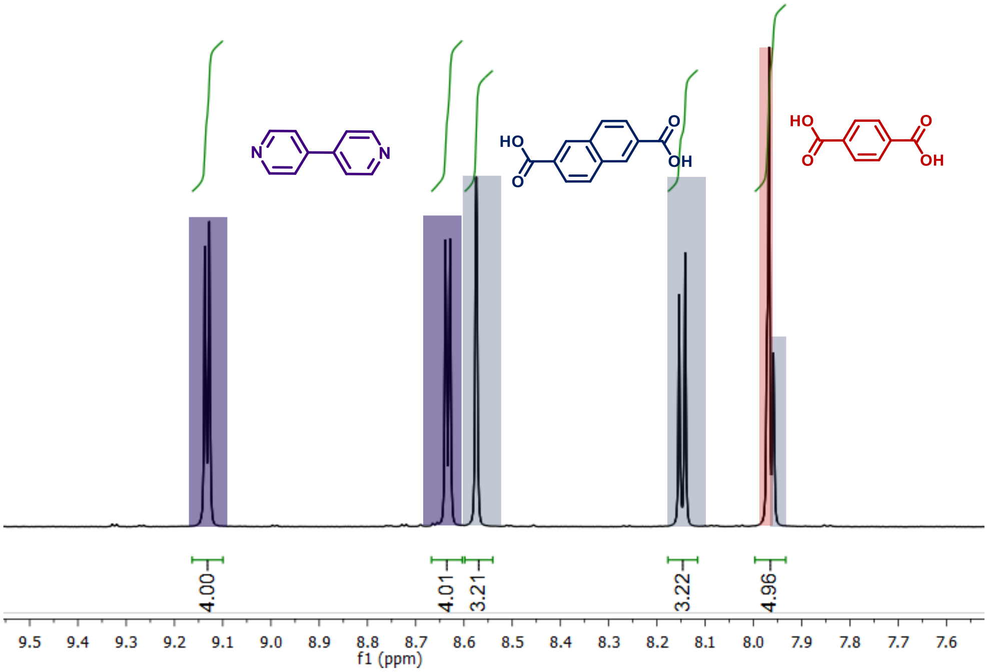

Figure S2. Aromatic region of ^{1}H NMR spectra for digested UMCM-15.

4. Structural modelling and X-ray diffraction analyses

Powder X-ray diffraction data were collected on a Bruker D8 Advance Diffractometer in parallel beam mode. The CuKα radiation source was operated at 40 V and 40 mA. As-synthesized sample was ground and evenly dispersed on a low background quartz plate. The diffraction patterns were collected from 4 to 50 in 2θ at a 0.5 sec/step scan rate.

Based on indexing results using MDI Jade, a model was constructed in the triclinic crystal system (space group 1) assembling the building units using Materials Studio 7 (Accelrys). A geometry optimization was performed applying the Forcite module using UFF force field. The convergence conditions from coarse to ultra-fine were applied sequentially using default parameters. To compensate for the electron density contribution from the solvent in the pores, 20 oxygen atoms were added at random positions. The simulated powder pattern was generated from the model structure and refined against the experimental data using a full pattern Pawley refinement. The Pawley refinement was applied to the model sequentially with specimen displacement, background, lattice parameters, and peak profile using the Pseudo-Voigt function. The refinement was conducted sequentially with convergence quality from coarse to ultra-fine to give the final plot.

Table S1. Pawley refinement results of UMCM-15

Sample name	Rwp	Rwp (without background)	Rp

UMCM-15	4.39%	4.91%	2.80%

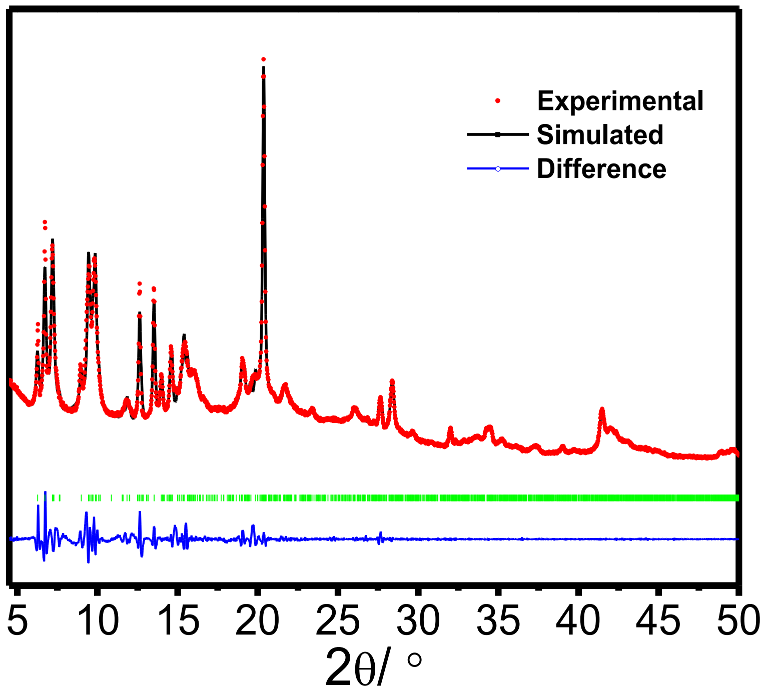

Figure S3. Pawley refinement results from simulated and experimental powder X-ray diffraction pattern of UMCM-15.

5. Nile red dye diffusion experiments

MCP crystals were immersed in *N*,*N*-dimethylformamide (DMF) solution saturated with Nile red dye and containing additional solid dye solution at room temperature for 1 day and then washed with fresh DMF five times followed by immersion in mineral oil. Optical micrographs of crystals after dye impregnation were taken with a Spot Flex camera fixed to a Leica DMLP microscope. The crystals were sectioned to confirm if dye had penetrated to the centers of the crystals as opposed to only being confined to the outer surfaces.

6. Thermogravimetric analysis of UMCM-15

Thermogravimetric analyses were performed on a TA Q50 equipment. Samples were activated before experiments. The temperature was ramped from 25 °C to 600 °C with a rate of 2 °C/ min under a flow of N_2 gas.

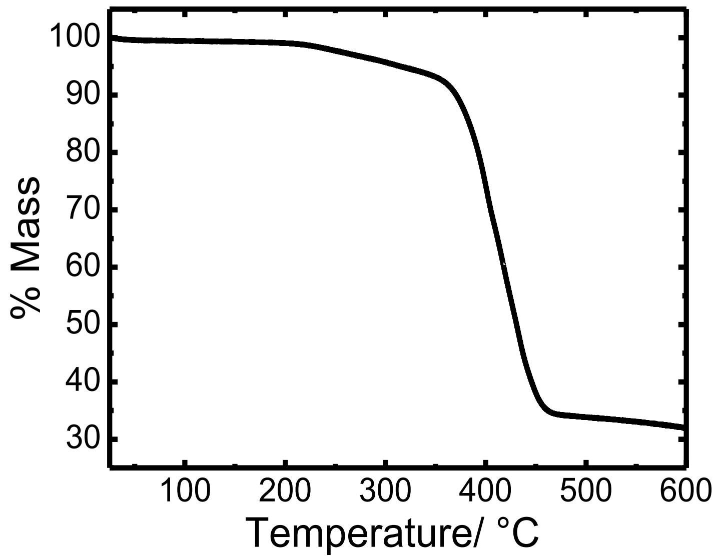

Figure S4. TGA trace of activated UMCM-15.

7. Gas sorption measurement

All materials were exchanged in fresh DMF for 12 hr followed by exchanging with dichloromethane for 24 hr. The solid was finally dried under reduced pressure (10^{-2} Torr).

N_2 adsorption/desorption isotherms were measured volumetrically at 77K in the range of $1.00 \times 10^{-5} \leq P/ P_0 \leq 1.00$ with an Autosorb-1C outfitted with the micropore option by Quantachrome Instruments (Boyton Beach, Florida, U.S.A.) 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 Gases and used as received.

Ar sorption experiments were performed in order to determine pore size distribution of UMCM-15 at 87K in the range of $1.00 \times 10^{-5} \leq P/ P_0 \leq 1.00$. Ultra-high purity Ar (99.999%) was purchased from Cryogenic Gasses. Pore size distributions were calculated applying Non-linear Density Functional Theory (NLDFT) zeolite/silica equilibrium transition kernel for Ar sorption at 87K based on cylindrical pore model as implemented in version 1.2 of the ASWin software package.

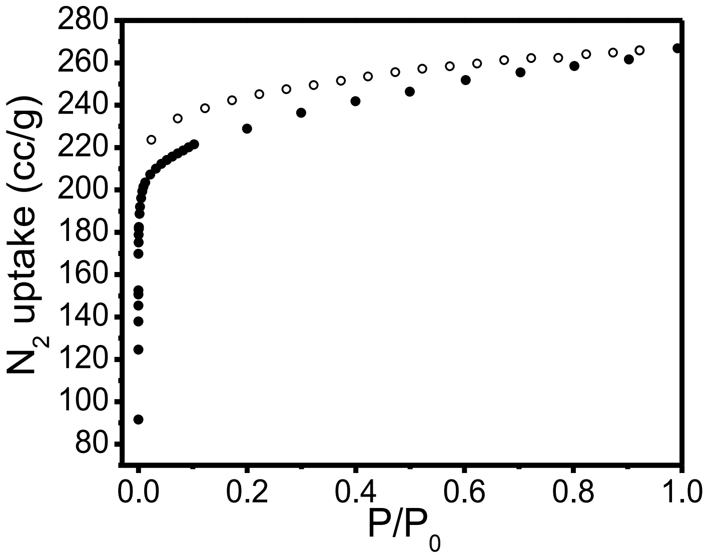

Figure S5. Nitrogen isotherm of activated UMCM-15 showing hysteresis.

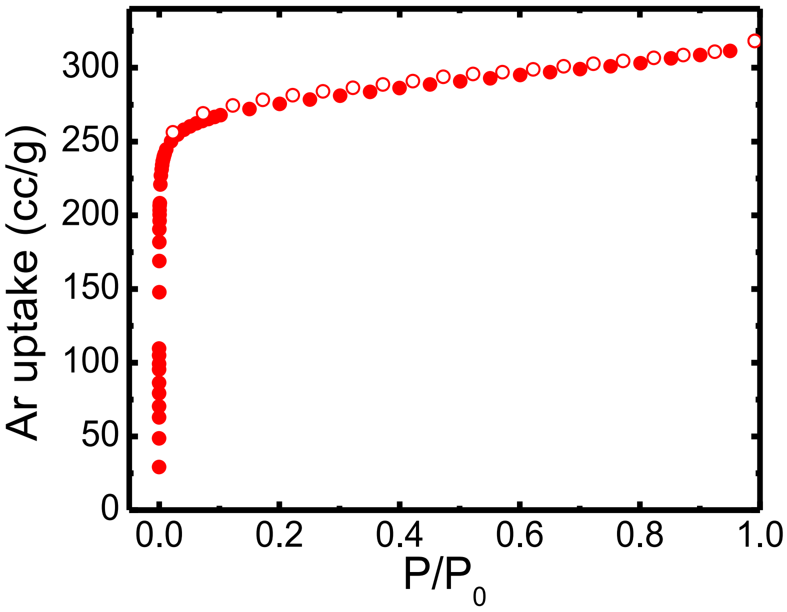

Figure S6. Ar sorption isotherm of activated UMCM-15.

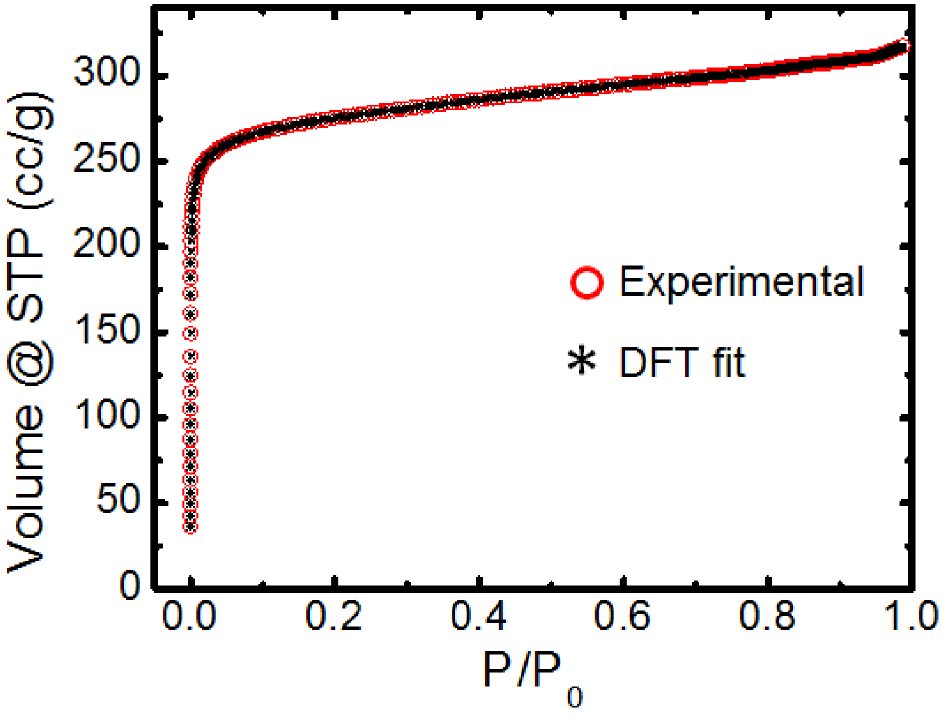

Figure S7. NLDFT model of Ar sorption isotherm of UMCM-15 based on a kernel for zeolite and silica with spherical/ cylindrical pores (fitting error of 0.046%). No more accurate NLDFT model was available.

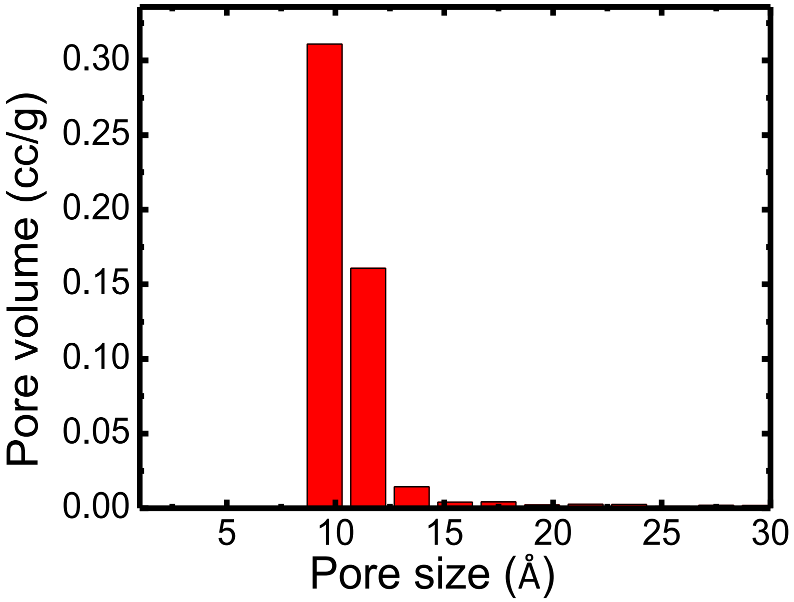

Figure S8. Pore distribution of activated UMCM-15 obtained from Ar sorption isotherm and subsequent NLDFT fitting.

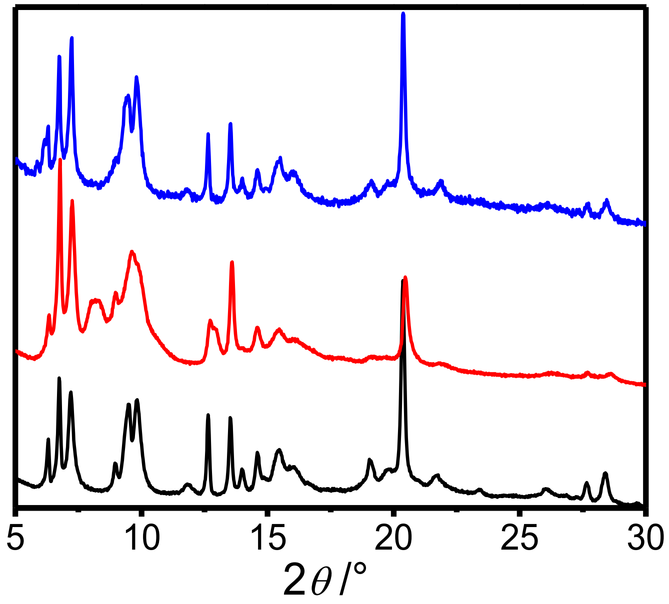

Figure S9. Powder X-ray Diffractograms of UMCM-15 (as synthesized: black, activated: red, resolvated: blue)