

A Mesoporous Metal-Organic Framework Based on a Shape-Persistent Macrocycle

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Supporting Information

General Methods and Materials	S2
Synthesis of Macrocyclic Ligand 1	S3
¹H NMR Spectrum of Ligand 1	S4
Synthesis of Zn-MCMOF	S4
X-Ray Crystallographic Analysis of Zn-MCMOF	S5
Fourier-Transform Infrared Spectrum of Zn-MCMOF	S6
Thermogravimetric Analysis of Zn-MCMOF	S7
Supercritical CO₂ Activation of Zn-MCMOF	S7
Gas Adsorption Isotherms	S8
Distribution of Pore Sizes	S9
Powder X-Ray Diffraction Patterns	S11
Production of the 3D Printed Model of the Crystal Structure of Zn-MCMOF	S11
References	S12

General Methods and Materials

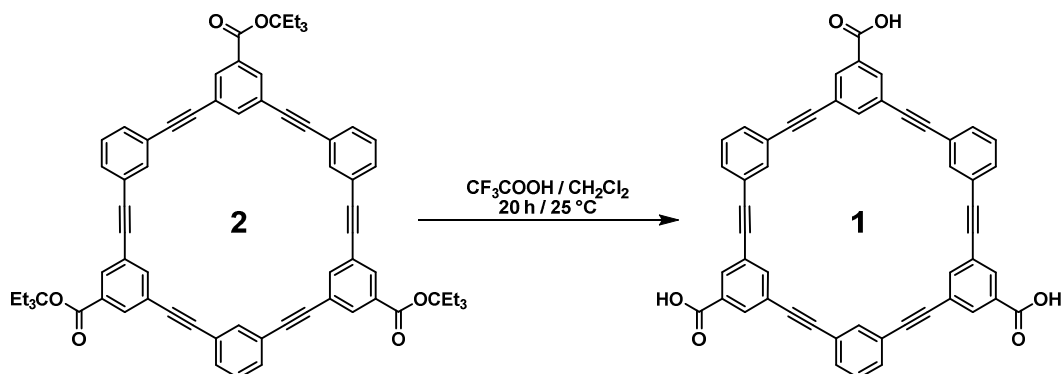
Round bottom flasks were used as reaction vessels for the synthesis of precursors, while standard scintillation vials were used as vessels for **Zn-MCMOF** synthesis. ^1H NMR spectra were recorded on the JEOL ECA-500 spectrometer using the peaks of TMS or residual solvent as standards (DMSO- d_6 : 2.50 ppm). Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer using Pike MIRacle Micrometer pressure clamp. High resolution mass spectral (HRMS) analyses were performed in the Mass Spectrometry Facility at the University of Texas at Austin using Micromass Autospec Ultima or Agilent Technologies 6530 Accurate Mass QtofLC/MS mass spectrometers. Microanalyses were conducted by Intertek USA, Inc. Thermogravimetric analyses (TGA) were carried out on a TA Instruments TGA 2050 thermogravimetric analyzer at a temperature ramping rate of 2 °C/min under the flow of N_2 gas. Powder X-ray diffraction (PXRD) data were collected at 25 °C on a Phillips X'pert Pro diffractometer. Capillary PXRD measurements were performed on a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector and an Incoatec 30 Watt Cu microsource with compact multilayer optics. Simulated PXRD patterns were calculated with the Material Studio software package^[1] employing the structure model from the single crystal data obtained.

The following starting materials and solvents were obtained from the respective commercial sources and used without further purification: dichloromethane, absolute EtOH (Aldrich); trifluoroacetic acid (Oakwood); $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar); *N,N*-dimethylacetamide (TCI). Ultra high purity grade (99.999%) N_2 , O_2 , CO_2 , He, and bone-dried cupercritical CO_2 with siphon tube were purchased from Matheson Tri-Gas.

Experiments are presented in the order following the discussion of the manuscript.

Compound numbers are identical to those in the main text of the manuscript.

Synthesis of Macrocyclic Ligand 1



Heptacyclo[37.3.1.1^{4,8}.1^{11,15}.1^{18,22}.1^{25,29}.1^{32,36}]octatetraconta-
1(43),4,6,8(48),11,13,15(47),18,20,22(46),25,27,29(45),32(44),33,35,39,41-octadecaen-
2,9,16,23,30,37-hexayne-6,20,34-tricarboxylic acid (1)

A 100 mL flask equipped with a magnetic stirring bar was charged with triester precursor **2**^[2] (0.96 g, 0.93 mmol) and CH_2Cl_2 (50 mL). Resulting clear solution was treated with trifluoroacetic acid (5 mL) under vigorous stirring. Reaction mixture was then vigorously stirred at 25 °C for 20 h. The crude triacid **1** that was formed as the precipitate during the reaction was filtered off and the solid was washed with fresh CH_2Cl_2 (3×30 mL). Obtained white solid was dried in vacuo for 2 h to provide the product (0.65 g, 96% yield). ¹H NMR (500 MHz, $\text{DMSO-}d_6$, 125 °C) δ 8.20–7.40 (m, 21H) ppm. HRMS (CI negative mode) *m/z*: calculated for $[\text{C}_{51}\text{H}_{24}\text{O}_6]^-$ 732.1573, found 732.1581. Due to the extremely low solubility of the product in all common deuterated solvents (including $\text{DMSO-}d_6$ at high temperature) all attempts to record a meaningful ¹³C NMR spectrum were unsuccessful.

¹H NMR Spectrum of Ligand 1

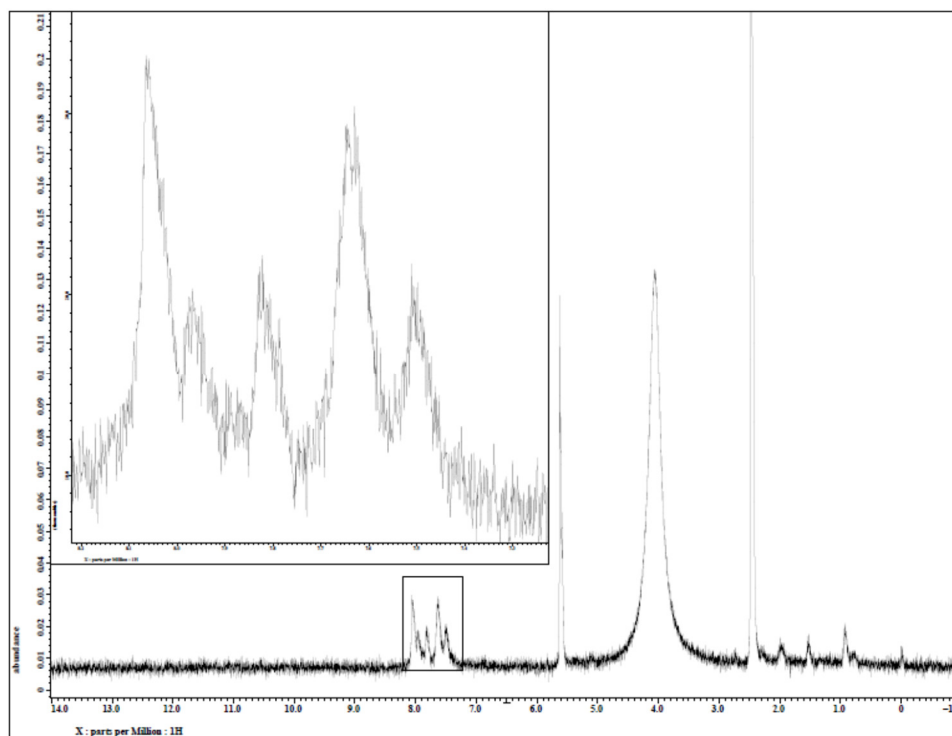


Figure S1. ¹H NMR spectrum of macrocyclic ligand **1**.

Synthesis of Zn-MCMOF

Macrocyclic ligand **1** (20 mg, 0.027 mmol) and Zn(NO₃)₂·6H₂O (14 mg, 0.047 mmol) were added to a 20 mL glass scintillation vial. DMA (8 mL) was added to the solids, and the mixture was sonicated for 10 min. The vial was capped and placed into an oven at 100 °C for 1 d, after which time yellowish crystals could be obtained. After cooling down, the liquid was decanted and replaced with fresh DMA three times in 1 d. The isolated crystals were soaked in absolute EtOH for 3 d, with EtOH being replaced every day. Supercritical CO₂ drying was then performed on wet crystals. Based on the activated sample, yield of 87% (20 mg) could be estimated, taking the macrocyclic ligand as the limiting reagent. FT-IR (neat): $\tilde{\nu}$ = 3605 (b), 3063 (b), 1699 (w), 1557 (s), 1434 (s), 1393 (s), 890 (s), 788 (s), 679 (s) cm⁻¹. Anal. calcd (%) for C₁₀₂H₄₂O₁₄Zn₃: C 72.53, H 2.49; Found: C 71.38, H 2.77.

X-ray Crystallographic Analysis of Zn-MCMOF

Preliminary diffraction experiments were performed at BL13BC1 beamline in NSRRC. The final structure data collection was performed at ChemMatCARS beamline at the Advanced Photon Source of the Argonne National Laboratory. The diffraction data was collected on a Bruker D8 diffractometer with an APEX-II CCD detector using phi scans. Data collection was 99.9% complete to 11.25° in θ . A total of 147936 reflections were collected covering the indices, $-26 \leq h \leq 25$, $-24 \leq k \leq 26$, $-26 \leq l \leq 26$. Indexing and unit cell refinement indicated a *P*-centered, cubic lattice. The space group was found to be $P4_132$ (No. 210). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms, except those in the severely disordered benzene ring (C10–C15), were refined anisotropically by full-matrix least-squares (SHELXL-97). Restraints were used both for the geometry (DFIX) and the displacement parameters (DELU). Benzene rings of the macrocyclic ligand **1** were both treated and refined as rigid bodies (AFIX 66). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. The SQUEEZE function of the PLATON program was used to remove disordered solvent.

Empirical formula	$C_{102}H_{42}O_{14}Zn_3$
Formula weight	1687.47
Temperature	296(2) K
Wavelength	0.49594 Å
Crystal system	Cubic
Space group	$P4_132$
Unit cell dimensions	$a = b = c = 33.261(4)$ Å $\alpha = \beta = \gamma = 90^\circ$
Volume	$36,796(8)$ Å ³
<i>Z</i>	4
Density (calculated)	0.305 Mg/m ³
Absorption coefficient	0.072 mm ⁻¹

F(000)	3424
θ range for data collection	0.60° to 11.25°
Index ranges	$-26 \leq h \leq 25, -24 \leq k \leq 26, -26 \leq l \leq 26$
Reflections collected	147,936
Independent reflections	3141 [$R(\text{int}) = 0.1088$]
Completeness to $\theta = 11.25^\circ$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6445
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3141 / 29 / 126
Goodness-of-fit on F^2	1.12
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0648, wR_2 = 0.1774$
R indices (all data)	$R_1 = 0.0892, wR_2 = 0.1879$
Absolute structure parameter	0.06(8)
Largest diff. peak and hole	0.118 and $-0.384 \text{ e}/\text{\AA}^3$

Fourier-Transform Infrared Spectrum of Zn-MCMOF

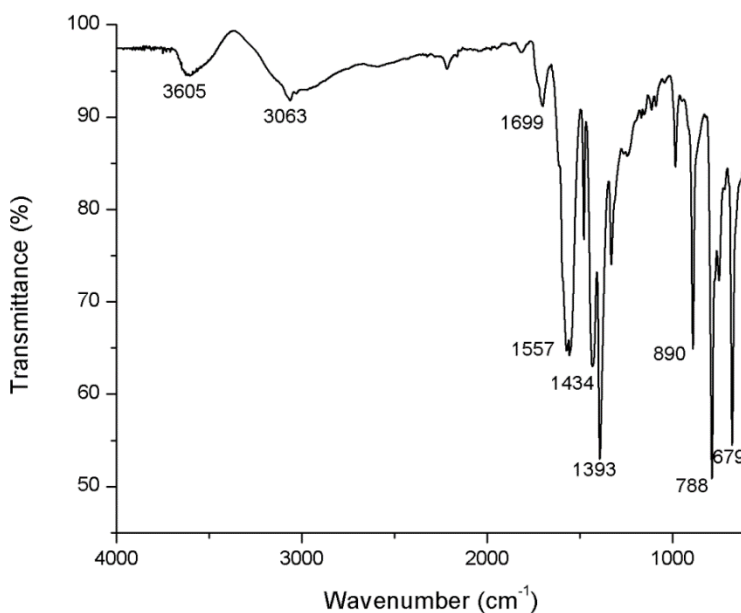


Figure S2. Fourier-transform infrared spectrum of Zn-MCMOF.

Thermogravimetric Analysis of Zn-MCMOF

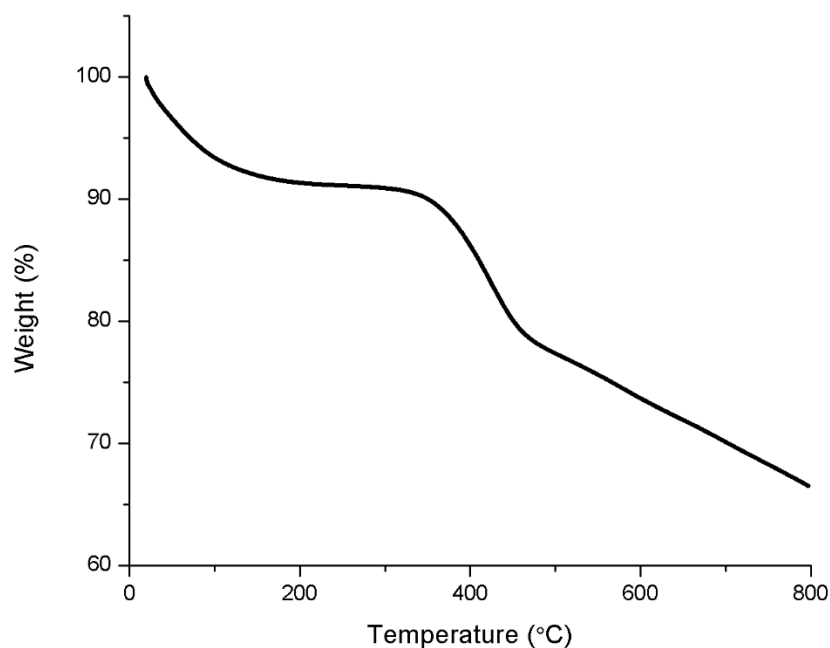


Figure S3. TGA trace of Zn-MCMOF.

Supercritical CO₂ Activation of Zn-MCMOF

Absolute EtOH was added to the crystals of Zn-MCMOF after the mother liquor was decanted. The EtOH was then decanted and replaced daily for 3 d and the crystals were left in EtOH until the next step. Approximately 60 mg of crystals were transferred into a Tousimis Samdri-PVT-3D supercritical CO₂ dryer. Excess EtOH was decanted, the temperature was lowered to 0 °C, and the chamber was filled with liquid CO₂ (ultrahigh grade CO₂ with a siphon tube from Matheson Tri-Gas Inc. was used). The sample was soaked for 48 h, venting 10 times for 10 min. The chamber was then heated to 40 °C and the pressure in the chamber was above 1300 psi. The supercritical CO₂ was bled off for 24 h until the chamber was at ambient pressure. The chamber was opened and the sample was quickly sealed and taken into an Ar atmosphere glove box for further manipulations.

Gas Adsorption Isotherms

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure N₂ adsorption isotherms. Samples of macrocyclic ligand and Zn-MCMOF weighing between 50 and 100 mg were transferred to a preweighed sample tube, which was then capped by a seal frit. Samples were heated to 120 °C under high vacuum (10⁻³–10⁻⁴ Torr) for 15 h. The evacuated sample tubes were weighed again, and the sample mass was determined by subtracting the mass of the previously tared tubes. Isotherms for the sorption of N₂ and O₂ were measured using a liquid nitrogen bath (77 K). Isotherms for the sorption of CO₂ were measured at 297 K and in a dry ice/isopropanol bath (195 K). Ultrahigh purity grade (99.999%) N₂ and He, oil-free valves, and gas regulators were used for all free space corrections and measurements. Relative pressure (P/P_0) range for BET analysis was taken from 5×10⁻⁵ to 0.1. The adsorption and desorption isotherms (Figure S4–S9) were displayed in filled and empty symbol, respectively.

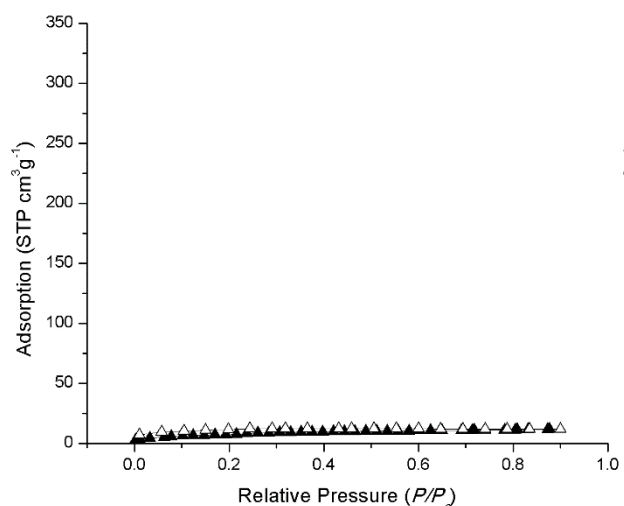


Figure S4. Adsorption/desorption isotherm for N₂ (77 K) in the powder of the macrocyclic ligand.

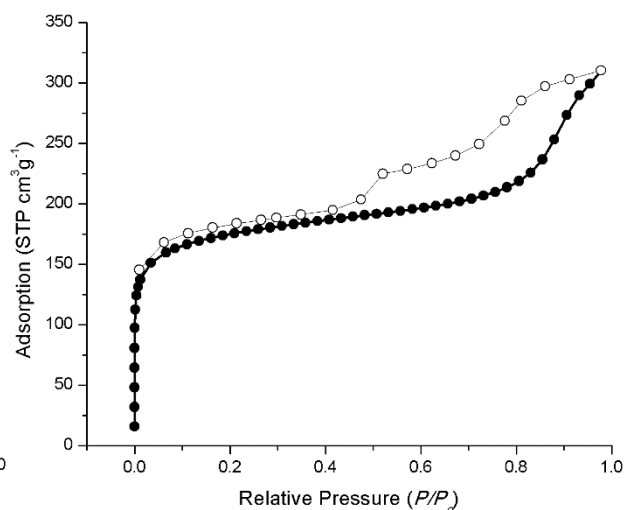


Figure S5. Adsorption/desorption isotherm for N₂ (77 K) in the crystals of Zn-MCMOF.

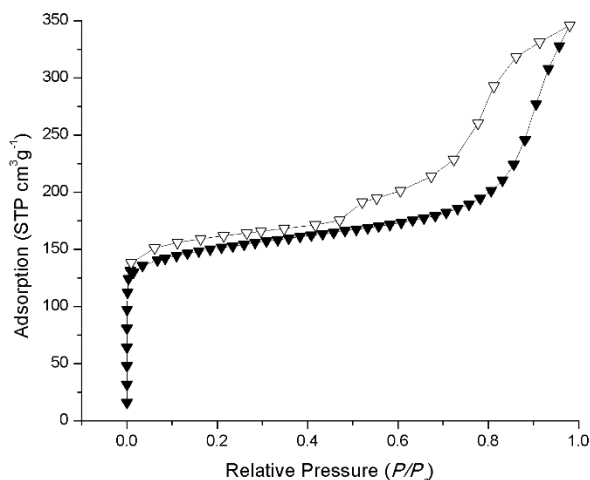


Figure S6. Adsorption/desorption isotherm for N_2 (77 K) in the resolvated **Zn-MCMOF**.

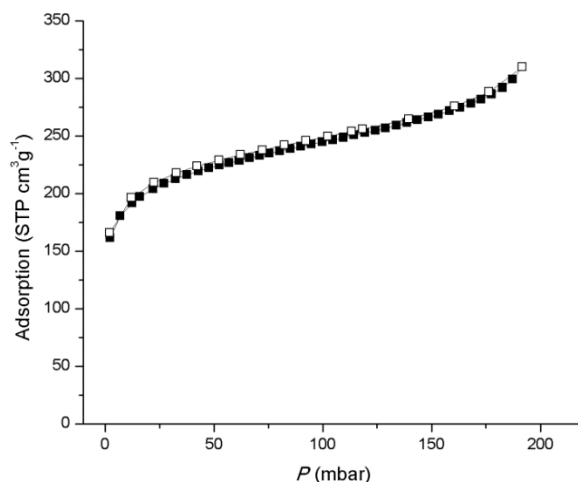


Figure S7. Adsorption/desorption isotherm for O_2 (77 K) in the crystals of **Zn-MCMOF**.

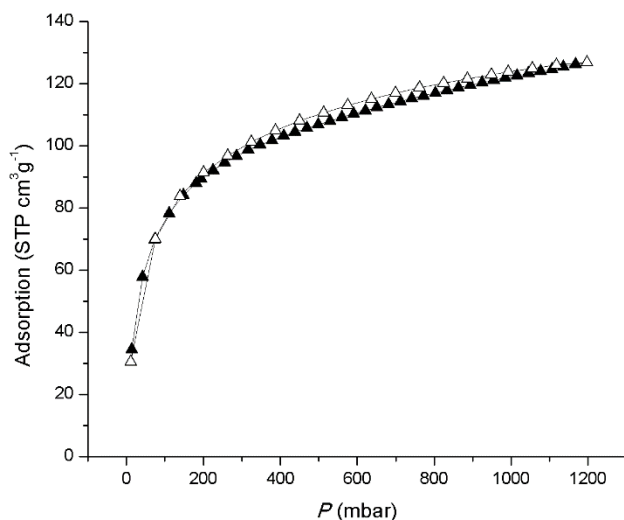


Figure S8. Adsorption/desorption isotherm for CO_2 (195 K) in the crystals of **Zn-MCMOF**.

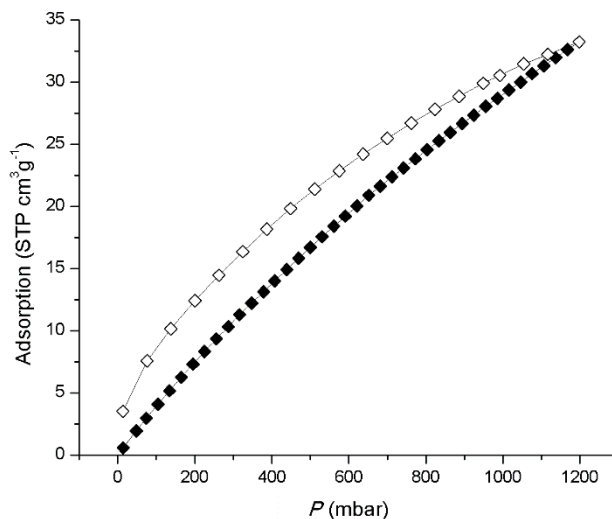


Figure S9. Adsorption/desorption isotherm for CO_2 (297 K) in the crystals of **Zn-MCMOF**.

Distribution of Pore Sizes

Micropore size distribution analysis was carried out using nonlocal density functional theory (NLDFT) method and normalized. Micropore area was calculated by t -plot micropore area from N_2 adsorption/desorption isotherm, and mesopore area was obtained by subtracting t -plot micropore area from BET specific surface area. Total pore volume was determined by the adsorption branch of N_2 isotherm curve at the $P/P_0 = 0.98$ single point.

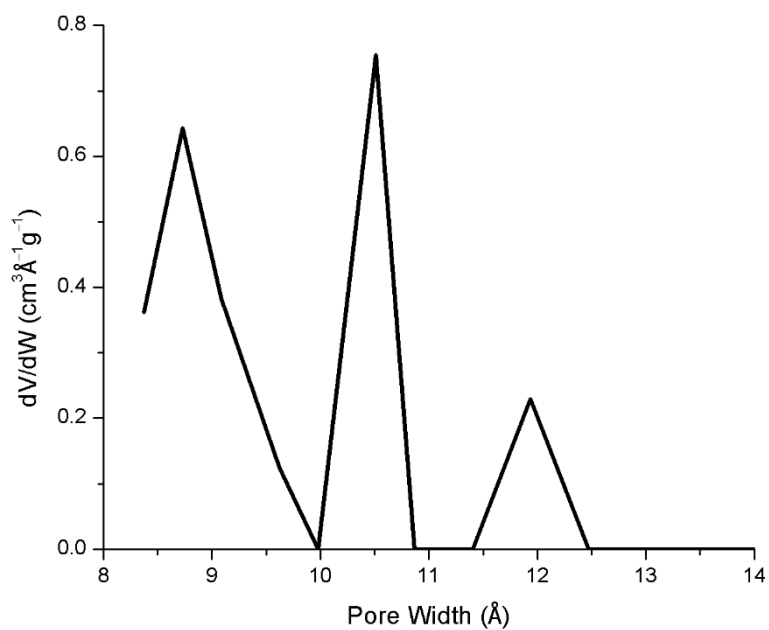


Figure S10. Micropore size distribution in **Zn-MCMOF**, as determined by the NLDFT method.

Powder X-Ray Diffraction Patterns

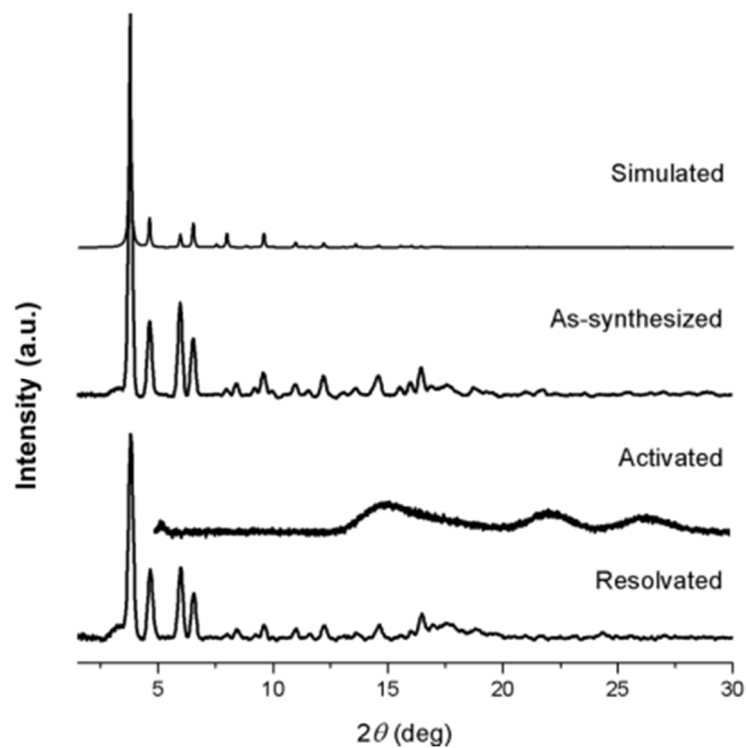


Figure S12. Powder X-ray diffraction (PXRD) patterns of Zn-MCMOF.

Production of the 3D Printed Model of the Crystal Structure of Zn-MCMOF^[3]

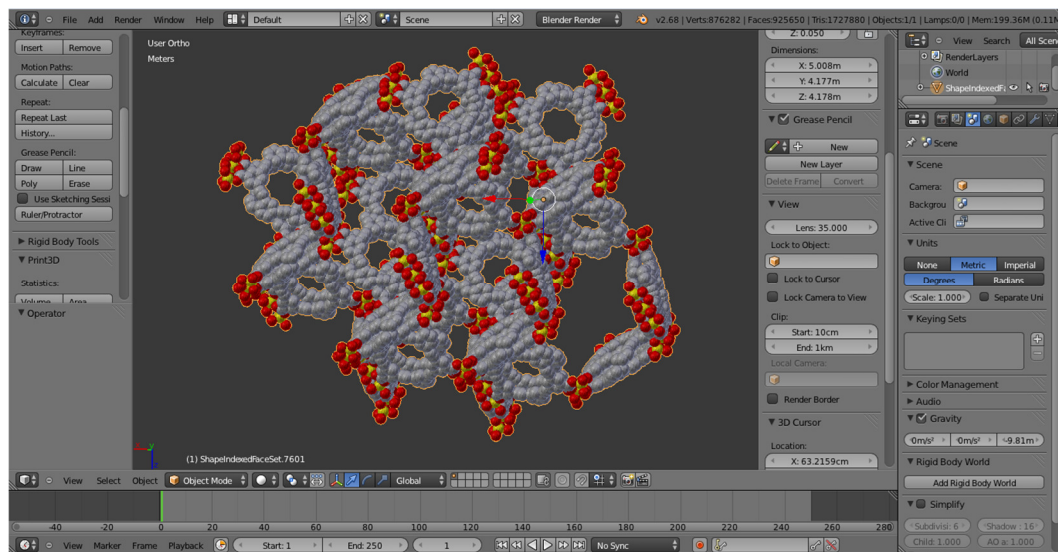


Figure S13. Processing of a model of the crystal structure of Zn-MCMOF prior to 3D printing.

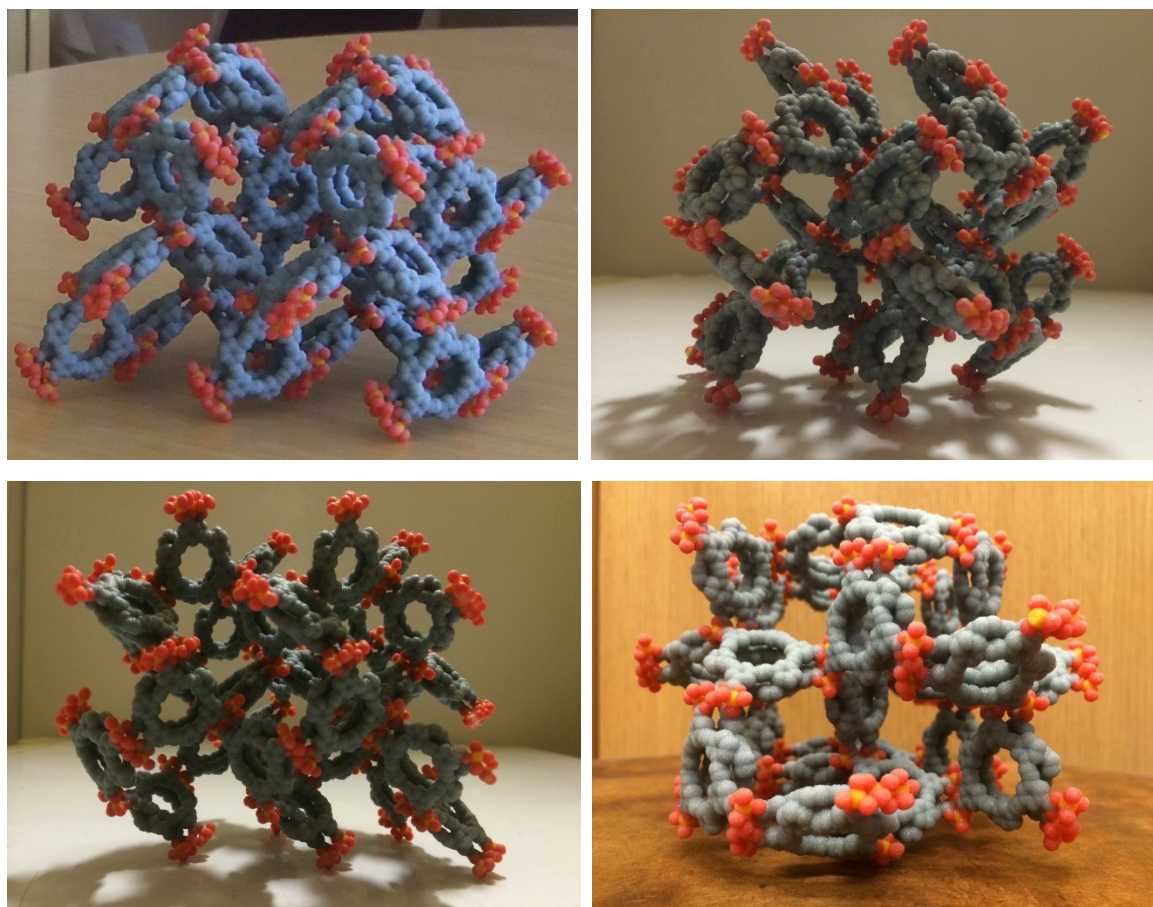


Figure S14. 3D printed model of Zn-MCMOF.

References

- [1] *Materials Studio* program, version 5.5; Accelrys, San Diego, CA, 2011.
- [2] I. Popov, T.-H. Chen, S. Belyakov, O. Daugulis, S. E. Wheeler and O. Š. Miljanić, *Chem. Eur. J.*, 2015, **21**, 2750.
- [3] T.-H. Chen, S. Lee, A. H. Flood and O. Š. Miljanić, *CrystEngComm*, 2014, **16**, 5488–5493.