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
'H 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

S1
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-d6: 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 N2 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); Zn(NO3)2·6H2O (Alfa Aesar); N,N-dimethylacetamide (TCI). Ultra high purity grade (99.999%) N2, O2, CO2, He, and bone-dried supercritical CO2 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[37.3.1.14,8.11,15.118,22.125,29.132]octatraconta-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 [0.96 g, 0.93 mmol] and CH₂Cl₂ (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 CH₂Cl₂ (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, DMSO-d₆, 125 °C) δ 8.20–7.40 (m, 21H ppm). HRMS (CI negative mode) m/z: calculated for [C₅₃H₅₄O₆]⁻ 732.1573, found 732.1581. Due to the extremely low solubility of the product in all common deuterated solvents (including DMSO-d₆ at high temperature) all attempts to record a meaningful ¹³C NMR spectrum were unsuccessful.
\textbf{Synthesis of Zn-MCMOF}

Macro cyclic ligand 1 (20 mg, 0.027 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (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 CO$_2$ drying was then performed on wet crystals. Based on the activated sample, yield of 87% (20 mg) could be estimated, taking the macro cyclic 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 C$_{102}$H$_{42}$O$_{14}$Zn$_3$: C 72.53, H 2.49; Found: C 71.38, H 2.77.

\textbf{Figure S1.} $^1$H NMR spectrum of macrocyclic ligand 1.
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 ≤ h ≤ 25, −24 ≤ k ≤ 26, −26 ≤ l ≤ 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.

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<td>Absorption coefficient</td>
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F(000) 3424

θ range for data collection 0.60 ° to 11.25 °

Index ranges −26 ≤ h ≤ 25, −24 ≤ k ≤ 26, −26 ≤ l ≤ 26

Reflections collected 147,936

Independent reflections 3141 \[ R(\text{int}) = 0.1088 \]

Completeness to θ = 11.25° 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 > 2σ(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 e/Å³

**Fourier-Transform Infrared Spectrum of Zn-MCMOF**

![Fourier Transform Infrared Spectrum](image)

**Figure S2.** Fourier-transform infrared spectrum of Zn-MCMOF.
Thermogravimetric Analysis of Zn-MCMOF

![Figure S3. TGA trace of Zn-MCMOF.](image)

Supercritical CO\textsubscript{2} 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 CO\textsubscript{2} dryer. Excess EtOH was decanted, the temperature was lowered to 0 °C, and the chamber was filled with liquid CO\textsubscript{2} (ultrahigh grade CO\textsubscript{2} 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 CO\textsubscript{2} 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 N$_2$ 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 N$_2$ and O$_2$ were measured using a liquid nitrogen bath (77 K). Isotherms for the sorption of CO$_2$ were measured at 297 K and in a dry ice/isopropanol bath (195 K). Ultrahigh purity grade (99.999%) N$_2$ and He, oil-free valves, and gas regulators were used for all free space corrections and measurements. Relative pressure ($P/P_o$) range for BET analysis was taken from $5\times10^{-5}$ 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 N$_2$ (77 K) in the powder of the macrocyclic ligand. **Figure S5.** Adsorption/desorption isotherm for N$_2$ (77 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 $P/P_o = 0.98$ 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

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

