Microporous Cyclen-Based Octacarboxylate Hydrogen-Bonded Organic Framework Exhibiting Selective Gas Adsorption

ABSTRACT: A microporous hydrogen-bonded organic framework (HOF) was successfully prepared by a cyclen-based octacarboxylate ligand H₈tacnip-Zn. The obtained three-dimensional structure presents a periodic double-layer unit that stacks to form a one-dimensional channel that buttresses discrete cavities (∼5.6 × 5.6 Å²). From the single crystal structure, the macrocycle-bound metal ion was proven to greatly enhance the rigidity of the cyclen-based ligand while adjusting the direction of the carboxyl groups. The indelible porosity of degassed HOF was elucidated by CO₂ sorption and selective gas adsorption. This work provides facile access to construct more porous HOFs based on a cyclen unit.

INTRODUCTION

Crystalline porous materials have attracted diverse research attention in terms of exploring novel multifunctional materials in the last two decades. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), which are constructed via coordination and covalent bonds, are two popular crystalline porous materials lately and are receiving increasing research attention in gas capture and separation, catalysis, energy storage, drug delivery, and sensing. However, the flexibility of the cyclen-based ligand contributes negatively by forming strong and directional interactions inside HOFs structures. Taking advantage of the reactive amine sites in azamacrocycle, a metal center could be introduced and act as a catalytic center, open binding site, or chromophore. More importantly, the chelating in the middle of the macrocycle could tremendously increase the rigidity of the cyclen-based ligand. To increase donating/accepting groups, an isophthalic acid group was selected to decorate the tetra-carboxyl ligand, affording a new octacarboxyl ligand H₈tacnip, which is anticipated to construct a robust HOF.

Herein, we report a robust microporous hydrogen-bonded metal-macroyclic framework HMMCF-1, comprising H₈tacnip-Zn ligands linked via the intermolecular hydrogen-bonding interactions and π−π interaction. The obtained 3-D structure displays a repeated double-layer unit (Scheme 1, repeated layer = A and B layer) which stacks to form one-dimensional aromatic columns that buttress discrete cavities (∼5.6 × 5.6 Å²). It was found that the macrocycle-bound metal ion greatly enhances the rigidity of the cyclen-based ligand while adjusting the direction of the carboxyl groups.

Received: June 30, 2019
Revised: August 23, 2019
Published: September 13, 2019

DOI: 10.1021/acs.cgd.9b00851
Scheme 1. Illustrative Scheme of the Molecular Structures of H₈tacnip together with Hydrogen-Bonded Metal Organic Framework Topologies

H₈tacnip = 5,5′,5″-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrasiphalic acid

Importantly, the desolvated framework manifests permanent porosity and selective adsorption of CO₂ over N₂.

■ EXPERIMENTAL SECTION

General Remarks. Highly pure commercially available reagents were obtained from Fisher Scientific or Sigma-Aldrich and used as received.

Synthesis of Dimethyl 5-Methylisophthalate. A methanol (100 mL) solution of 5-methyl isophthalic acid (10 g, 0.056 mol) was prepared first, and then sulfuric acid (2 mL, concentrated) was added at room temperature, and the mixture was refluxed overnight. The reaction mixture was cooled and poured into 1 L of water. The precipitate was filtered and washed by copious volumes of water. The solid product was collected and dried overnight in a vacuum. Dimethyl 5-(bromomethyl) isophthalate was obtained as a buff powder with the yield of ~75%.

Synthesis of Dimethyl 5-(Bromomethyl)isophthalate. Bromination of dimethyl 5-methylisophthalate (10 g, 48.03 mmol) was done in 100 mL of CCl₄ with N-bromosuccinimide (9.4 g, 52.83 mmol) and a trace of AIBN [2,2′-azobis(2-methylpropionitrile)]. The mixture was refluxed for 6 h and then cooled down and filtered. The solution was dried over sodium sulfate and evaporated to afford a yellowish solid, which was further purified by column chromatography using n-hexane/ethyl acetate (10:1). Yield: 6.5 g, 47%.

Synthesis of H₈tacnip. First, 1,4,7,10-tetracyclododecane (1.5 mmol, 258 mg) and methyl 4-(bromomethyl) benzoate (7.2 mmol, 1.65 g) was dissolved in 100 mL of acetonitrile. Then, solid K₂CO₃ (1.5 g, 10.85 mmol) was introduced, and the suspension was refluxed for 24 h. The solvent was removed by a vacuum, and the residue was partitioned between CH₂Cl₂ and water. The organic layer was collected and washed by brine, dried over sodium sulfate, and recrystallized from hexane/ethyl acetate mixed solvent to yield crystalline product of Me₈tacnip (0.813 g, 54%). Solution of Me₈tacnip 0.997 g (1.0 mmol) and ZnCl₂ (1.36 g, 10.0 mmol) in 50 mL of DMF was refluxed for 3 h. The mixture was then cooled to RT, and 100 mL of H₂O was added. The resultant precipitate was filtered and washed thoroughly with water. The produced solid was dissolved in methanol (50 mL) and mixed with potassium hydroxide (0.50 g, 8.9 mmol) aqueous solution (25 mL). After being refluxed for one night, the volatile component was evaporated under reduced pressure, and the remaining solution was neutralized with HCl (1 M).

The precipitated solid was collected and washed thoroughly with deionized water. After being dried in vacuum oven, H₈tacnip-Zn was obtained as a white powder.

Synthesis of HMMCF-1. H₈tacnip-Zn (5.0 mg, 0.0053 mmol) was dissolved in a solution of 1,4-dioxane (0.8 mL) and H₂O (0.2 mL) with its pH adjusted to 5 using hydrochloric acid. After being sonicated for 1 h, the mixture was loaded into a Pyrex tube, sealed under a vacuum, and heated to 100 °C for 48 h. A very low yield of needle-shape crystals was obtained (Figure 1c, yield: 9.0% based upon ligand).

Physical Measurements. The powder X-ray diffraction (PXRD) data for HMMCF-1 were collected using a Bruker D8 Advance, Cu Kα radiation of 40 mA, 40 kV, λ = 0.15418 nm, 2θ scanning range of 2–40°, a scan step size of 0.02° and a time of 3 s per step. HMMCF-1 crystals were pretreated by acetone and chloroform, and then degassed for 24 h to 6 μm Hg at room temperature to provide an activated phase. Various gas sorption isotherms of HMMCF-1 were determined on a Micromeritics ASAP 2020 surface area analyzer, and the measurement temperature was maintained at 273 K with an ice–water bath and 296 K with a water bath.

RESULTS AND DISCUSSION

Synthesis of H₂tacctip and HMMCF-1. The esterification reaction of 5-methyl isophthalic acid in methanol solvent afforded dimethyl 5-methylisophthalate. Then, the bromination reaction between dimethyl 5-(bromomethyl)isophthalate and N-bromosuccinimide (NBS) produced dimethyl 5-(bromomethyl)isophthalate. Next, Me₈tacnip was prepared by the reaction of 1,4,7,10-tetracyclododecane and dimethyl 5-(bromomethyl)isophthalate in MeCN. The metal center was introduced by refluxing Me₈tacnip with metal salt in DMF. H₈tacnip-Zn (Figure 1a) was obtained by hydrolysis in the presence of KOH and acidified using HCl. Colorless crystals of HMMCF-1 (Figure 1c) were obtained by mixing H₂tacctip-Zn, 1,4-dioxane, and H₂O in a pyrex tube and then heating in oven at 100 °C and autogenous pressure for 48 h. The incorporation of the zinc ion in the middle of cyclen proved to be crucial for increasing the rigidity of ligand and assembling robust HOFs. Virtually, without the chelating of metal in the middle of the octacarboxylate ligand, only amorphous materials can be formed.

Crystal Structure of HMMCF-1. Single-crystal X-ray diffraction (SCXRD) study revealed that HMMCF-1 belongs to the tetragonal system with the I4mm space group. The intermolecular interactions, present in HMMCF-1, consist mainly of a combination of strong/weak hydrogen bonding along with π–π interactions. The isophthalate pendant carboxylic acid associate with one another in a cyclic tetramer.
arrangement (Figure 1b); the tetrameric assembly exhibits strong hydrogen bonding interactions, with donor-acceptor distances of 2.56 Å. The overall cycle is approximately planar, in which all atoms falling within 0.2 Å of the mean plane defined by the eight carboxylic acid carbons. Extended propagation of these cyclic tetramer arrangements leads to a pattern of a two-dimensional sheet parallel to the crystallographic ab plane, enclosing square cavities in a checkerboard-type arrangement. Parallel-displaced π−π interactions between the aromatic rings of the isophthalate pendant exist perpendicularly to the hydrogen bonding sheets, with a minimum carbon−carbon distance of 3.571 Å. Stacking of a series of double layers forms one-dimensional aromatic columns that buttress discrete cavities bracketed by macrocyclic moieties.

The phase purity of HMMCF-1 was confirmed by PXRD analysis. As shown in Figure 3, the PXRD patterns of HMMCF-1(Zn) are consistent with the calculated pattern derived from the SCXRD. After treatment over the temperature range 80−180 °C, the resulting materials are consistent with the original species, thereby establishing the robust nature and thermal stability in this temperature range. Moreover, the crystals of HMMCF-1 were treated in water for 24 h, and the PXRD pattern of immersed sample reveals that HMMCF-1 is very stable in water. The aqueous stability mainly comes from the compensation of π−π interactions. The formation of parallel-displaced π−π interactions between the aromatic rings stabilizes the framework even though the hydrogen bonding was influenced by the penetration of water.

**Adsorption and Selectivity.** The combination of hydrogen bond and π−π interactions results in excellent thermal stability, as shown from the PXRD patterns at different temperature ranges (Figure 3). HMMCF-1 also retains structural integrity and crystallinity upon solvent exchange as well as removal of guest molecules under a vacuum. During the crystalline growth, high boiling point solvents were avoided to prevent its influence in self-assembly process. After solvent exchange with acetone and chloroform, HMMCF-1 was degassed at RT under a high vacuum for 24 h to remove the solvent molecules located in the cavities. As shown in Figure 3, the PXRD pattern of activated sample retains its crystallinity, which is very coherent with that of the as-synthesized phase, indicating the robust nature of HMMCF-1.

The Langmuir surface area is deduced to be 113 m²/g. CO₂ uptake is ~45 cm³/g at 196 K and 1 atm, and the experimental pore volume of HMMCF-1 was calculated as 0.11 cm³/g. The CO₂ adsorption isotherms were collected to investigate the adsorption properties of as-obtained HMMCF-1. Given the limited N₂ uptake, the separation ratios of CO₂ versus N₂ are calculated from the ratio of the initial slopes of the adsorption isotherms, which are 5.0 at 273 K and 5.3 at 298 K.

**CONCLUSION**

To conclude, HMMCF-1 was successfully constructed through a rational design strategy. On the basis of complementary hydrogen bonding and π−π interactions, HMMCF-1 shows high chemical and thermal stability, as revealed in the SCXRD and PXRD results at different temperature ranges. The activated HMMCF-1 sample exhibits permanent porosity and a remarkable selectivity for CO₂/N₂ selective adsorption. This work shows the promise to construct variety of cyclen
containing organic ligands to fabricate porous HOFs based on cyclen unit (Scheme 1). Further applications of cyclen-based HOFs are under investigation.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00851.

Synthetic procedures of related compounds and X-ray diffraction data (PDF)

Accession Codes

CCDC 1937392 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: sqma@usf.edu.

ORCID®

Shengqian Ma: 0000-0002-1897-7069

Author Contributions

C. Stackhouse and J. Ren contributed equally.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge NSF (DMR-1352065) and the University of South Florida for financial support of this work. The authors would like to express their sincere appreciation to the Deanship of Scientific Research at King Saud University for funding this research through Grant No. RG-1435-010.

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