


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

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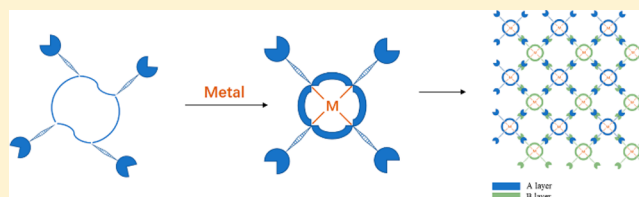
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Supporting Information

ABSTRACT: A microporous hydrogen-bonded organic framework (HOF) was successfully prepared by a cyclen-based octacarboxylate ligand $H_8tacnip$ -Zn. The obtained three-dimensional structure presents a periodic double-layer unit that stacks to form a one-dimensional channel that buttresses discrete cavities ($\sim 5.6 \times 5.6 \text{ \AA}^2$). 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 CO_2 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.^{1–14} Unlike the above-mentioned crystalline porous materials, hydrogen-bonded organic frameworks (HOFs) are relatively new crystalline porous materials built by organic building blocks connected based on weak intermolecular interactions.^{15–20} The permanent porosity of HOFs was not developed until 2010, which could be attributed to the weak and complicated interaction patterns inside them. The primary advantage for HOFs is their facile synthesis via crystallization, and more importantly they can be simply recycled and processed using a solution chemistry approach, hence making them unique porous materials for various applications and device fabrications.²¹

Given the “soft” and “flexible” nature of the interactions inside HOFs, together with the presence of immense donating/accepting groups, the design of topologies and controlled assembly of HOFs in single-component systems can be challenging and usually results in amorphous materials. In this case, the precise design of a ligand is required to ensure it is chemically and geometrically adaptable to provide strong and directional interactions.²²

By functionalization of the parent macrocycles, cyclen (1,4,7,10-tetraazacyclododecane) derivatives are one of the most extensively studied ligands in coordination chemistry.^{23–26} 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 tetraazamacrocycle, affording a new octacarboxyl ligand 5,5',5''-((1,4,7,10-tetraazacyclododecane-1,4,7-tetrayl) tetrakis (methylene)) tetra-isophthalic acid ($H_8tacnip$), which is anticipated to construct a robust HOF.

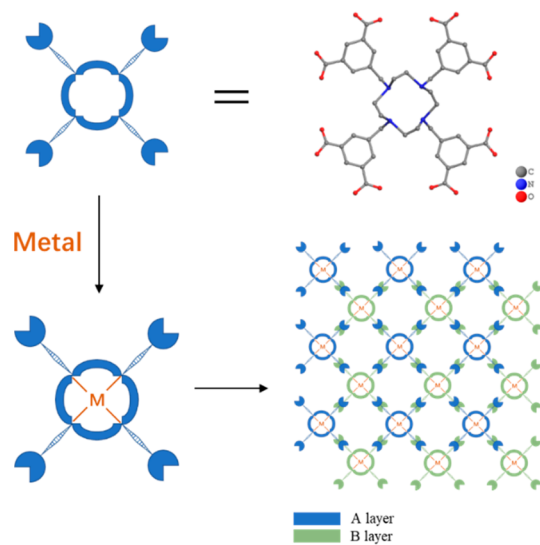
Herein, we report a robust microporous hydrogen-bonded metal-macrocycle framework HMMCF-1, comprising $H_8tacnip$ -Zn ligands linked via the intermolecular hydrogen-bonding interactions and π - π interaction. The obtained 3-D structure displays a repeated double-layer unit (Scheme 1, repeated layer = A and B layer) which stacks to form one-dimensional aromatic columns that buttress discrete cavities ($\sim 5.6 \times 5.6 \text{ \AA}^2$). 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.

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Scheme 1. Illustrative Scheme of the Molecular Structures of H_8 tactnip^a together with Hydrogen-Bonded Metal Organic Framework Topologies



^a H_8 tactnip = 5,5',5''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis (methylene) tetraisophthalic acid

Importantly, the desolvated framework manifests permanent porosity and selective adsorption of CO_2 over N_2 .

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 CCl_4 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 H_8 tactnip. 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 K_2CO_3 (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 CH_2Cl_2 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 Me_8 tactnip (0.813 g, 54%). Solution of Me_8 tactnip 0.997 g (1.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in 50 mL of DMF was refluxed for 3 h. The mixture was then cooled to RT, and a 100 mL of H_2O 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, H_8 tactnip-Zn was obtained as a white powder.

Synthesis of HMMCF-1. H_8 tactnip-Zn (5.0 mg, 0.0053 mmol) was dissolved in a solution of 1,4-dioxane (0.8 mL) and H_2O (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).

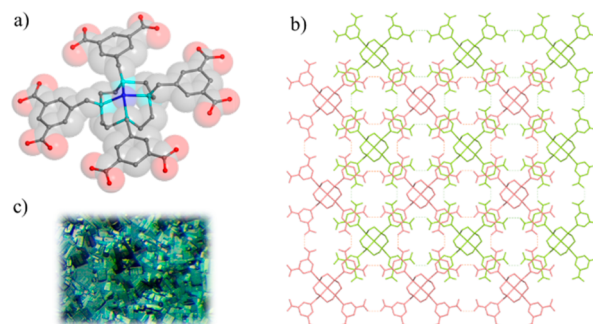


Figure 1. (a) Building block of H_8 tactnip-Zn, (b) two neighboring 2D supramolecular grids in different colors, (c) microscopic picture of the as-synthesized HMMCF-1.

Physical Measurements. The powder X-ray diffraction (PXRD) data for HMMCF-1 were collected using a Bruker D8 Advance, $Cu K\alpha$ radiation of 40 mA, 40 kV, $\lambda = 0.15418$ 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 μ m 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 H_8 tactnip 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, Me_8 tactnip 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 Me_8 tactnip with metal salt in DMF. H_8 tactnip-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 H_8 tactnip-Zn, 1,4-dioxane, and H_2O 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.

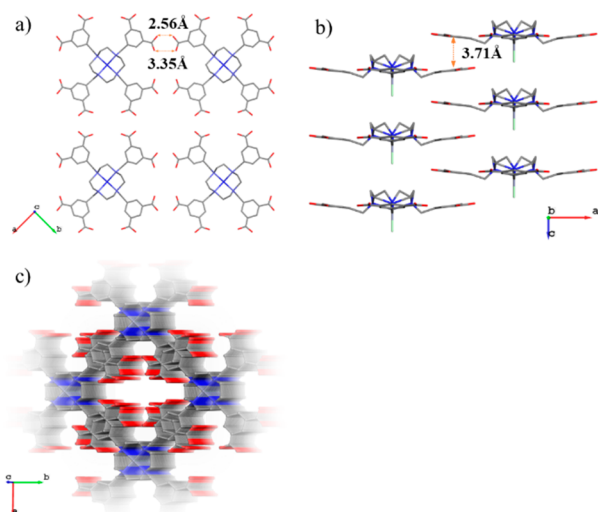


Figure 2. SCXRD structure of HMMCF-1 showing (a) a two-dimensional supermolecular sheet connected via intermolecular hydrogen bond, (b) parallel-displaced π – π interactions between the aromatic rings of the isophthalate pendant, and (c) packing of the 3D framework.

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

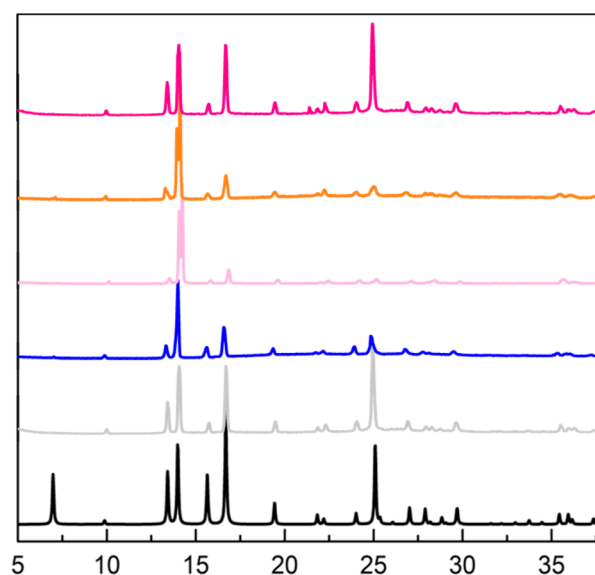


Figure 3. Powder X-ray diffraction patterns of HMMCF-1 showing a calculated pattern (black), as-synthesized HMMCF-1 (gray), the phase after treatment at 80 °C (blue), 180 °C (pink) overnight in air, the phase after treatment in water (orange), and upon the removal of guest molecules (red).

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.

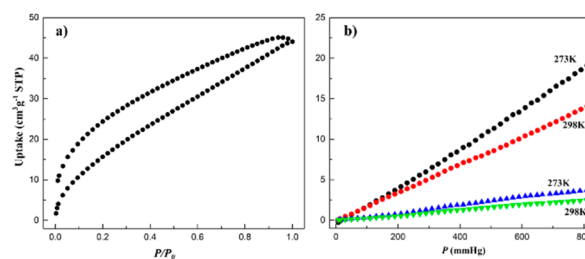


Figure 4. (a) Adsorption/desorption isotherms for CO₂ in HMMCF-1 at 195 K; (b) adsorption isotherms of HMMCF-1 for CO₂ (black and red) and N₂ (blue and green) at 273 and 298 K.

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.

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Notes

The authors declare no competing financial interest.

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