

A Highly Porous Interpenetrated Metal–Organic Framework from the Use of a Novel Nanosized Organic Linker

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Supporting Information

ABSTRACT: The initial use of a novel elongated tricarboxylic acid H₃hmpib in metal–organic framework (MOF) chemistry resulted in a [Zn₄O(hmpib)₂] MOF (UCY-1) with pyrite topology. The compound displays a remarkably high internal surface area despite its double-interpenetrated structure as well as high CO₂ uptake and selective adsorption for it over CH₄.

The research activity on metal–organic frameworks (MOFs) has expanded tremendously in the past decade. This is not surprising because this unique class of materials revealed a plethora of new structural topologies and extraordinary physical properties.^{1–4} The key for the fascinating properties of MOFs is their high porosity, which can be realized because of the robustness of their structures. Highly porous MOFs display very useful properties and potential applications in various important fields, including gas storage and separation,^{5–10} catalysis,¹¹ drug delivery,¹² sensing, etc.¹³

An apparent strategy toward highly porous MOFs consists of the use of elongated polytopic organic ligands. A significant drawback of this approach is the tendency to isolate MOFs with structures of limited robustness that tend to collapse upon guest removal. However, properly designed extended organic molecules with rigid linkages can stabilize quite robust MOFs with exceptionally high permanent porosity.^{14–18}

We have designed, synthesized and report here a novel nanosized tricarboxylic acid H₃hmpib [H₃hmpib = 4,4',4''-(1E)-[4,4',4''-(hydroxymethanetriyl)tris(benzene-4,1-diyl)tris(azan-1-yl-1-ylidene)]tris(methan-1-yl-1-ylidene)tribenzoic acid; Figure 1]. This ligand contains imine (CH=N) linkages that can restrict to some degree the flexibility of this largely extended organic molecule and may provide sufficient rigidity to the structure of MOFs. Indeed, we demonstrate the capability of the hmpib³⁻ ligand to stabilize highly porous MOFs through isolation of a new nanoporous MOF material. Herein, we present the synthesis, structure, and gas sorption data for [Zn₄O(hmpib)₂], denoted as UCY-1 (UCY = University of Cyprus), which displays a highly porous double-interpenetrated structure. UCY-1 represents a rare example of a catenated MOF with quite high internal surface area (~2600 m²/g) and also

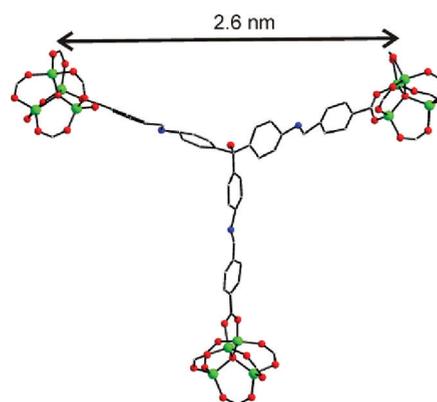


Figure 1. The ligand hmpib³⁻ connected to three SBUs in UCY-1. Color code: Zn, green; O, red; N, blue; C, gray.

displays high CO₂ uptake and selectivity for it over CH₄ at near-ambient temperature.

The H₃hmpib ligand was synthesized via a Schiff base condensation of tris(4-aminophenyl)methanol (pararosaniline base) with 4-formylbenzoic acid in ethanol. Compound UCY-1 was prepared by the reaction of Zn(NO₃)₂ or Zn(OAc)₂ and H₃hmpib in *N,N*-dimethylformamide at 100 °C. The compound crystallizes in the trigonal space group R3.¹⁹ The structure contains the octahedral cluster [Zn₄O(COO)₆] as the secondary building unit (SBU; Figure 1). The cluster is formed by a Zn₄O tetrahedron and six μ₂-COO⁻ groups from six hmpib³⁻ ligands and extends infinitely, creating a (3,6)-connected net, with the clusters and ligands representing the 6-c and 3-c nodes, respectively. Accordingly, the charge-balanced framework formula is [Zn₄O(hmpib)₂]. The distance between two neighboring SBUs (expressed as the separation between the μ₄-oxo groups of two adjacent SBUs) that are bridged by the same tricarboxylato ligand is ~2.6 nm (Figure 1). The structure is double-interpenetrated, consisting of two interwoven identical nets with pyrite (pyr) topology and Schläfli symbol {6³}₂{6¹².8³} (Figure S1 in the Supporting

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Information, SI). Despite the interpenetration, compound UCY-1 displays a highly porous structure (Figure 2, top).

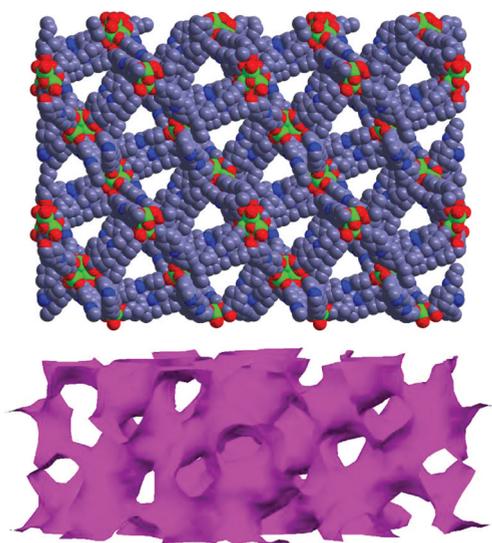


Figure 2. Top: Space-filling representation of the structure of UCY-1. Color code: Zn, green; O, red; N, blue; C, gray. Bottom: Representation of the pore network of UCY-1 (only pores and channels with diameter ≥ 4 Å are shown).

The solvent-accessible volume calculated by *PLATON*²⁰ is 57652 Å³, corresponding to 76.8% of the unit-cell volume. The 3D structure contains large cavities with a maximum diameter of ~ 13.7 Å, as found by *PLATON* (taking into account the van der Waals radii of the atoms). A representation of the voids using the structure visualization program *MERCURY*²¹ reveals a continuous and complex 3D pore network, where the large cavities communicate through relatively wide channels with a diameter ≥ 4 Å (Figure 2, bottom). As expected, the hmpib³⁻ ligands deviate from planarity. Specifically, the phenyl rings of the core Ph₃COH of the ligands are significantly tilted toward each other with dihedral angles of approximately 70–90°. However, the phenyl rings of each PhN=CHPhCOO⁻ moiety are less tilted toward each other (dihedral angles of approximately 8–45°) presumably because of the presence of the semirigid N=CH functionalities. The hydroxylic groups of half of the ligands are involved in relatively strong hydrogen bonds (O...O 2.7–3.0 Å). These hydrogen bonds are formed between the two different interpenetrated nets. Specifically, each Zn₄O(COO)₆ of one net is hydrogen-bonded (through its carboxylic oxygen atoms) with the OH group of one ligand of the second net. Thus, the structure of UCY-1 could be alternatively described as an unprecedented trinodal (3,4,7)-connected net with Schläfli symbol {4³.6¹².8⁶}{4³.6³}{6³} considering that each SBU is involved in six covalent and one hydrogen-bonding interactions with seven ligands, half of which now serve as 4-c nodes (Figure S2 in the SI). The latter net can be simplified down to a uninodal 15-c net with Schläfli symbol {3³³.4⁶⁰.5¹²}, by contracting the 3-c and 4-c nodes to the 8-c nodes (Figure S3 in the SI).

Although several examples of MOFs with pyr topology have been reported,^{9,22–29} the combination of double interpenetration^{9,22,25,28} and hydrogen-bonding interactions between the interpenetrated nets, such as that observed in UCY-1, is quite uncommon for such networks. At this point, we should note that the hmpib³⁻ ligand is one of the most extended

tricarboxylic ligands ever used for the construction of MOFs, significantly longer than many reported polyaromatic tricarboxylic acids such as TCA,²² BTB,³⁰ etc. In fact, the hmpib³⁻ ligand is comparable in size to the BBC ligand employed in the synthesis of MOF-200, an exceptionally porous material recently reported.¹⁶ Because of the presence of the highly extended organic linkers hmpib³⁻, compound UCY-1 displays the most open version of the pyr structure ever reported.

The large free volume in UCY-1 prompted us to investigate the possibility of removing the guest molecules and accessing the pore space. To avoid partial framework hydrolysis, all solvent-exchange reactions were performed inside a moisture-free, nitrogen-filled glovebox. These investigations revealed that CH₂Cl₂ is the most appropriate solvent to remove the guest molecules without structural collapse. Nitrogen adsorption–desorption recorded at 77 K revealed a type I isotherm, typical of a microporous material, as shown in Figure 3. The apparent

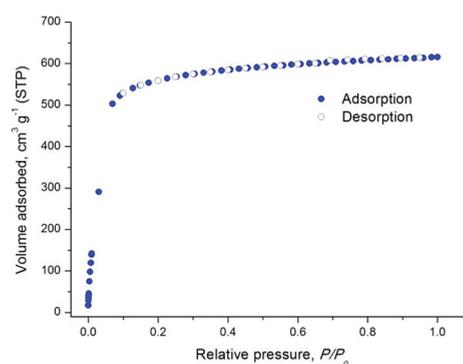


Figure 3. Nitrogen sorption isotherm of UCY-1 recorded at 77 K.

Langmuir surface area is 2591 m²/g (BET surface area 2067 m²/g), and the total pore volume is 0.95 cm³/g at 0.983 *p*/*p*₀. The observed surface area is close to the calculated Connolly surface (3000 m²/g) obtained from the crystal structure using a Connolly radius of 1.2 Å, indicating an almost complete evacuation of the pore space while maintaining framework integrity. The estimated pore-size distribution obtained by applying the Dollimore–Heal³¹ calculation method is 12.7 Å (Figure S5 in the SI), which correlates well with the crystal structure of UCY-1.

To further investigate the gas sorption properties of UCY-1, gas adsorption isotherms were measured for H₂, CO₂, and CH₄ at different temperatures. The hydrogen uptake at 1 bar and 77 K is 0.77 wt % (Figure S6 in the SI), which is comparable to the values found at the same conditions (i.e., 1 bar and 77 K) for many MOFs, being promising for hydrogen storage.³² More interestingly, UCY-1 shows a completely reversible, high CO₂ adsorption at near-ambient temperature (Figure S7 in the SI). The CO₂ uptake at 1 bar and 273 K is 1.4 mmol/g, while at 298 K is 0.98 mmol/g. For comparison, the corresponding values at 273 K for MOF-5 and ZIF-100 are 1.5 and 1.7 mmol/g, respectively.³³ The CH₄ uptake values are 0.47 and 0.33 mmol/g at 273 and 298 K, respectively (Figure S7 in the SI). The isosteric heats of adsorption at zero coverage for CO₂ and CH₄, calculated using the Clausius–Clapeyron equation, are 18 and 15 kJ/mol, respectively (Figure S8 in the SI). Analysis of the adsorption data using the ideal adsorption solution theory³⁴ (see the SI) reveals that the CO₂/CH₄ selectivities in UCY-1 are 4.4 at 298 K and 4.2 at 273 K, in the low-pressure limit (near-zero coverage). As expected, the selectivity gradually

drops with increasing pressure (Figure S9 in the SI). At ~ 500 Torr, the corresponding values at 298 and 273 K are 2.8 and 3.0, respectively.

Clearly, the use of the nanosized organic linker H₃hmpib containing the efficiently rigid imine functionalities is a rational method for the construction of robust open-framework materials. This was evidenced by isolation of UCY-1, which is the initial example of a MOF with the H₃hmpib ligand. This new MOF exhibits a double-interpenetrated structure with pyr topology, in which an uncommon interconnection of the two interwoven pyrite nets via hydrogen-bonding interactions is observed. UCY-1 displays a remarkably high internal surface area despite the double interpenetration of its structure. This obviously results from the highly extended hmpib³⁻ ligands largely separating the SBUs as well as the close proximity of the interpenetrated nets due to the hydrogen-bonding interactions between them. The high CO₂ uptake and its selective adsorption over CH₄ at near-ambient conditions are also important properties of UCY-1. Currently, further investigations on the use of the H₃hmpib ligand for isolation of new porous MOFs are in progress, and these results will be presented in the near future.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF format), representations of the topology (Figures S1–S3), details for gas sorption studies (experimental details and Figures S4–S9), and synthetic procedures for H₃hmpib and UCY-1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) Single-crystal X-ray diffraction data for UCY-1: trigonal, space group R3, $a = b = 52.143(4)$ Å, $c = 31.870(3)$ Å, $V = 75043(10)$ Å³, $Z = 3$, $\rho_{\text{calcd}} = 0.445$ g/cm³, $T = 100.0(3)$ K, and $2\theta_{\text{max}} = 50$. The refinement of 1334 parameters on 49 650 independent reflections out of 83 073 measured reflections ($R_{\text{int}} = 0.0833$) led to $R1 = 0.0402$ [$> 2\sigma(I)$], $wR2 = 0.0807$ (all data), and $S = 0.944$ with largest difference peak and hole of 0.149 and -0.116 e/Å³. Electron density contributions from disordered guest molecules were handled using the SQUEEZE procedure from the PLATON software suite. CCDC 817155 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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