A Simple and Rational Approach for Binodal Metal–Organic Frameworks with Tetrahedral Nodes and Unexpected Multimodal Porosities from Nonstoichiometric Defects

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Supporting Information

ABSTRACT: The fact that asymmetrically substituted dicarboxylate is capable of forming two different coordination modes is exploited to synthesize a binodal metal–organic framework containing tetrahedral nodes, and thus [H₂N-(CH₃)₂][Zn₅(hbdc)₆(dabco)] (hbdc = 2-hydroxyterephthalate, dabco = 1,4-diazabicyclo[2.2.2]octane) possesses the (8,4)-coordinated fluorite topology. This simple approach is verified by using symmetrically substituted ligand, 2,5-dihydroxyterephthalic acid to synthesize a uninodal, 4-coordinated net whose tetrahedral nodes lead to the rare lonsdaleite topology. It has been found that 1 readily loses some of the neutral ligand and cations during the activation processes without collapsing the whole framework, and multimodal porosities are observed due to the nonstoichiometric defects.

INTRODUCTION

Metal–organic frameworks (MOFs) occupy a somewhat unique position in network solids in that available building blocks are not only infinite in varieties, but they also vary greatly in terms of their chemical and physical properties. As a result, possibilities for practical applications have been proposed in numerous areas, such as separation, storage, catalysis, electronics, and the delivery of biological molecules.1 The highly versatile nature of the crystalline porous materials is probably best exemplified by myriad variations in framework types; however, as O’Keeffe and co-workers have pointed out, only those MOFs having simple and high-symmetry topologies are plausible targets for designed synthesis.

The targeted synthesis of porous MOFs with a highly symmetric, binodal topology presents intricate challenges due to greater uncertainties of nodal geometries compared to uninodal systems. Therefore, without the ability to predict crystal structures a priori, practical approaches for the designed and rational synthesis of such MOFs should rely on experience-based knowledge of simple and well-defined building blocks, such as di-, tri-, or tetranuclear metal carboxylate clusters.

We have recently initiated systematic investigations toward new binodal MOFs, and reported a highly symmetric (8,6)-coordinated net unprecedented in MOFs.3 The MOF was obtained by linking two heterometallic secondary building units (SBUs) with an asymmetrically substituted dicarboxylate ligand. We hereby describe an even simpler method using only one kind of metal, along with a similar ligand, 2-hydroxyterephthalic acid (H₂hbdc). This ligand, we expected, is capable of forming two different SBUs within one framework when a coordinatively versatile metal, such as Zn²⁺, is used (Scheme 1a). This approach is verified by synthesizing a uninodal 4-coordinated net with symmetrically substituted ligand, 2,5-dihydroxyterephthalic acid (H₂dhbdc) (Scheme 1b).

EXPERIMENTAL SECTION

Materials and Methods. All the reagents and solvents were commercially available and used as received. The synthesis described below is the result of optimizations with many different parameters,

Scheme 1. Expected Connectivities for Substituted Dicarboxylate Ligands

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including heating profiles, solvents, additives, and stoichiometries between reagents. A simultaneous differential scanning calorimetry-gravimetric analysis (DSC-TGA) was carried out on a SCINOCS S-1000 instrument with a heating rate of 5 °C/min in air. Fourier-transform nuclear magnetic resonance spectra were obtained using a Bruker 400 MHz spectrometer.

\[ \text{H}_2\text{N(CH}_3\text{)}_2\text{[Zn}_2\text{(hbdc)}_3\text{(dabco)}] \] (1). To a solution containing Zn(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O (133.0 mg, 0.45 mmol), H\textsubscript{2}hbdc (81.4 mg, 0.45 mmol) and 1,4-diazabicyclo[2.2.2]octane (dabco) (16.6 mg, 0.15 mmol) in DMF (3.0 mL) were added, along with a small amount of deionized water (5 μL). The solution mixture was stirred at room temperature for 1 h, and then heated to 85 °C for 16 h in a sealed glass vial. After filtering off a small amount of polycrystalline residue, the solution was allowed to stand at room temperature in a capped vial to produce truncated octahedron-shaped single crystals. The product was collected after 5–7 days and soaked in dichloromethane before drying under vacuum overnight (51.0 mg, 40%).

\([\text{H}_2\text{N(CH}_3\text{)}_2\text{][Zn}_2\text{(hbdc)}_3\text{(dabco)}] \] (2). A solution containing Zn(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O (63.7 mg, 0.21 mmol), H\textsubscript{2}hbdc (61.9 mg, 0.31 mmol), and dabco (11.7 mg, 0.10 mmol) in DMF (3.0 mL) was sealed in a glass vial and heated to 105 °C for 6 h. The solution was quickly filtered while warm, and then allowed to stand at room temperature in a capped vial. Large hexagonal block-shaped crystals began to form within several hours. The product was collected after 1 day and soaked in dichloromethane before drying under vacuum overnight (25.6 mg, 27%).

**RESULTS AND DISCUSSION**

On the basis of our experience of MOFs synthesized from M\textsuperscript{2+}, simple dicarboxylate and diamine ligands,\textsuperscript{8} we expected that new MOFs with mixed nodal figures of either paddlewheel and tetrahedral or pinwheel and tetrahedral could be obtained from the asymmetrically substituted hbdc ligand (Scheme 1a). Therefore, Zn\textsuperscript{2+} was reacted with H\textsubscript{2}hbdc and dabco under solvothermal conditions in DMF, and truncated-octahedron shaped crystals of an apparently singular phase were obtained.

X-ray crystallography on the single crystals establishes the formula as \([\text{H}_2\text{N(CH}_3\text{)}_2\text{][Zn}_2\text{(hbdc)}_3\text{(dabco)}] \) (1) for the framework. Analysis for the contents of C, H, N, and Zn corroborates with this formulation, and X-ray powder diffraction studies further support the bulk purity of the product (Figure 1).

![Figure 1. Debye–Scherrer diffraction patterns for 1 (λ = 1.000 43 Å).](image)

The crystal structure of 1 was solved with the cubic space group Pa-3, in which the asymmetric unit contains 5/6 Zn\textsuperscript{2+} ion over three sites, one hbdc dianion, 1/3 dabco, and 1/3 dimethylammonium cation. Two of the three independent Zn\textsuperscript{2+} ions constitute a trinuclear pinwheel SBU with the general formula \([\text{Zn}_3\text{(O}_2\text{C)}_6\text{(dabco)}] \), and the last Zn\textsuperscript{2+} ion forms a mononuclear tetrahedral node supported by three carboxylates and a nitrogen of the dabco ligand. In accordance with our expectation, the two different SBUs are bridged by hbdc ligand (Figure 2a).

Topologically, the 8-connecting pinwheel SBU adopts the nodal geometry of a cube, as shown in Figure 2b, and on average, there exist two tetrahedral nodes for every pinwheel SBU. The overall packing structure of the new MOF (Figure 2c) can thus be simplified as a binodal (8,4)-net with the cubic and tetrahedral nodes in a 1:2 ratio. The default net having this connectivity is that of fluorite (CaF\textsubscript{2}) with the net symbol flu in the RCSR database,\textsuperscript{16} and flu is indeed the topology underlying...
the net of 1 (Figure 2d). The flu net is one of the most fundamental and frequently observed structure types in binary ionic solids, and has first been replicated in MOFs by one of us. Since then, many other MOFs have been reported as having the flu topology; however, all the examples known to date contain multitiopic ligands playing the role of either 4- or 8-connecting node. Therefore, to the best of our knowledge, is the first case in which two unique SBUs define both nodes of the fluorite net.

Our synthetic approach—the derivation of mononuclear tetrahedral center through the 2-substituted carboxylate moiety—may be adopted as a general strategy for Zn-carboxylate-based new MOFs. In order to demonstrate this, we reacted Zn$^2+$, dabco and symmetrically substituted ligand, 2,5-dihydroxyterephthalate (dhbdc) under a condition similar for 1 (Scheme 1b), and were able to isolate large hexagonal block shape crystals as the only product (Figure 3a).

The X-ray diffractions by these single crystals are extremely weak and poor, even at 100 K under a synchrotron radiation. According to our best interpretation of the data with a limited resolution, the new MOF is built upon tetrahedral Zn$^2+$ coordinated by three carboxylates and a dabco nitrogen atom, as in the case of 1 (Figure 3b). The uninodal 4-coordinated net has an anionic framework with the formula $[\text{Zn}_2(\text{dhbdc})_3(\text{dabco})]^2-$ (2), and possess the topology of lonsdaleite (lon), also known as the “hexagonal diamond” (Figure 3c,d).

The charge-balancing dimethylammonium cations in 1 are believed to be a decomposition product of DMF, and are found at locations close to the pore walls. The solvent-accessible voids estimated after considering the cations is 55% of the total crystal volume. The Connolly surface of 1 created with the probe radius of 1.4 Å is depicted in Figure 2c. The figure clearly shows that adjacent pores are interconnected through windows and channels. Solvent molecules occupying these voids can be readily replaced by low-boiling solvents, such as dichloromethane, and removed under mild conditions. The onset of the thermal decomposition of the framework is observed at around 250 °C according to simultaneous DSC-TGA analysis (SI Figure S2).

The activated solid of 1 was subject to nitrogen sorption measurements at 77 K, and the results, shown in Figure 4, revealed rather unusual features.

The overall shape is type I typical for microporous materials; however, hysteresis and unlimited adsorption are observed at high P/P$_0$, which are the characteristics of meso- or macroporous materials. Because the microporous nature of 1 is unambiguously established by X-ray crystallography, we attributed the atypical features to physical defects in the framework caused by the activation processes. In order to verify this hypothesis, we measured $^1$H NMR spectra of 1 after digesting the solid in NaOH/D$_2$O solutions (Figure S5).

For comparison, samples were prepared by slightly different activation processes, such as the number of solvent-exchange steps and evacuation temperatures. To our surprise, the results
were inconsistent from measurement to measurement, even though only hand-picked single crystals were used to ensure the purity of the samples. More specifically, the integrated ratio of protons from dabco with respect to the hbdc diaminio varies significantly depending on the activation temperatures (60, 80, and 100 °C for Figure Sb, a, and c, respectively). This is possible when the neutral diamine ligand had been partially removed from the framework by the heating processes. Note that all atoms of the dabco ligand are well-defined with no sign of a partial occupancy or disorder in the original crystal structure. The integration of protons for the dimethylammonium cations also shows large variations in which the numbers decrease as the solvent-exchange steps increase from Figure Sa–c. Therefore, it can be concluded that the framework of I readily loses some of the ligands during the activation processes, and the meso- and macropores created in the framework are responsible for the unusual hysteresis and unlimited uptake in the nitrogen sorption isotherms. It may be interesting to note that despite the nonstoichiometric nature of the defects in the framework, the nitrogen sorption profile is highly reproducible with almost identical features over the whole pressure range. This was confirmed by N2 sorptions measured for four independent samples (SI Figure S3). The fact that some ligands in porous MOFs can be removed without collapsing the whole framework may be a general phenomenon that has been overlooked in the past, and underlines the versatility of MOFs as porous materials.

The highest values of the BET and Langmuir surface areas for I estimated from the nitrogen adsorption are 1042 and 1168 m$^2$/g, respectively. The uptake capacity for H2 at 77 K and 1 bar is modest with 166 cm$^3$/g (STP) or 1.5 wt %. At 273 K, the sorption of CO2 reaches to 16.7 wt % at 1 bar, and is selective against CH4, N2, or O2 at that temperature. For comparison, the highest uptake of CO2 at 298 K and 1 bar has been reported for a series of materials known as MOF-74 or CPO-27 (20–28 wt %).19

In conclusion, a simple and rational approach has been adopted to synthesize a new MOF in which two independent SBUs are linked by asymmetrically substituted ligands to form the fluorite topology. Although this material readily loses some of the ligands that constitute the framework, the stability as a porous solid is maintained and multimodal porosities are observed. The fact that tetrahedral Zn nodes can readily be reproduced using the 2-hydroxycarboxylate moiety may be a useful guide for the designed synthesis of new MOFs with high-symmetry topologies.

**ASSOCIATED CONTENT**

1 Supporting Information

Plots of TGA and N2 sorption data for I, and snapshots of single-crystal diffractions by 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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(13) Our approach may not be universally applied to carboxylate-based MOFs because the selection of nodality depends also on synthetic conditions. For example, a uninodal MOF can be built from hbdc and dabco ligands. See, for example: Chen, Z.; Xiang, S.; Arman, H. D.; Li, P.; Zhao, D.; Chen, B. Eur. J. Inorg. Chem. 2011, 2227.

(14) Only the framework atoms are unambiguously defined because of the low quality of diffractions. See Experimental Section and SI Figure S1 for more details. A full characterization of its material property, including gas sorptions, will be published later.


(16) Adding a stoichiometric amount of dimethylammonium salt during the synthesis results in the formation of unknown impurities, implying that the slow formation of the cation is a key step in the selection of the final structure.


(18) It is plausible that the counter cations have been gradually exchanged by NMR-transparent protons during the solvent-exchange steps.