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Targeted Synthesis of a Prototype MOF Based on $Zn_4(O)(O_2C)_6$ Units and a Nonlinear Dicarboxylate Ligand

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A surprisingly small number of topologies are known in metal−organic frameworks (MOFs) that possess $Zn_4(O)(O_2C)_6$ building units. One of such MOFs having a simple, nonlinear dicarboxylate ligand, 5-methylisophthalate (mip), is targeted and successfully synthesized. The framework, $[Zn_4(O)(mip)_3]$, is based on a nonuniform, uninodal six-connected net and is featured by complicated meshlike pores with narrow passages. Gas sorption studies reveal the potentials as a prototype from which new MOFs having interesting properties can be derived.

Coordination chemistry is at the center of studies on open-work crystalline solids known as metal−organic frameworks (MOFs), and this area of research has experienced exceptional growth in the past decade with high prospects for practical applications.[1] Considering the explosive interests and efforts devoted to this area, the structural diversity of MOFs based on $Zn_4(O)(O_2C)_6$ secondary building units (SBUs) is remarkably simple. Except for MOF-5 and its isoreticular series reported by Yaghi and co-workers,[2] only a few cases are known in the literature to have the tetranuclear SBUs.[3] It is also noticed that most of those MOFs are built either from linear dicarboxylate or from multicarboxylate ligands on an extended polyaromatic backbone. The lack of topological variety may give a notion that the μ_4-O-centered tetrazinc unit can be formed only under specific and unpredictable reaction conditions. Linking $Zn_4(O)(O_2C)_6$ units with simple, nonlinear dicarboxylate linkers will therefore enrich the structural chemistry of MOFs significantly and may result in whole new sets of MOFs having interesting properties, such as the efficient storage of gases.[4]

Recently, we reported that dinuclear paddlewheel SBUs give MOFs having completely different pore structures depending on whether the linker is isophthalate or terephthalate.[5] Therefore, we targeted the synthesis of $Zn_4(O)(O_2C)_6$-based MOFs with easily available bent dicarboxylate ligands. In this Communation, we report the synthesis, structure, and basic properties of a new MOF having the formula $Zn_4(O)(mip)_3$, where mip is a 5-methylisophthalate dianion.

Typical solvothermal reactions of Zn^{2+} and $H_2(mip)$ in *N*,*N*-dimethylformamide (DMF) or *N*,*N*-diethylformamide (DEF) give a clear solution without the formation of any crystalline product of importance, if at all. The same reaction, however, produces large, polyhedral crystals in good yields when an organic base is added to the initial reaction mixture in DMF.[6] The crystalline products are $[Zn_4(O)(mip)_3(DMF)_2]\cdot 3DMF\cdot H_2O$ according to the X-ray crystallographic analysis.[7] The guest and coordinated solvent molecules can be removed by thermal evacuation, and therefore the final formula of the evacuated framework is

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(6) Synthesis of $[Zn_4(O)(mip)_3(DMF)_2]\cdot 3(DMF)\cdot (H_2O)$: To a DMF (15.0 mL) solution containing $Zn(NO_3)_2\cdot 6H_2O$ (0.423 g, 1.42 mmol) and H_2mip (0.191 g, 1.06 mmol) was added NEt_3 (0.148 mL, 1.03 mmol). The initially formed white precipitate was dissolved after stirring for 1 h at room temperature. The solution was then heated to 100 °C for 2 days to produce large, polyhedral crystals (0.304 g, 72%). The yields vary between 60 and 80% depending on the reaction scale. The elemental analysis was carried out for an evacuated sample. Anal. Calcd for $[Zn_4(O)(C_9H_6O_4)_3]\cdot 2H_2O$: C, 38.24; H, 2.61; N, 0.00. Found: C, 38.17; H, 2.97; N, 0.00.

10.1021/ic801906e CCC: $40.75

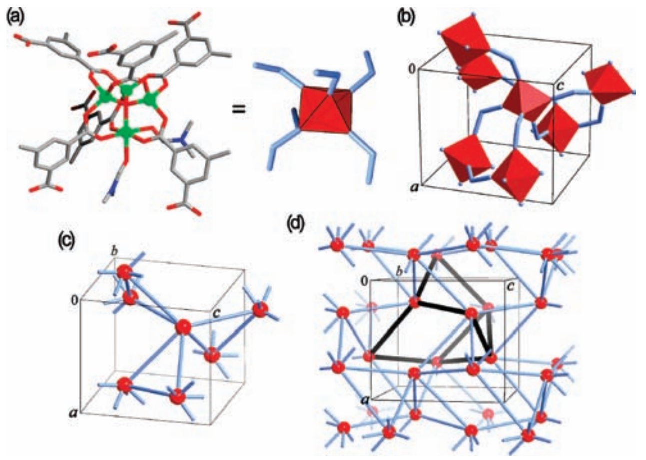

Figure 1. (a) X-ray structure of the SBU (H atoms have been omitted) and its topological model. (b) Fragment of the net stylized according to part a. (c and d) Ball-and-stick representations of part b and the extended net. The natural tile[10] composed of one triangular and three pentagonal faces is emphasized by black edges.

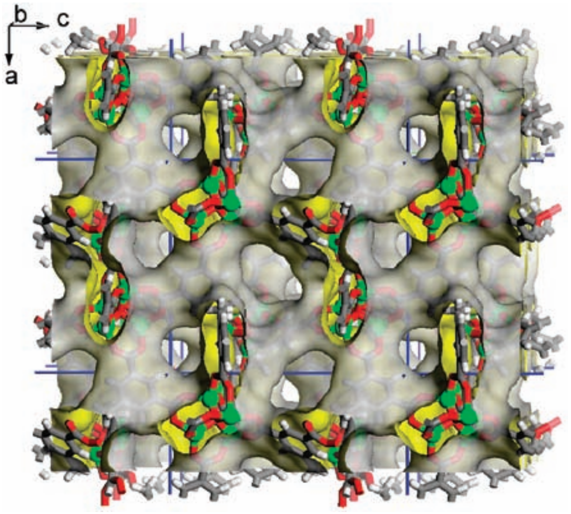

Figure 2. Connolly surface of $[Zn_4(O)(mip)_3]$ with a probe radius of 1.4 Å. Guest and coordinated solvent molecules are omitted. Blue lines are the unit cell edges.

$[Zn_4(O)(mip)_3]$. The homogeneity and purity of the bulk product, which are evident even by visual inspection, have been confirmed by elemental analysis and powder X-ray diffraction (XRD; Figure S3 in the Supporting Information).

We figure that the addition of a noncoordinating organic base is essential to the successful synthesis and that this method may be applied to other dicarboxylate ligands. MOF-5, for example, can be synthesized similarly in DMF containing a small amount of triethylamine. Note that without triethylamine, solvothermal reactions of Zn^{2+} and terephthalic acid in DMF produce predominantly a paddlewheel-based 2D square-grid net[8] instead of MOF-5, which is best synthesized in DEF. We presume that the slight increase of the OH^- concentration due to the raised pH plays a key role in the controlled formation of the μ_4-O bridge of the six-connecting SBU.

The structure of the tetranuclear building unit shown in Figure 1a reveals that one of the four Zn^{2+} ions is not in the usual tetrahedral environment with two DMF molecules coordinated to it. The asymmetric coordination environment causes a slight distortion in the overall geometry of the octahedrally connecting SBU (Figure 1b). The network structure of $[Zn_4(O)(mip)_3]$ requires more than routine attention to comprehend and is found to be a rare example of uninodal six-connected nets.[9] The distorted octahedral SBUs linked by mip ligands form two kinds of essential circuits (triangles and pentagons) and one kind of natural tile (Figure 1c,d). Detailing the network structure further leads to a conclusion that the underlying topology is one of the 14 semiregular 3D nets and is inherently chiral.[10] To our best knowledge, the topology having the net symbol of **lcy** has been observed only once prior to this work in entire extended solids.[11]

The genuine virtue of $[Zn_4(O)(mip)_3]$ as a porous MOF lies not on the rarity of the network topology but in the way the void spaces are developed. A close examination of the solvent-accessible surface reveals that it does not allow straight open channels with a meaningful free passage (Figure 2). Instead, pores of varying sizes (<1 nm) and irregular shapes are interconnected through relatively narrow windows measuring 4−6 Å. Similar to the case of the network structure, the pore structure of $[Zn_4(O)(mip)_3]$ defies a simple description, and thus it may have to be concluded that highly corrugated channels of less than 1-nm width are interconnected and propagate throughout all directions.

The solvent molecules included in the as-synthesized crystals can be safely replaced with other low-boiling solvents, and they can be removed by heating the material under vacuum. The thermogravimetric analysis (TGA) of a $CHCl_3$-exchanged sample shows a plateau in the range 230−400 °C after a weight loss of about 38% (Figure S2 in the Supporting Information). In order to establish the activation conditions for gas sorption studies, we measured the powder XRD after heating the $CHCl_3$-exchanged sample to 110 °C under vacuum for 14 h. The resulting XRD pattern shows a number of strong peaks at the positions expected from the simulation based on the single-crystal structure (Figure S3 in the Supporting Information). The porous framework of $[Zn_4(O)(mip)_3]$ activated as such shows reversible uptakes of various gases. For example, the saturated sorption of N_2 (77 K) and Ar (87 K) displays typical type I behavior without a notable hysteresis, common features of microporous materials (Figure 3).

The Langmuir (Brunauer−Emmett−Teller) surface areas deduced from the N_2 and Ar sorption data are similar, with

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(7) Crystal data for $[Zn_4(O)(mip)_3(DMF)_2]\cdot 3DMF\cdot H_2O$: formula $C_{42}H_{55}N_5O_{19}Zn_4$, $M = 1195.39$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 16.215(3)$ Å, $b = 17.174(3)$ Å, $c = 18.104(4)$ Å, $V = 5042$ (2) Å^3, $Z = 4$, $T = 173$ K, $\rho_{calcd} = 1.575$ g/cm^3, $F(000) = 2456$, μ(Mo Kα) = 1.958 mm^{-1}, 10 253 independent reflections, 9713 observed [$I > 2\sigma(I)$]; R1 = 0.0596, wR2 = 0.1642 (all data).

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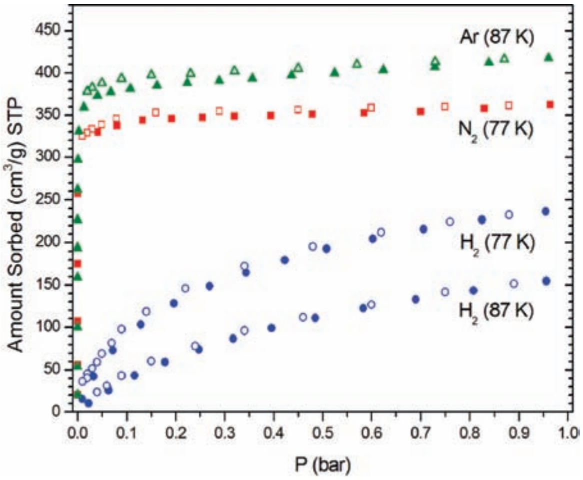

Figure 3. Gas sorption isotherms measured at 77 K (N_2 and H_2) and 87 K (Ar and H_2). Filled and open symbols denote the sorption and desorption, respectively.

1556 (1062) and 1591 (1013) m^2/g, respectively. The estimated total pore volumes are also similar, with 0.56 and 0.53 cm^3/g from the N_2 and Ar sorption data, respectively. These values are equivalent to the porosity of 60 and 57% when the crystallographic density of the void framework (1.07 g/cm^3) is taken. The analysis of the crystal structure gives reasonably close values: the solvent-accessible void of 52%[12] or the free volume of 55% from the Connolly surface of the framework.[13] Therefore, it appears that most of the void spaces of [$Zn_4(O)(mip)_3$] can be accessed and occupied by small gas molecules.

The H_2 sorption of [$Zn_4(O)(mip)_3$] shows a considerable uptake of 236 cm^3/g (STP) or 2.1 wt % at 77 K and 0.96 bar. Assuming that the adsorbed H_2 has the liquid density at normal boiling point (70.973 kg/m^3), the H_2 adsorbed in [$Zn_4(O)(mip)_3$] would fill 53% of the total pore volume (0.56 cm^3/g). This is higher than a series of pillared square-grid MOFs based on paddlewheel SBUs.[14] The isosteric heat of H_2 adsorption for [$Zn_4(O)(mip)_3$] is 10.2−8.2 kJ/mol at low coverage condition (0.01−0.1 wt %), which is comparable to or slightly higher than other known examples in MOFs (Figure S5 in the Supporting Information).[15]

Note that the absolute amount of H_2 uptake is of less importance here because the isotherm is far from being saturated, and 77 K and 1 bar are not realistic storage conditions for H_2 gas.[16] Instead, it may be more insightful to compare the apparent surface coverage by H_2 with those of other MOFs having the same tetranuclear SBU. Yaghi's IRMOFs, for instance, possess a primitive cubic topology and very high surface areas in the range 1501−4590 m^2/g; however, their H_2 uptakes are not higher than 1.9 wt % under the same conditions.[2] Other MOFs based on the same SBU and extended tri- or tetracarboxylate ligands also show similar or lower H_2 uptake than [$Zn_4(O)(mip)_3$].[3]

We showed in a recent study that extending organic linkers of an MOF having highly constrained SBUs and narrow channels results in a significant improvement in the H_2 sorption capacity.[17] We expect a similar scenario for [$Zn_4(O)(mip)_3$] in which the methyl groups of mip ligands and the relatively short spacer of a 1,3-substituted phenyl ring impose strains on the connectivities between SBUs. These analyses suggest that the isoreticular chemistry of [$Zn_4(O)(mip)_3$] is very much worth the effort and that one of the related MOFs such as the one having 2,7-naphthalenedicarboxylate instead of isophthalate linkers, which is yet to be synthesized, may show unprecedented H_2 sorption capacities. Our current research is focused on this goal.

In brief, we targeted and successfully synthesized a porous MOF based on $Zn_4(O)(O_2C)_6$ SBUs and bent dicarboxylate ligands. The uninodal, six-connected net of [$Zn_4(O)(mip)_3$] has a topology rarely seen in extended solids. The complex meshlike pore structure is responsible for the efficient and considerable H_2 uptake for such a modest surface area. More importantly, the open-framework solid [$Zn_4(O)(mip)_3$] may become a prototype from which numerous new MOFs can be derived. The future development in its isoreticular series may be very interesting.

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Supporting Information Available: Experimental details, plots of IR, TGA, XRD, and enthalpy of H_2 adsorption, and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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