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Made in Water: A Stable Microporous Cu(I)-carboxylate Framework (CityU-7) for CO_2, Water, and Iodine Uptake

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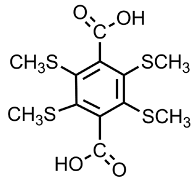
Supporting Information

ABSTRACT: Using water as the sole solvent, the bifunctional molecule tetrakis(methylthio)-1,4-benzenedicarboxylic acid (TMBD) was reacted with $Cu(CH_3CN)_4BF_4$ to form a robust microporous metal−organic framework (MOF, CityU-7) featuring Cu(I) ions being simultaneously bonded to the carboxyl and thioether donors. The MOF solid is stable in air and can be easily activated by heating, without the need for treatment with organic solvents. The subnanoscopic pores (ca. 0.6 nm) of the host net allow for uptake of CO_2 and H_2O but exhibit lesser sorption for N_2 at 77 K. The microporous net can also be penetrated by I_2 molecules.

In the study of metal−organic frameworks (MOFs) as a promising class of porous materials, water stability and environmentally friendly, green assembly of MOF solids are two topics of industrial and academic importance.[1−6] For example, most MOF solids are solvothermally prepared using organic solvents (e.g., dimethylformamide (DMF)) and acid/base additives such as HCl or amines, limiting their production on commercial scales. It is therefore of interest to develop MOF materials that can be directly assembled by using water as the sole solvent without use of any additives. Here we report a microporous MOF material (denoted as CityU-7) that is conveniently made by heating water, $Cu(CH_3CN)_4BF_4$, and the sulfur-equipped dicarboxylic linker H_2TMBD (Scheme 1).

Scheme 1. Linker H_2TMBD



H_2TMBD

The synthesis of CityU-7 as a water-stable MOF also offers fundamental insight into materials design. In general, better water stability can be achieved by enlisting hard−hard (e.g., as in Cr^{3+}, Zr^{4+}-carboxylate) bonding[7−12] or using softer coordination bonds based on, for example, nitrogen donors and metal ions including Cu(I) and other transition metals.[13−19] That is to say, most Cu(I)-based MOF solids are constructed through N-donor linkers such as pyrazolate and pyridine,[20−24] while Cu(I)-carboxylate links are rarely featured in MOF structures.[25,26] This observation is partly due to the soft nature of Cu(I) that tends to refrain from the hard carboxyl group and partly due to Cu(I) being prone to oxidization and disproportionation.

Part of our long-standing studies on the carboxyl−thioether duo (e.g., Scheme 1 and Scheme S1) is to access stable Cu(I)-carboxylate nets. Namely, the soft thioether groups serve to stabilize the soft Cu(I) center, while the rigid, charge-balancing carboxylate units bond with the Cu(I) cations to enhance the strength and directionality conducive to open-framework metal-carboxylate compounds. Previously, a nonporous, close-packed network based on Cu(I) and TMBD (denoted as Cu_2TMBD-*np*) had been reported.[27,28] The MOF solid of CityU-7 disclosed herein, with its distinct microporous features, represents a step forward in this direction.

CityU-7 was accidentally discovered as a minor phase (in the form of large block-like brown single crystals) using a recipe for synthesizing the nonporous Cu_2TMBD-*np*, for example, by heating $Cu(NO_3)_2{\cdot}3H_2O$ (3.0 mg), H_2TMBD (3.5 mg), and water (0.5 mL) in a sealed glass tube at 140 °C for 48 h.[27] The Cu(I) ions apparently were generated in situ from redox reactions between the Cu(II) ions and the TMBD sulfide units, a type of reaction that often occurs under the conditions of hydro(solvo)thermal reactions.[29,30] The Ag(I) analog of CityU-7, that is, Ag_2TMBD, was also obtained, albeit in poor yields, because of severe ligand oxidation by the Ag(I) ions.[31] While

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studying Cu_2TMBD-*np*, we had attempted to increase the yield of the porous CityU-7. All attempts utilizing Cu(II) as reactants had not been successful. In our continuing search we realized that a nonoxidizing Cu(I) salt such as $Cu(CH_3CN)_4BF_4$ should be investigated, as higher Cu(I) concentrations may accelerate reaction with the TMBD linker for forming a kinetically controlled, porous product.

Indeed, by heating H_2TMBD (7.0 mg, 0.020 mmol), $Cu(CH_3CN)_4BF_4$ (18.9 mg, 0.060 mmol), and water (1.0 mL) in a sealed Pyrex tube at 120 °C for 24 h, we obtained a yellow-greenish power that turned out to be a polycrystalline sample of pure porous CityU-7, as verified, for example, by the PXRD (powder X-ray diffraction) patterns and SEM imaging (scanning electron microscope; showing square-prismatic crystallites of ca. $5 \times 5 \times 10$ μm^3) (Figure 1). The access to pure bulk samples of CityU-7 has greatly facilitated the study of its properties as a porous material.

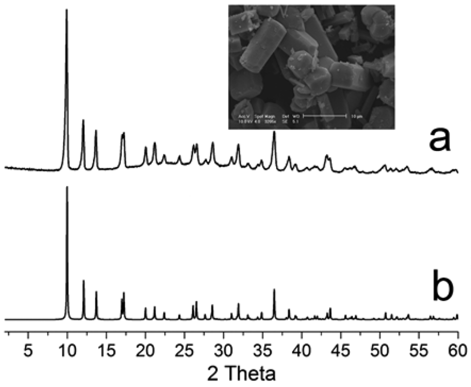

Figure 1. PXRD patterns (Cu Kα, λ= 1.5418 Å) of (a) a powder solid sample of CityU-7 (with the SEM image shown in the inset) and (b) a simulation from the single-crystal structure.

The single-crystal structure of CityU-7 adopts the space group $P4_2/ncm$ (no. 138). The Cu(I) atoms occur in pairs (Cu···Cu distance: 3.172 Å; Figure 2a), with each pair being symmetrically bridged by two straddling carboxyl groups (Cu–O distance: 2.032 Å) to form half of a paddle wheel, which is a familiar motive in Cu(II)-based MOF structures. Each Cu(I) is also chelated by two sulfur atoms (Cu–S distances: 2.235, 2.413 Å) to complete (together with the two O donors) a roughly tetrahedral geometry that is typical of the Cu(I) d^{10} electronic configuration. Treating the center of the Cu pair as a tetrahedral node and the center of the TMBD linker as a square planar node (Figure 2b), one obtains a four-connected net of the PtS type (Figure 2d). Substantial cavity volume was observed in the crystal structure (Figure 2c), which is filled by disordered water molecules. If overlapping spheres with van der Waals radii (1.20, 1.70, 1.52, 1.80, 1.40 Å for H, C, O, S, Cu, respectively) are placed at the atomic positions, then the void fraction is calculated to be 45.5%.

The framework composition of CityU-7 was revealed by the crystal structure to be charge-neutral Cu_2TMBD, that is, $Cu_2C_{12}H_{12}S_4O_4$, which is isomeric with the previous nonporous Cu_2TMBD-*np*. Such a composition is also supported by chemical analysis; that is, the product $Cu_2(C_{12}H_{12}S_4O_4)(H_2O)_2$ yields the following: calcd [C (28.17%), H (3.15%), S (25.07%)], found [C (28.44%), H (3.00%), S (23.02%)]. Thermogravimetric analysis (TGA (Figure 3) on the polycrystalline sample indicated no weight loss up to 250 °C, with a stable weight percentage of ~30% above 850 °C, being consistent with the formation of a Cu_2O residue (e.g., calculated from $Cu_2C_{12}H_{12}S_4O_4$: 30.1%).

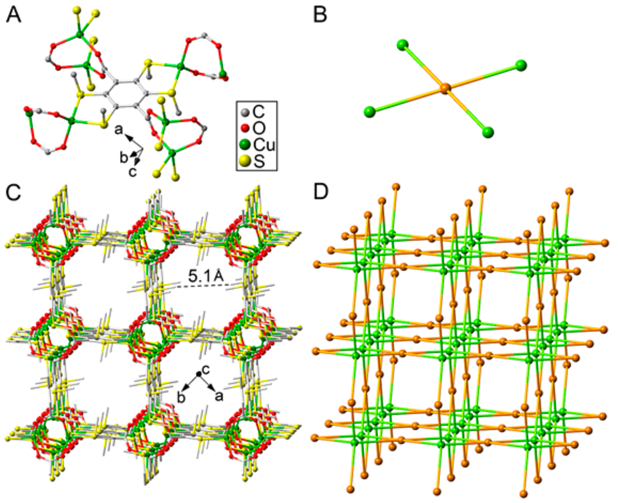

Figure 2. (a) Local coordination environment of linker TMBD and Cu(I) centers in the crystal structure of CityU-7. (b) Corresponding topological representation of panel a, with the TMBD treated as a node (orange sphere) connected by four half-paddle-wheel Cu_2 nodes (greenish yellow spheres). (c) Overview of the 3D net of CityU-7, with the same color code as panel a. The dotted line indicates the window size of the open channel. (d) Topological representation of panel c, with the same color code as panel b, showing the bonding geometries of the TMBD linker (square planar) and metal nodes (tetrahedral).

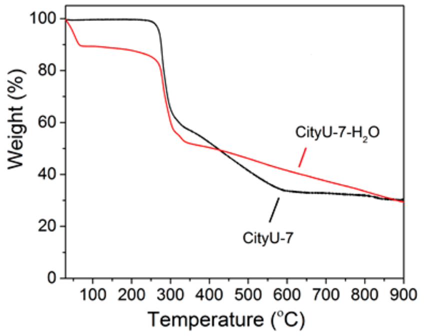

Figure 3. TGA plots of CityU-7 and CityU-7-H_2O.

CO_2 sorption at 273 K (pressure range: from 8×10^{-3} to 780 mmHg) on CityU-7 (activated by heating under vacuum at 90 °C, no need for solvent exchange) revealed a typical type-I gas adsorption isotherm (Figure 4) with a BET surface area of 197 m^2/g. NLDFT analysis on pore-size distribution and pore volume (Figure S2) indicated an average pore width of 0.48 nm and a modest micropore volume of 0.149 cm^3/g. The small pore size thus uncovered is consistent with the ultramicroporous character of the crystal structure and helps to explain the lesser N_2 sorption (measured at the lower temperature of 77 K; Figure S3). Despite the relative pressure (p/p_0) and pore filling being low at 273 K for CO_2, the BET surface area thus determined has been found to be reasonable for uniformly ultramicroporous sorbents,[32] even though sorption at lower temperatures (e.g., 195 K)[33] ought to afford more complete pore filling.

The micropores of CityU-7 can also be penetrated by I_2 molecules. For example, when a powder sample of CityU-7 (5.0

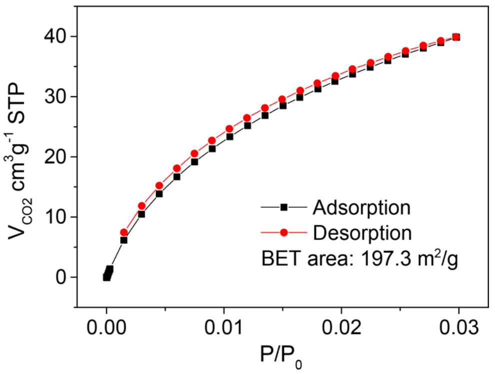

Figure 4. CO_2 isotherm at 273 K of a CityU-7 sample.

mg) was added to a hexane solution of I_2 (2.0 mL, 178 mg·L^{-1}; total I_2 0.356 mg), >99% of the I_2 solute was removed from the solution within 6 h (see Figure S4 for the calibration curve). For a sample fully loaded with I_2 (e.g., by immersing in a saturated I_2/hexane solution for 15 h, denoted as CityU-7-I_2), TGA indicates a distinct step (as compared with the original CityU-7 sample; see Figure S5) of weight losses of ∼15% below 250 °C, suggesting a formula $Cu_2TMBD·0.5I_2$. The PXRD pattern of the I_2-loaded sample shows the diffraction peaks at angles corresponding to the original lattice of CityU-7 but with increased intensity observed for the higher angle peaks (Figure S6), which is consistent with the added electron intensity associated with the I_2 guests. The I_2 guests can be largely evacuated by heating under vacuum at 130 °C, as shown by the EDX elemental analysis (cf. Figures S7−S9) and the recovered PXRD intensity profile in pattern c of Figure S6. This pattern, however, features a distinct hump at 2θ of 20−35, pointing to some amorphous phase. Also, the evacuated sample (CityU-7-I_2-re) differs from the original CityU-7 sample in TGA graphs (Figure S5), further indicating the incomplete recovery of the CityU-7 phase by evacuating on the CityU-7-I_2 sample.

The activated sample of CityU-7 can also take up water molecules. For example, by immersing CityU-7 in saturated water vapor at room temperature for 12 h, TGA of the resultant sample CityU-7-H_2O (see Figure S11 for the PXRD patterns) exhibits a rapid weight loss of ∼10% from RT to 65 °C (Figure 3), corresponding to the formula $Cu_2TMBD·3H_2O$. The water sorption isotherm for CityU-7 (Figure S10), on the contrary, indicates a maximum uptake of 96.7 cm^3/g (STP conditions; equivalent to ∼7.2% w/w of water in CityU-7-H_2O) at P/P_0 = 0.95.

In conclusion, we have succeeded in assembling a microporous Cu(I)-carboxylate framework (CityU-7) by enlisting chelating thioether units. The microporosity of CityU-7 is demonstrated in the CO_2 and N_2 sorption and the I_2 uptake tests. Besides the green advantage of water-based synthesis and activation procedures, the small pore size of the robust CityU-7 solid may prove to be useful for selective sorption of small molecules of more topical interests (such as acetylene from ethylene).[34−53] Furthermore, one may use thiol analogs of DMBD (with −SH replacing −SMe) to install covalent Cu−S bonds to enhance electronic interaction and to access anionic frameworks with ion exchange properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00481.

Synthetic and experimental details, additional TGA plots, EDX data, PXRD patterns, and X-ray crystallographic data in CIF format of CityU-7. (PDF)

Accession Codes

CCDC 1825009 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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