

Microporous Metal Organic Materials: Promising Candidates as Sorbents for Hydrogen Storage

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Materials that effectively store hydrogen are needed for use in fuel cell powered vehicles. Among the various candidate storage technologies including porous sorbents, reversible metal hydrides, chemical hydrides, compressed gas, and liquefaction, none is capable of meeting the DOE cost and performance targets.¹ Porous metal coordination structures represent a promising new entry to the field of hydrogen storage materials.² To fully exploit this new field, relationships between structure and storage properties must be developed to guide the further rational design and synthesis of tailored materials with significantly improved hydrogen adsorption capability. In this light, we have explored a new type of sorbent, microporous metal coordination materials (MMOMs) with pore dimensions comparable to the length scale of the molecular diameter of hydrogen.

The MMOMs share physical characteristics similar to those of single-walled carbon nanotubes (SWNTs) that have been under intense investigation as storage materials. Both are lightweight and composed of open channels based on aromatic carbon. In addition, MMOMs possess several advantageous features over SWNTs that are particularly promising for improving hydrogen adsorption. For example, the MMOMs incorporate metals that can bind hydrogen much more strongly than graphitic carbon, but not as strongly as when a true chemical bond forms as in the case of metal hydrides. Furthermore, the organic components can be modified to induce stronger interactions with H₂. The open channels in MMOMs are perfectly ordered, allowing effective access of hydrogen to the interior space. The internal surfaces of MMOMs can easily be modified to change the channel curvature, thus enhancing the H₂-sorbent interactions.³ The "one-pot" synthesis is simple, cost-effective, and highly reproducible. More importantly, the structures of these materials, including the metal building unit, pore dimension, shape, size, and volume, can be systematically tuned for the purpose of modifying and improving hydrogen uptake and adsorption/desorption properties.

In this Communication, we report the synthesis, structure, and room-temperature hydrogen adsorption of a novel MMOM, [Cu-(hfipbb)(H₂hfipbb)_{0.5}] [H₂hfipbb = 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid)] (**1**). Crystals of **1** were grown in reactions of hydrated copper nitrate salt and excess H₂hfipbb in deionized water at 150 °C.^{4a} The structure of **1** is a 3D interpenetrating framework containing unique and perfectly ordered microporous 1D open channels (microtubes) built upon a Cu₂(hfipbb)₄(H₂hfipbb)₂ paddlewheel building unit.⁵

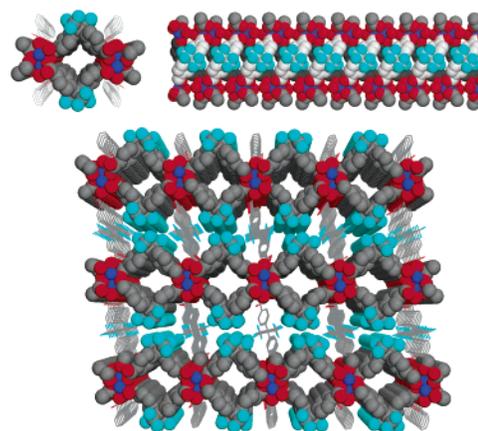


Figure 1. Views of structure **1**. Top left: cross section of a single microtube. Blue balls, Cu; red balls, O; gray balls, C; light blue balls, F. Top right: side view of a single microtube. Bottom: Three-dimensional packing of microtubes.

The coordination geometry of each copper is square pyramidal with respect to the five ligands. Two copper atoms share four carboxylate groups of the hfipbb ligands located in the equatorial plane to form a paddlewheel-shaped motif with a Cu–Cu distance of 2.645 Å. Each paddlewheel unit connects to four adjacent paddlewheel units via the four remaining carboxylate groups of hfipbb ligands to form an undulated 2D neutral network with a 4⁴ topology. The adjacent 2D layers are connected by monodentate carboxylate groups of H₂hfipbb ligands binding to the apical position of the metals to generate a 3D network. The metal network based on Cu₂ dimer has a highly distorted α -polonium topology.⁶ Two identical 3D networks interpenetrate to give rise to the final structure containing ordered arrays of 1D microtubes packing along the (10 $\bar{1}$) direction. Two views of a single microtube are depicted at the top section of Figure 1. The bottom section of the same figure shows how these microtubes pack to give rise to a 3D structure. The salient features of these microtubes are that they contain curved internal surfaces featuring small windows ($\sim 3.5 \times 3.5$ Å, excluding the van de Waals radius of carbon) and larger cages ($\sim 5.1 \times 5.1$ Å). This is similar to the RPM1 system we reported earlier.⁷ Thermogravimetric (TG) analysis of **1** showed that the as-prepared sample was stable to 330 °C.^{4b} The unusually high thermal stability is presumably a result of interpenetration.^{6,8}

The hydrogen adsorption isotherm of **1** was obtained at 25 °C using a pulse mass analyzer according to a previously described procedure.⁹ The instrument measures mass changes by an inertial technique for a packed bed of adsorbent in a flowing stream of hydrogen (99.999%) as a program ramps the pressure from 1 to 48

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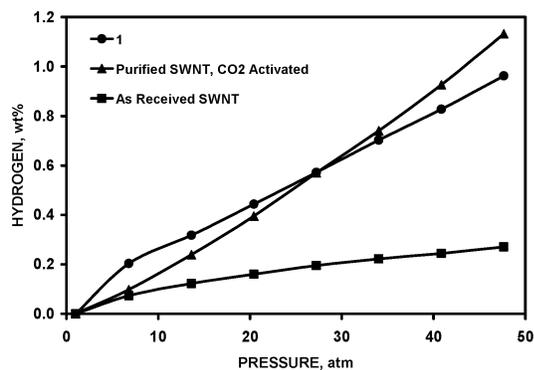


Figure 2. Room-temperature hydrogen adsorption isotherms for **1**, as compared to as-received SWNT and purified SWNT that was activated by CO₂ oxidation.⁹ The lines are drawn to guide the eye.

atm. The isotherm is the average of eight complete pressure cycles. The amount of hydrogen adsorbed was stable throughout the 20 min hold time at each pressure and returned to baseline when pressure was reduced from its highest point to one atmosphere. Thus, the full amount of hydrogen taken up is delivered when the pressure is released. As shown in Figure 2, structure **1** adsorbed close to 1 wt % hydrogen at 48 atm. This puts it in the class with the best performing carbon nanotubes that we have examined. For example, included in Figure 2 are data for two samples of SWNTs. The material received as prepared by the laser ablation method has a relatively low storage capacity. After purification by nitric acid oxidation,¹⁰ then activation by partial oxidation in CO₂, followed by heating to 700 °C, the storage capacity reached above 1.1 wt % at 48 atm.⁹ In contrast to this extensive pretreatment, the MMOM required no activation procedure other than heating (190 °C) to remove material adsorbed on the surface.

As a further comparison, we also measured hydrogen uptake in MOF-5 (pore dimensions approximately 7.7 × 7.7 Å) using the same conditions. The material was synthesized according to the published procedure.¹¹ The hydrogen isotherm taken by our procedure essentially agrees with that reported, which covered a range of pressures up to 20 atm. We have extended the isotherm to higher pressures and find a storage capacity of 1.65 wt % at 48 atm. The accessible volume of MOF-5 (about 76.8% based on our calculations) is 6.6 times that of **1** (11.6%), but MOF-5 only takes up 1.8 times the amount of hydrogen. This suggests that pore volume is not the sole factor that determines the amount of gas adsorbed. The quality of the pores that contribute to the pore volume must be considered as well. One critical aspect of pore quality is the relative size of the pores with regard to the gas that is taken in. An optimal material would have pores that fit the size of the gas molecules well and have the largest possible pore volume. Note the differences in the pore dimensions and shapes of the two structures. Positive evidence for a restricted pore size in **1** was found by comparing isotherms we have obtained for methane with those for hydrogen. In the case of **1**, the molar ratio of methane to hydrogen sorbed at 48 atm was 0.75, while for the larger pore size material of similar structure it was 1.7.¹² Based on the adsorption results on the pure gases, this represents a striking inversion of selectivity that is apparently related to the pore dimensions.

Note also that **1** gives a significantly higher volume density,¹ 0.0147 g H₂/cm³, as compared to 0.0099 g H₂/cm³ for MOF-5. This also points to a more effective use of available pore volume by the material with smaller pore size. Thus, tailoring pore size to fit the molecular diameter of the stored molecule seems to have virtue. This result points toward more optimal designs for MMOMs that retain a small pore size but have larger total pore volumes. In this way, it may be possible to approach the DOE target value (0.036 g H₂/cm³ for 2005¹) without resorting to pressures much higher than those used here.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) (a) Reaction of Cu(NO₃)₂·3H₂O (0.024 g, 0.1 mmol) with excess H₂fhfipbb (0.122 g, 0.31 mmol) and deionized water (5 mL) in the molar ratio of 1:3.1:2.778 at 150 °C for 12 hours resulted in column-like blue crystals of **1**. The product was washed with DMF (10 mL × 3) to remove excess H₂fhfipbb, followed by washing with deionized water (10 mL × 3) and drying in air. Yield: 60 mg, (92.3%). (b) Element analysis: found (%) C = 46.95, H = 1.98, N = 0.16; calc. C = 47.08, H = 2.00, N = 0.00. IR (cm⁻¹): 1690 (vs), 1634 (s), 1616 (s), 1574 (s), 1565 (sh), 1541 (m), 1514 (s), 1418 (vs), 1393 (s), 1333 (s), 1300 (w), 1254 (m), 1215 (s), 1182 (m), 1138 (s), 1022 (vs), 969 (s), 959 (sh), 933 (s), 860 (m), 849 (sh), 804 (m), 778 (s), 745 (w), 727 (s), 694 (w), 635 (w), 560 (w), 543 (s), 497 (w). Thermal gravimetric analysis of **1** showed no weight loss until 330 °C, indicating that the microtubes in the structure are guest-free. The framework collapsed after the sample was heated above this temperature. Sample purity was checked and confirmed by PXRD on all powder samples.
- (5) Crystal data of **1**: C₅₁H₂₆Cu₂F₁₈O₁₂, *M* = 1299.80, monoclinic, space group *P2₁/n*, *a* = 18.723(4), *b* = 7.271(1), *c* = 20.481(4) Å, β = 107.02(3)°, *V* = 2666.1(9) Å³, *Z* = 4, *F*(000) = 1296, *D_c* = 1.619 g cm⁻³, μ(Mo Kα) = 0.921 mm⁻¹, 375 variables refined on *F*² with 3397 observed reflections collected at 295 K (θ_{max} = 26.0°) with *I* ≥ 2σ(*I*) yielding *R*₁ = 0.0441, *wR*₂ = 0.0685.
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