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A Porous Coordination Copolymer with over 5000 m^2/g BET Surface Area

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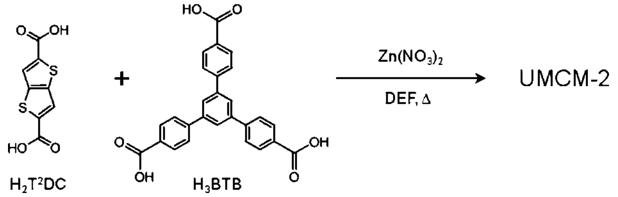
The past decade has seen a revolution in the production of high surface area materials enabled by breaking from traditional sorbents such as zeolites and activated carbons and embracing microporous coordination polymers (MCPs). The first material to exceed surface areas of the best activated carbons was MOF-177.[1] This material typifies the most common strategy for the production of high surface area MCPs, namely linker variation. Other important factors controlling surface area include identity of the metallic secondary building unit (SBU)[2] and topology of the polyreticular framework.[3] Motivating most of these advances is the quest to find more efficient sorbents. In particular, gravimetric hydrogen storage capacity is a property that has been correlated with surface area for MCPs,[4] and significant improvement will be needed to achieve U.S. Department of Energy system targets of 6.0 wt% (45 g/L) by 2010.[5]

Surface area measurements are typically based on N_2 sorption at 77 K; the Langmuir or Brunauer−Emmer−Teller (BET) model is typically used to interpret the data.[6] The basic assumption for the Langmuir model is that adsorbates pack in a monolayer, whereas the BET model accommodates multilayers. Because most porous materials have large enough pores to allow more than one adsorbed layer, the Langmuir surface area leads to overestimation, and the BET surface area calculation is more reliable.[7] Although thousands of MCPs have been reported, few materials possess BET surface areas over 4000 m^2/g and, perhaps consequently, most materials can not even achieve 6 wt% excess H_2 uptake at 77 K.[4]

This communication illustrates the application of coordination copolymerization for the synthesis of ultrahigh surface area materials. H_2BDC is the organic linker which makes MOF-5 when combined with Zn(II) ions. Utilizing H_3BTB under identical synthetic conditions yields MOF-177. Our previous finding for the combination of H_2BDC with H_3BTB in the presence of zinc was that both components are incorporated into a completely new type of structure (UMCM-1; University of Michigan Crystalline Material), which has both cage-like micropores and one-dimensional mesoporous channels.[8]

Scheme 1. Synthetic Process for UMCM-2



As a strategy to increase the surface area of the basic UMCM-1 structure, replacement of the ditopic linker with thieno[3,2-b]thiophene-2,5-dicarboxylate (T^2DC) was explored. Pure T^2DC reacts to generate IRMOF-20, which shows the highest surface area in the IRMOF series.[9] The length of T^2DC is 1.3 times longer than that of BDC. Combining T^2DC with BTB in the presence of zinc did not result in an extended structure isomorphous with UMCM-1; this combination resulted in a completely new phase, and at a ratio of 1:1 (T^2DC/BTB) a hexagonal plate-like phase was obtained (Scheme 1). A single crystal X-ray diffraction study of these plates showed that the product crystallizes in the hexagonal space group $P6_3/m$. The framework of the material consists of Zn_4O metal clusters linked together by two T^2DCs and four BTBs arranged in an octahedral geometry. In the structure, T^2DC linkers are disposed both opposite to each other and adjacent to each other leaving the other four positions occupied by BTB linkers (Figure 1a). Comparison of the bulk powder XRD pattern to the simulated pattern calculated from the single crystal data confirms that a single, phase-pure material forms in the region where the mole ratio of T^2DC/BTB is between 3:2 and 1:1. The formula of this product was determined as $Zn_4O(T^2DC)(BTB)_{4/3}$ from a combination of elemental analysis and thermogravimetric analysis (TGA) of as-synthesized crystals which were exchanged in CH_2Cl_2 and then evacuated at room temperature (Figure S1). This product is denoted as UMCM-2. Analysis of the structure reveals two different microporous cages (Cages I and III in Figure 1c) and a mesoporous cage (Cage II, Figure 1c). Cage I has the same geometry as the microporous cage of UMCM-1 which is constructed from six ditopic linkers (BDC), five tritopic linkers (BTB), and nine Zn_4O clusters. Cage II, the mesoporous cage, has an internal dimension of approximately 2.6 nm × 3.2 nm (subtracting the van der Waals radii of the atoms). Cage III is defined by alternating cages of I and II (Figure 1b).

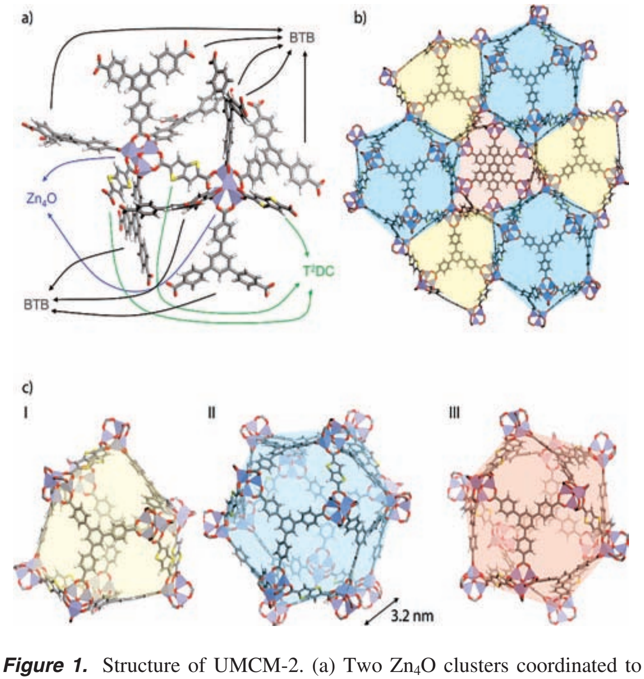


Figure 1. Structure of UMCM-2. (a) Two Zn_4O clusters coordinated to three T^2DC linkers and eight BTB linkers. (b) Structure of UMCM-2 viewed along the *c*-axis. (c) Microporous cages (I and III) and a mesoporous cage (II).

10.1021/ja809985t CCC: $40.75 © 2009 American Chemical Society

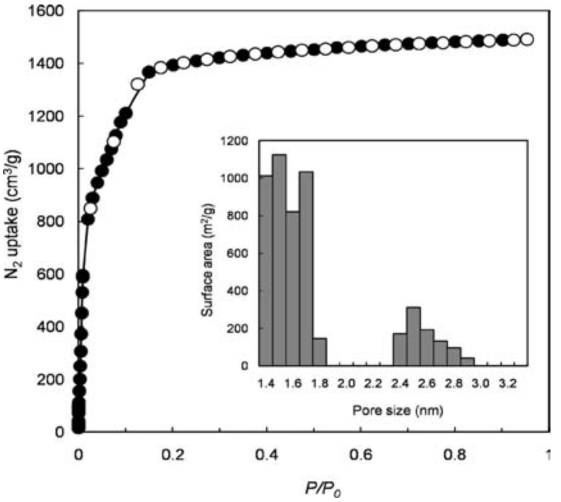


Figure 2. Nitrogen adsorption isotherm at 77 K for UMCM-2 (●, adsorption; ○, desorption). Inset: Pore size distribution calculated after fitting DFT models to argon gas adsorption data at 87 K.

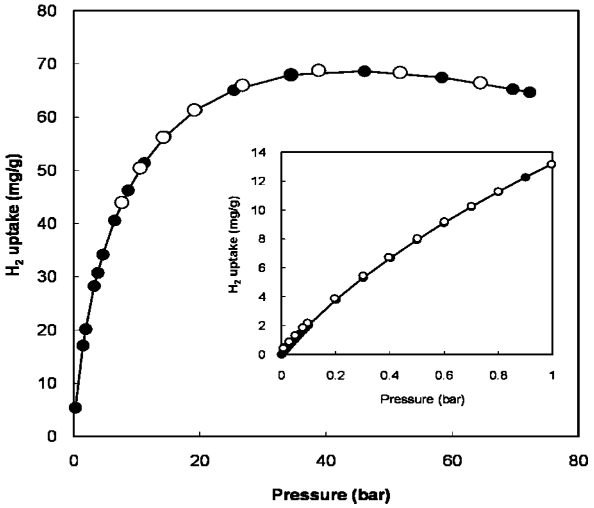


Figure 3. Hydrogen sorption isotherm at 77 K for UMCM-2 (●, adsorption; ○, desorption). Inset: isotherm from 0 to 1 bar.

The N_2 sorption isotherm of UMCM-2 is shown in Figure 2. From the secondary uptake at the region $P/P_0 \approx 0.15$, the isotherm could be classified as type IV. UMCM-2 exhibits exceptionally high N_2 uptake (ca. 1500 cm^3/g), and by applying the BET model up to the first plateau ($P/P_o \approx 0.1$), the apparent surface area is calculated to be 5200 m^2/g (a similar treatment using the Langmuir model affords a surface area of 6060 m^2/g). This value is significantly higher than that of any other porous material reported to date. A pore size distribution analysis by DFT methods using Ar gas at 87 K showed that there is a narrow distribution of micropores at 1.4−1.6 and 1.6−1.8 nm and a mesopore at 2.4−3.0 nm (Figure 2). These pore sizes are consistent with the three types of cages observed in the crystal structure.

TGA measurement recorded minimal weight loss up to 400 °C (Figure S1). Based on the TGA analysis result, 300 °C was applied for evaluating changes of crystallinity and porosity at high temperature, and no significant changes in the powder XRD pattern were observed after heating (Figure S10). These measurements suggest that no dramatic structural changes took place and the N_2 sorption isotherm after heating at 300 °C was unperturbed (Figure S5), indicating that the framework of UMCM-2 was thermally stable.

The H_2 sorption isotherm at 77 K shows type I behavior with no hysteresis and no noticeable change in properties upon repeated cycling (Figure 3). UMCM-2 shows an excess gravimetric H_2 uptake of 68.8 mg/g (6.9 wt% based on MCP) at 46 bar (Figure 2). Thus UMCM-2 shows high H_2 uptake, but not greater than MOF-177, providing evidence that for mesoporous materials surface area is not adequately predictive of hydrogen storage performance.[10] The heat of adsorption is between 4.2 and 6.4 kJ/mol at low coverage, indicating that the affinity is similar to that of other Zn_4O-based MOFs (Supporting Information).[11]

In summary, the coordination of the linkers T^2DC and BTB with zinc produces a new porous material with microporous and mesoporous cages. The N_2 uptake and surface area of UMCM-2 exceeds those of the materials derived from the pure linkers and demonstrates the highest values to date suggesting a very bright future for coordination copolymerization.

Acknowledgment. The authors would like to thank Dr. William W. Porter III for assistance with X-ray data collection and funding provided by the U.S. Department of Energy through the National Energy Technology Laboratory, under Award No. DEFG26-04NT42121.

Supporting Information Available: Synthetic procedures, crystallographic data, powder X-ray diffraction data, thermogravimetric analysis, Ar sorption isotherms, and heat of adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA809985T