

1. Adsorption sites in MOFs. The primary adsorption sites for Ar and N₂ within metal-organic framework-5 (MOF-5), a cubic structure composed of Zn₄O(CO₂)₆ units and phenylene links defining large pores 12 and 15 Å in diameter, have been identified by single crystal X-ray diffraction. Refinement of data collected between 293 and 30 K revealed a total of eight symmetry-independent adsorption sites. Five of these are sites on the zinc oxide

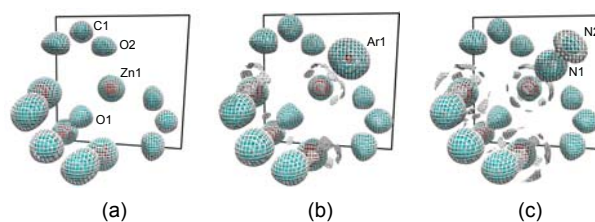
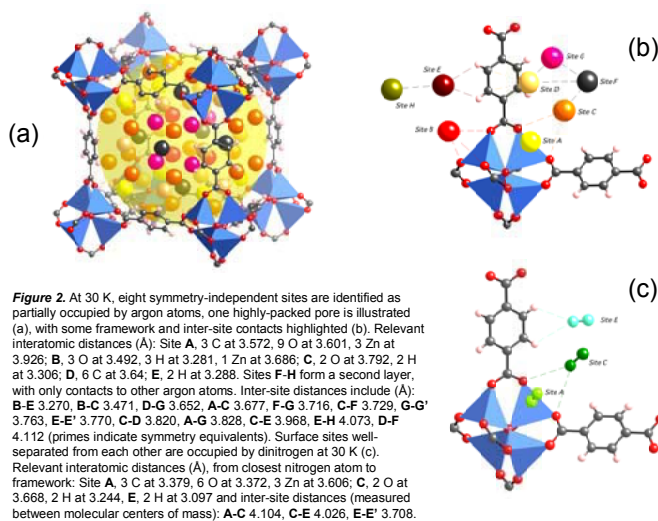
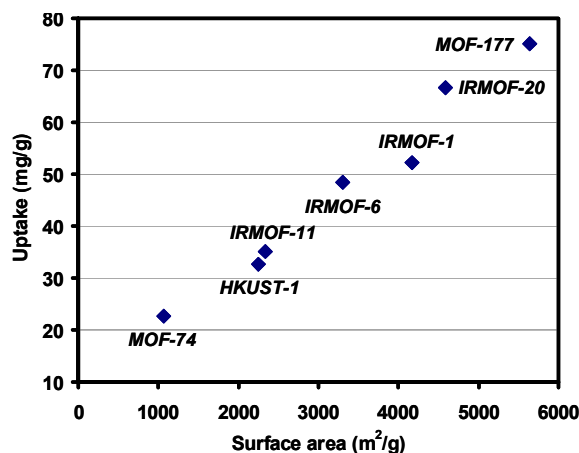


Figure 1. Three-dimensional electron density maps (F_{obs}) of the primary adsorption site in MOF-5, calculated from X-ray diffraction data collected from single crystals loaded under gases. At 293 K, only regions of electron density assigned to the framework are observed, including the Zn₄O cluster and three carboxylates (a), while at 30 K, regions of electron density ascribed to adsorbed argon (b) or dinitrogen (c) are also prominent. At 30 K, Fourier ripples around the Zn atoms are observed. Contours ($e^{-}/\text{\AA}^3$): silver > 3, blue > 5, red > 25.



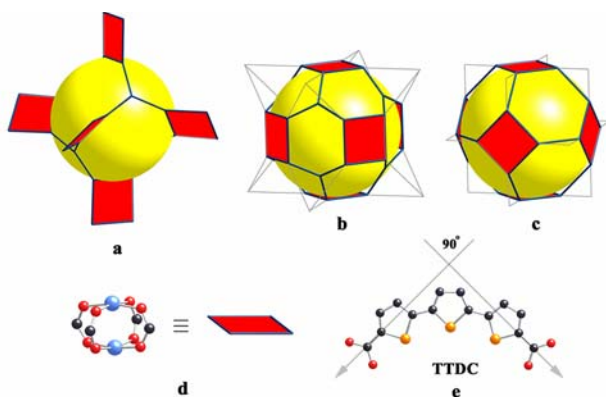
unit and the organic link; the remaining three sites form a second layer in the pores. The structural integrity and high symmetry of the framework is retained throughout, with negligible changes resulting from gas adsorption. This has facilitated the design of specific frameworks for storage and separation of gases as well as the separation of polar and nonpolar, and aromatic organics.

2. Hydrogen storage. Understanding the relationship of surface area to hydrogen uptake is a very important aspect of achieving the DOE goals for hydrogen storage. Under this grant, we find a clear relationship between hydrogen storage capacity and surface area (reported in JACS 2006). We reported adsorption data collected for seven MOF materials at 77 K which leads to saturation at pressures between 25 and 80 bar with uptakes from 2% to 7.5%. In this study we show that the saturation uptake of H₂ in MOFs correlates well with surface area and that viable volumetric densities in highly porous structures can indeed be achieved.

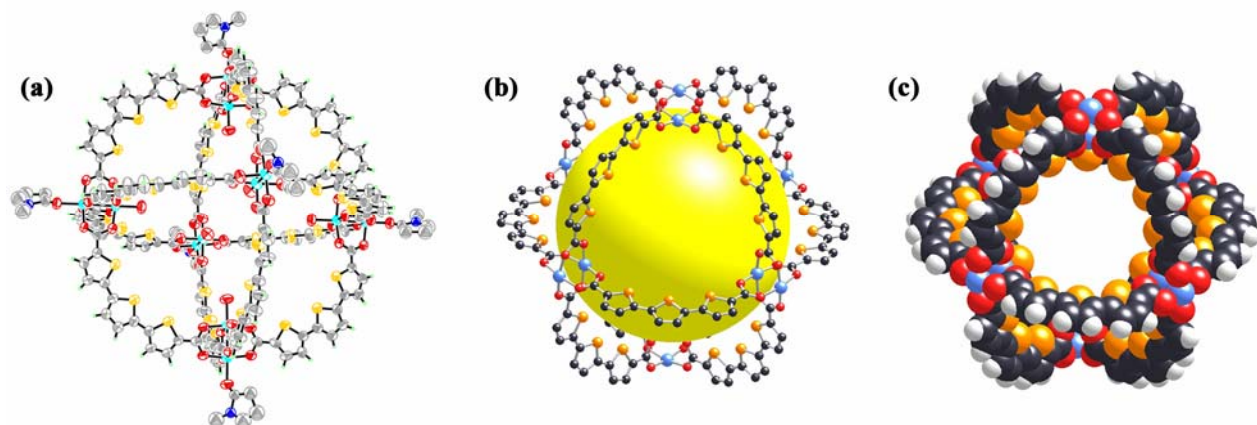


3. Porous polyhedra. A more recent development focused on designing and using small porous molecules that can be employed in solution to trap and separate organics and small gas molecules. The remainder of the report will discuss this aspect; although the publications listed below are indicative of the tremendous success we have achieved in the last year on this project.

A number of designed 3-D discrete molecular shapes have been assembled by joining metal ions with organic linkers. Success of such syntheses is critically dependent on identifying chemical units with specific geometry that would assemble into a target structure. In this context, for a square unit, there are *only* three truncated 3-D discrete shapes that can be assembled in which all squares and all links are equivalent: octahedron, cuboctahedron, and icosidodecahedron. Our studies concerns the truncated octahedron for which two construction strategies have been previously implemented wherein either alternative faces, **a**, or all faces, **b**, of the octahedron are built from triangular organic linkers, and vertices from protected squares (Pd^{2+} , Pt^{2+} , Mo_2^{4+}), **a**, or unprotected squares, **b**. Here, we report the construction of a truncated octahedron of the third type, **c**, from $\text{Cu}_2(\text{CO}_2)_4$ building blocks, in which the carboxylate carbon atoms define a *rigid* square, **d**, and 2,2':5',2''-terthiophene-5,5''-dicarboxylate (TTDC) having a linking angle very close to 90° when in the *cis,cis* conformation, **e**. We further show that molecular structures of this kind can be designed to have truly porous architectures and remarkable capacity for adsorption of gases, as evidenced by this compound's Type I gas sorption isotherm.



To prepare truncated octahedron, **c**, we used reactions known to produce the $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel unit. These were uncovered in an earlier study involving the use of such units with 1,3-benzenedicarboxylate to produce a 25 Å-sized truncated cuboctahedron, metal-organic polyhedron-1 (MOP-1). Reaction of equimolar amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and H_2TTDC at 85 °C for 24 hours in a mixture of NMP (2-methyl-1-pyrrolidinone) and DMA (*N,N*-dimethylacetamide) gives green crystals of $[\text{Cu}_{12}(\text{TTDC})_{12}(\text{NMP})_6(\text{H}_2\text{O})_6] \cdot 13\text{NMP} \cdot \text{DMA} \cdot \text{H}_2\text{O}$ (termed MOP-28). The structure of MOP-28 was determined by single crystal X-ray diffraction studies. Each MOP-28 molecule is composed of 6 $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel building blocks and 12 *cis,cis*-terthiophene linking units (Fig. 1a-c).



The reproducibility of the isotherm was confirmed by repeating adsorption-desorption cycle three times. Significantly, all gas molecules can be removed as observed from the desorption branch of the plot. A small H4 type hysteresis loop is also observed in the isotherm. Given the location of the lower closure point of the loop ($P/P_0 = 0.21$), the hysteresis must be attributed to causes other than capillary condensation of N_2 in large pores. From the adsorption branch of the isotherm, Langmuir surface area of 1,100 m^2/g and pore volume of 0.39 cm^3/g (Dubinin-Radushkevitch model) have been obtained. The amount of N_2 adsorbed in the pores (337 mg/g) corresponds to 57 N_2 molecules per truncated octahedron. It is remarkable that MOP-28 being a solid composed of discrete molecules, exhibits porosity similar to that of extended metal-organic frameworks. To our knowledge, MOP-28 is the most porous *molecular* structure and stands among the first metal-organic polyhedra to be characterized by gas sorption.

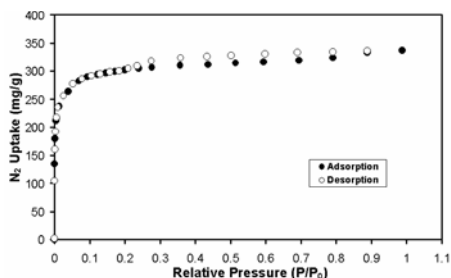


Figure 2. Nitrogen sorption isotherm (77K) for MOP-28.

Publications acknowledging DOE support

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- Gas Adsorption Sites in a Large-Pore Metal-Organic Framework, J. Rowsell, E. Spenser, J. Eckert, J.A. K. Howard, O. M. Yaghi, *Science*, **2005**, *309*, 1350.
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- A Route to High Surface Area, Porosity and Inclusion of Large Molecules in Crystals, H. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. Matzger, M. O’Keeffe, O. M. Yaghi, *Nature*, **2004**, *427*, p. 523.