

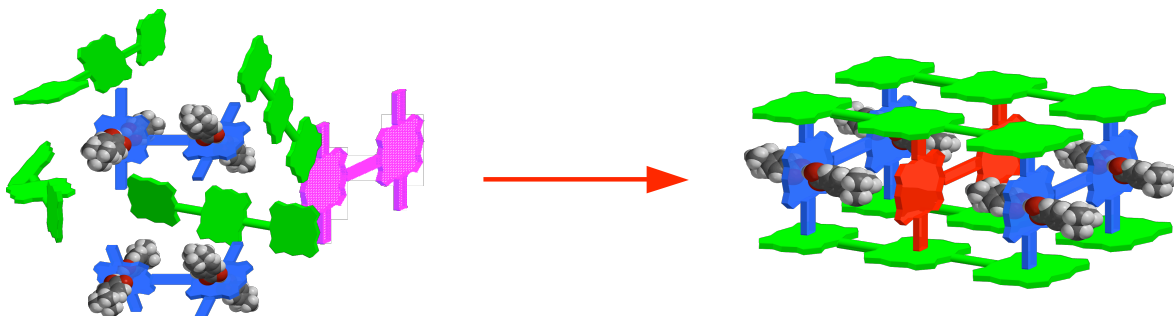
Final Report for Grant. No. DE-FG02-ER15244 “Supramolecular-Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities”

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The premise of this project was that coordination chemistry could be used to devise new kinds of microporous materials and that these materials could exhibit nanoscale porosity and selective chemical separation capabilities. Our initial materials focus was on aggregates of discrete hollow molecules, especially molecular squares. Subsequently our focus turned largely toward permanently microporous metal-organic frameworks (MOFs). Our approach emphasized coupling predictive & explanative computational modeling to materials design, synthesis, and property characterization. Results from the project were presented in ca. 30 papers. The accompanying proposal highlights additional significant unpublished results. Presented below are representative project results.

Experimental I. Hollow molecules. Hollow molecules proved to be very useful for creating freestanding membranes (liquid/liquid interfacial polymerization) and ultrathin microporous films (layer-by-layer coordinative assembly). Both kinds of materials were found to exhibit size-selective transport of condensed-phase molecular permeants, i.e. molecular-sieving behavior.[7,15] As part of this work, the applicability of x-ray standing wave and x-ray fluorescence methods for characterizing thin films on the nanometer scale was demonstrated.[8,10] Additionally, an unusual approach, based on wall-jet electrochemistry, was developed for quantifying rates of molecular transport through films. Rate/structure correlations, in turn, were used to establish mechanisms of transport.[7]

The spontaneous assembly of well-defined nanoscale box structures comprising 16 porphyrins was demonstrated; see schematic representation below.[27] The most sophisticated versions of the assembly scheme enlist both orthogonal coordination and steric self-sorting phenomena to produce monodisperse box structures. The ability of synchrotron radiation to provide structural information via *solution-phase* molecular diffraction was demonstrated.[18,27]

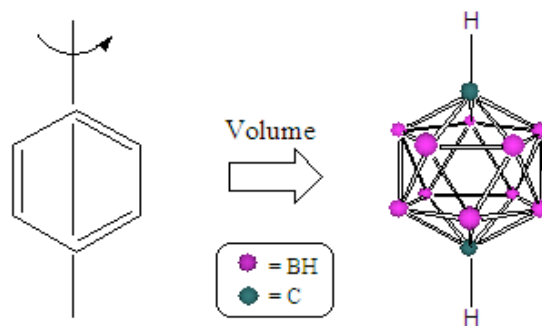


Experimental II. Metal-organic frameworks. Metal-organic frameworks (MOFs) synthesized in a building block approach from linker and corner units offer the opportunity to design materials with high surface areas for adsorption applications. They are characterized by complete uniformity of pore and channel size (for any given material), but broad tunability of pore and channel size, as well as chemical composition, across a range of materials. The well-defined structures of crystalline MOFs greatly facilitate the application of complementary computational modeling methods, as described in the next section of the report.

Much of our work here has focused on developing families of robust, permanently microporous, and potentially highly functional MOFs. We explored the following five ideas synthetically:

1. Frameworks based on anisotropic pillared paddlewheels. Cubic MOFs based on carboxylated struts are characterized by very good mechanical stability. Analogous pyridine-based MOFs, in contrast, are often subject to pore collapse upon removal of solvent. We have discovered that by employing pillared (pyridine) paddlewheel (carboxylate) architectures, we can capture the stability of carboxylate-based materials while enlisting the chemical diversity of pyridine-derived struts.[9] We have now synthesized more than two dozen MOFs of this kind, encompassing a broad range of channel sizes.

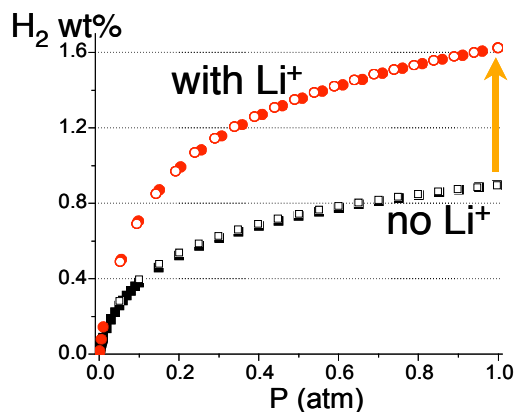
2. Carborane-based frameworks. These new materials are unusually robust and display high heats of adsorption for hydrogen, likely due to cavity-size modulation caused by the unusual 3D steric demand of the carborane units; see sketch.[21]



p-carborane versus phenyl ring

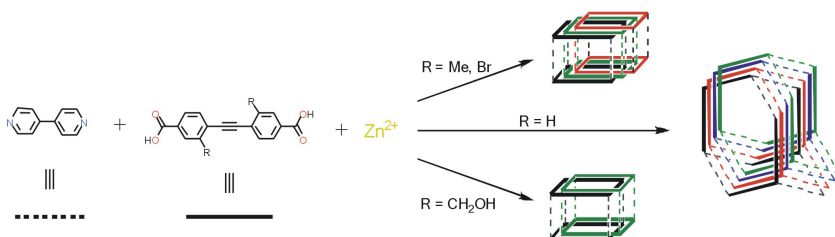
3. Framework reduction. We have shown that chemical reduction of framework struts by alkali metals, together with uptake of charge-compensating alkali cations leads to spectacular increases in hydrogen loading and substantial increases in heats of adsorption.[22]

4. Post-synthetically modifiable frameworks. We have used the idea of post-synthetic elaboration to introduce very specific



functionality to otherwise generic frameworks. In one version of this approach, materials featuring coordinatively unsaturated metal sites were designed and synthesized. These sites, which are initially achiral, were then modified with chiral ligands. Exposure of the modified material to a stream of racemic alcohol showed that the material is capable of separating the mixture into component enantiomers.[19] We see this as a potentially very powerful general approach to obtaining superior materials for separations.

5. Structural diversity via ligand elaboration. MOFs constructed from chemically similar components often exhibit isorecticular behavior. The classic examples are Zn_4O units + linear carboxylates; these generally yield simple cubic MOFs. We have observed that closely chemically related struts featuring very high aspect ratios can be made to behave much differently, yielding a broad range of mixed-ligand structures with widely varying degrees of catenation based on very small changes in strut substituents.[23]



We have taken advantage of the tunability outlined in strategy 1 to build materials that imbibe target molecules in size-selective fashion and then process them catalytically to produce chiral products. Specifically, we examined the selective uptake and conversion of olefins to epoxides in work [17] that was recently highlighted in *Chemical & Engineering News*. The catalysis aspects of this work we have now transitioned to other sponsorship in order to focus the DOE effort more completely on the use of MOFs for separations.

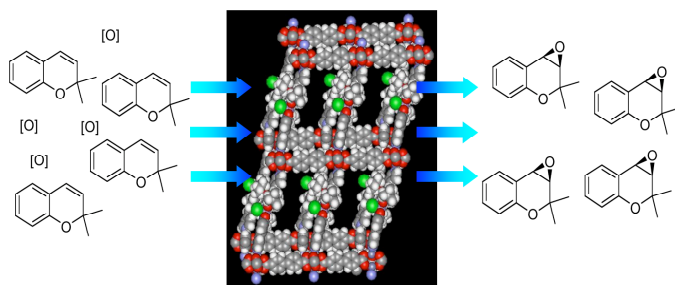


Figure 1. Enantioselective epoxidation of olefins utilizing a manganese salen MOF.

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Computational modeling. We have developed molecular models that

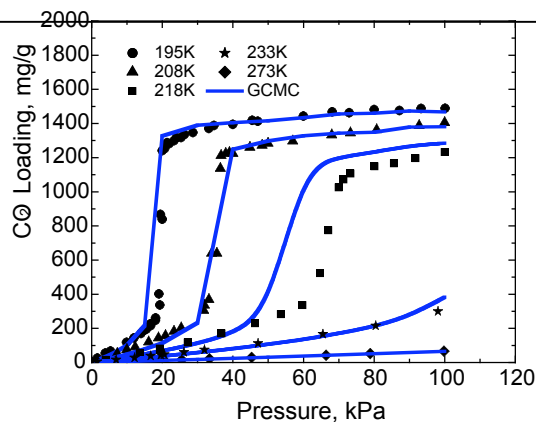


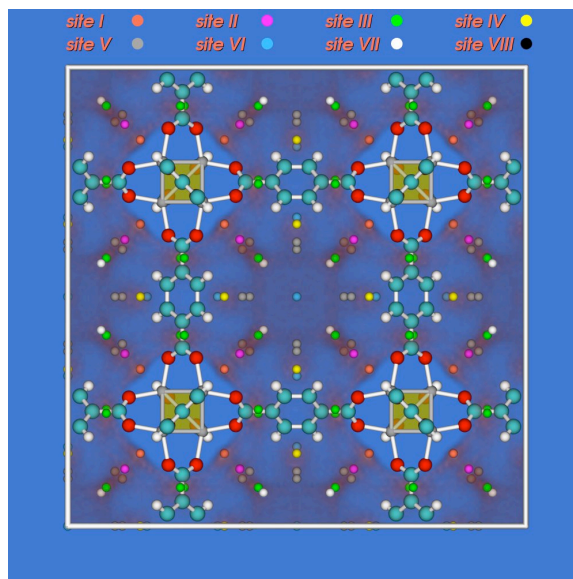
Figure 2. Comparison of GCMC simulations and experimental adsorption isotherms for CO₂ in MOF-5 [25].

predict adsorption of methane [2], hydrogen [14], argon [28], nitrogen [28], and CO₂ [25] in several cubic carboxylate MOFs in very-good-to-excellent agreement with experiment. See, for example Figure 2. It should be noted that the simulations in Figure 2 are true predictions; they are not fit to the experimental data. The modeling is now sufficiently compelling that we can use it to determine accurately the ideal upper bounds of MOF sorbate loading, and in turn determine whether we are fully accessing the MOF interior experimentally.

With these models, we have also successfully begun exploring mixture sorption [1]. Grand canonical Monte Carlo (GCMC) simulations show that MOFs are promising materials for removing trace amounts of n-butane from methane, an important separation for upgrading of natural gas. Detailed analysis of the molecular-level details also allowed us to propose new, not-yet-synthesized MOFs that are predicted to perform even better than existing MOFs.

In addition to reproducing the experimental isotherms, we have recently shown that simulations also predict the positions and occupations of the adsorption sites of argon and nitrogen in good agreement with experiments in IRMOF-1 [28]. At 30 K, the molecules are localized around their crystallographic sites, while at room temperature the molecules are spread throughout the pore volume as shown in [Figure B](#).

With simulations one can explore a large number of different materials much more quickly than with experiments, with the hope of obtaining deeper insights into the structure/property relationships. We performed GCMC simulations of hydrogen adsorption at 77 K in a series of 10 structurally related metal-organic frameworks. The effects of surface area, free volume, and heat of adsorption on hydrogen uptake were investigated by performing simulations over a wide range of pressures on this set of materials, which all have the same framework topology and surface chemistry but varying pore sizes. The results reveal the existence of three adsorption regimes: at low pressure (loading), hydrogen uptake correlates with the heat of adsorption; at intermediate pressure, uptake correlates with the surface area; and at the highest pressures, uptake correlates with the free volume [14]. These studies resolved seeming contradictions in the literature about whether hydrogen uptake by MOFs correlates with the surface area.



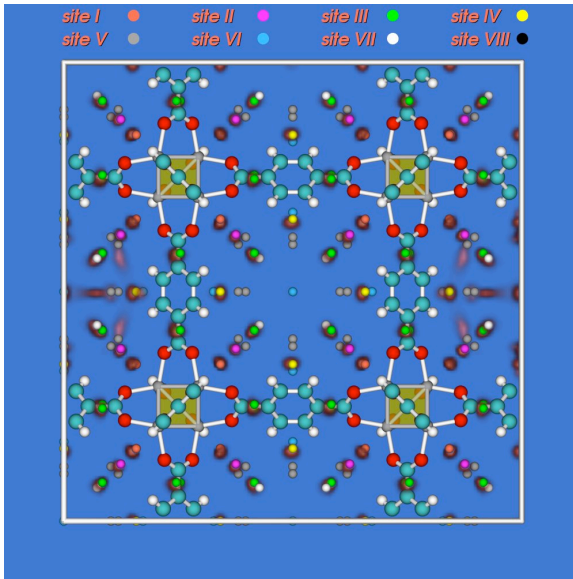


Figure B. Sitings of argon in IRMOF-1 at 288 K per unit cell simulations (brown patches) and compared to the experimental data (colored dots, sites I – VIII). Left: simulations at 30 K; right: simulations at 288 K.

Recently, we extended this investigation to adsorption at room temperature [24]. By artificially increasing the heat of adsorption in our simulations in a systematic way, we developed a correlation between the density of adsorbed hydrogen and the heat of adsorption. From this, we prepared a graph showing

combinations of heat of adsorption and free volume that meet target gravimetric and volumetric hydrogen storage amounts (Figure C). The graph suggests that if new materials can achieve a heat of adsorption of 10 to 15 kJ/mol with a free volume between 1.6 and 2.4 cm³/g, gravimetric uptake of 6% could be achieved. Our results for IRMOFs-9 and -10 suggest that catenation is not a promising option to increase the heat of adsorption because the loss in free volume is not sufficiently offset by the increased heat. Thus alternate methods of increasing the heat of adsorption, such as introduction of cations, should be considered [21].

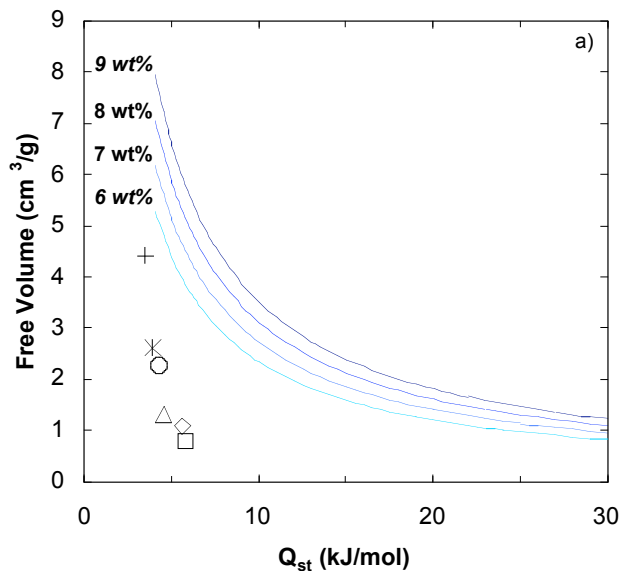


Figure C. Requirements for target gravimetric loadings at 120 bar and 298 K. \triangle IRMOF-1; \diamond IRMOF-9; $*$ IRMOF-10; \circ IRMOF-14; $+$ IRMOF-16; \square Cu-BTC.

Some MOFs are reported to have incredibly high surface areas – as high as 4500 m²/g. The high surface area is part of what makes these materials attractive for applications such as adsorption separations. The BET analysis is the standard method for determining surface areas from nitrogen adsorption isotherms and was originally developed for multilayer gas adsorption onto flat surfaces. MOF surfaces are far from flat, and in some MOFs adsorption occurs

through a pore-filling mechanism rather than by layer formation. Thus, it is unclear whether BET surface area numbers reported for these materials are truly meaningful. To test this widely used characterization method, we performed grand canonical Monte Carlo simulations to predict adsorption isotherms for nitrogen in a series of MOFs [20]. The predicted isotherms were used as pseudo-experimental data to test the applicability of the BET theory for obtaining surface areas for microporous MOFs. BET surface areas calculated from the simulated isotherms agree surprisingly well with the accessible surface areas calculated directly from the crystal structures in a geometric fashion. In addition, the surface areas agree well with experimental reports from the literature. These results provide a strong validation that the BET theory can be used to obtain surface areas of MOFs.

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