

Prospects for Nanoporous Metal-Organic Materials in Advanced Separations Processes

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Introduction

New materials spur new technologies. Nanoporous metal-organic materials — “soft materials” analogues of zeolites, but with all of the chemical diversity of carbon compounds — may be compelling examples of this path from materials to technologies. Research teams investigating this new class of materials are trying to develop adsorbents and membranes that will revolutionize small-molecule separations, as well as new kinds of catalysts that behave as powerful arrays of artificial enzymes. In addition, metal-organic materials hold promise to act as ultra-low-density sponges that can store and release extraordinary amounts of molecular hydrogen for next-generation vehicles.

Driving these materials discoveries are advances in supramolecular coordination chemistry and metal-based directed-assembly chemistry. These tools are enabling scientists and engineers around the world to construct imaginative new metal-organic materials in synthetically predictable ways. This article describes some of these materials and results to date that suggest their potential for performing, among other things, demanding chemical separations. Comprising the new materials are ones based on extended porous crystalline lattices, as well as others based on aggregates of individual hollow molecules. Each type appears to offer advantages for specific applications. What they have in common, however, are good permeability, high void volumes, and well defined tailorable cavities of uniform size — precisely the properties needed for catalysis, separations, and storage/release applications. This is still an emerging field, with many opportunities; numerous new materials are being made and the potential appears great, but the performance of metal-organic materials in industrially important technologies is still a mostly unexplored frontier.

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The New Materials: What They Are and What They Are Already Good For

Nanoporous metal-organic materials generally consist of metal or metal oxide vertices interconnected by rigid or semi-rigid organic molecules, as shown in Figure 1a. A large variety of metal-organic materials ranging from extended grid and network structures to discrete molecular triangles, squares, and cubes has been produced by various research groups, featuring different chemistries for the bonding of vertices with linkers. Figure 1 illustrates a few of the compounds made, but the extant variety of compositions, topologies, and unit cell sizes is much greater than shown.

The specific examples shown in Figure 1b are isorecticular metal-organic framework compounds (IRMOFs) developed by Yaghi and coworkers (Chen et al., 2001; Eddaoudi et al., 2002; Rosi et al., 2003). In general, IRMOF materials consist of zinc-oxygen complexes connected by molecular linkers (such as, 1, 4-benzenedicarboxylate in IRMOF-1), forming a regular, three-dimensional (3-D) lattice of cubic cavities. IRMOFs synthesized so far cover a range of pore sizes from 4 to 29 Å, void volumes between 55.8% and 91.1%, and densities from 1.00 to 0.21 g/cc, the lowest density to date for a crystalline material (Eddaoudi et al., 2002; Stein, 2003). Stability up to 400°C has been demonstrated for IRMOF-6 and other IRMOFs. Applications investigated to date for IRMOFs include methane storage (Eddaoudi et al., 2002; Düren et al., 2004) and hydrogen storage (Rosi et al., 2003).

Complementary to extended structures such as IRMOFs, are well-defined discrete hollow molecules that may be imagined as components of an ever growing chemical Lego set (Fujita et al., 1990; Stang and Olenyuk, 1997). Figure 1c illustrates a few of the now several hundred assemblies of this kind (Fujita, 1998; Sun and Lees, 2000; Dinolfo and Hupp, 2001). These can range in size from less than 5 Å to greater than 20 Å (cavity diameter), and they can exist in cationic, anionic, and neutral form. Many can be post-synthetically tailored to alter cavity sizes and chemical affinities as shown in Figure 1d, and a few

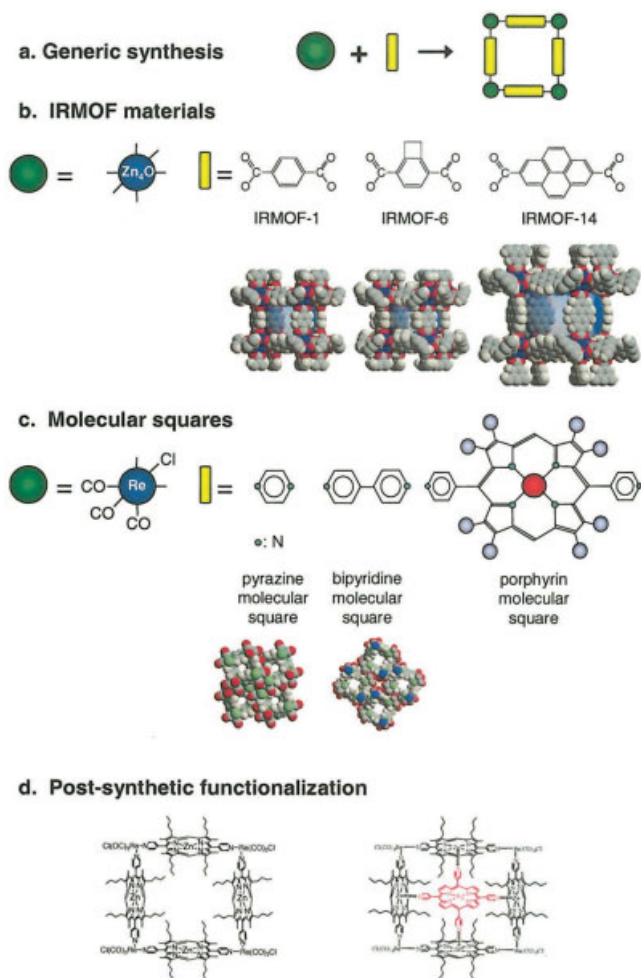


Figure 1. Examples of ligand-bridged metal-organic materials synthesized in a directed-assembly process.

(a) Representation of the assembly process (b) Building blocks and the resulting three-dimensional frameworks of different IRMOF materials. The empty lines at the Zn_4O vertices indicate where linkers bind. One complete, larger cavity of each IRMOF framework is shown. The transparent blue spheres were added to demonstrate the size of the cavity in the absence of network interpenetration, and to emphasize the open 3-D frameworks (c) Building blocks for representative molecular squares and the resulting crystalline structures for two of them (d) Tetrapyrrolyl porphyrin (in red) can be encapsulated within the Zn porphyrin square to modify the original cavity. Nitrogen atoms of the tetrapyrrolyl porphyrin bind to Zn atoms in the porphyrin walls of the square.

can be reversibly expanded and contracted in response to simple chemical stimuli. Some of the materials exist as pore-aligned crystalline compounds, whereas others are amorphous in the solid state. Among the demonstrated proof-of-concept applications, either in solution or as thin films, are chemical catalysis (Merlau et al., 2001), chemical sensing (Mines et al., 2002; Sun and Lees, 2000; Lee and Lin, 2002), size-selective membrane transport (Czaplewski et al., 2001), and light-to-electrical energy conversion (Splan et al., 2004).

Note that we use the term metal-organic material here to include both extended metal-organic frameworks (MOFs) and discrete metal-organic molecules such as, molecular squares. MOFs are sometimes referred to as coordination polymers in

the literature, and the discrete molecular compounds are sometimes called metallacycles. Note that we do not use the term organometallic, which implies a metal-carbon bond — something that is not always present in the kinds of structures considered in this article.

Predictable Synthesis via Directed Assembly of Molecular Building Blocks

One of the key objectives in the synthesis of new materials for separations, catalysis, and other applications is to design a material with tailored and functionalized characteristics (Bedard, 1999). However, in 1999, a panel of experts convened by the U.S. Dept. of Energy concluded that to date “tailoring of porous materials has proceeded largely in an empirical fashion rather than by design” (Barton et al., 1999). The beautiful variety of robust zeolite structures has inspired researchers to expand their range of compositions beyond aluminosilicates, and to explore for new framework topologies. In the 1980s aluminophosphates and metal aluminophosphate zeotypes were introduced, and the 1990s saw the introduction of many new frameworks, particularly with larger pores (Davis, 2002; Stein, 2003). However, devising a synthesis to achieve a targeted zeolite material is still an experimental challenge, usually requiring both good intuition and significant trial-and-error. Part of the difficulty is the complexity of the synthesis conditions, in which starting precursors undergo transformations that are not fully understood.

Synthesis of metal-organic frameworks (MOFs) attempts to avoid this complexity by assembling rigid molecular building blocks into ordered structures held together by strong bonds (Yaghi et al., 2003; Moulton and Zaworotko, 2001; Janiak, 2003; James, 2003). Strong bonding is essential for achieving permanent porosity. If bonding is weak, inter-network van der Waals interactions play too great a role and only nonporous, fully interpenetrated materials are obtained. Such nonporous materials are the predecessors of today’s nanoporous MOFs. They were often originally synthesized to test or illustrate interesting topological concepts (Barton et al., 1999; Vishnyakov et al., 2003). The evolutionary challenge here has been to mitigate the interpenetration phenomenon sufficiently to open up pores and channels — and to prevent the collapse of the resulting structures upon pore evacuation.

In most MOFs, organic linker molecules are rigid, and the functional groups that link to the vertices are in well-defined locations within the molecule, typically at the ends of the linker and at 180° to one another. Synthesis conditions are mild, and, thus, the structural integrity of the linkers is maintained in the final product. Because of the extensive literature and know-how from organic chemistry, an incredible variety of candidate linkers exists or can be made. The metal-containing vertices also play a crucial role in the ability to “design” a synthesis for a desired type of material. The vertices exploit the directional nature of metal-ligand interactions, and, therefore, provide the desired angle between the linker building blocks. They must also provide a certain degree of rigidity to this angle — otherwise the material may collapse. Indeed, an avoidable yet not uncommon problem with MOF materials is collapse when the solvent molecules from the synthesis are removed. Of course if this happens, the material is of limited utility as a nanoporous host for separations or catalysis. In other words, if

one is trying to create porous materials, they must really be porous under practical conditions. With the right chemistry, however, these problems can be overcome, as shown through some examples below.

A completely different way of defeating the problem of network interpenetration is to make individual ring-like molecules, each defining a cavity, and then use the cavities in aggregate to build up channels. The trick to getting the needed cyclic molecules is *directed assembly*. Metal ions predisposed to bind ligands efficiently, but only at certain sites (sites that define a right angle — the corner of a square), are combined 1:1 with ligands that can be bound at both ends (Stang and Olenyuk, 1997). One example is the reaction of $\text{Re}(\text{CO})_5\text{Cl}$ with pyridine-terminated ligands. The rhenium center readily loses two (and only two) carbonyls, replacing the rhenium-carbon bonds with more stable rhenium-nitrogen bonds at 90° to each other. The new bonds should not be too stable, however, or assembly mistakes — for example, making open-ended oligomers — cannot be undone. At the same time, the bonds have to be strong enough to prevent collapse of the resulting cavities when solvent molecules are removed. In the end, high-yield, essentially mistake-free products tend to be the outcome. The reasons are two. First, closed structures, like squares and triangles, maximize the number of metal-ligand bonds formed (an enthalpic advantage). Second, closed structures tend to be much less soluble, and their precipitation pulls the solution-phase reactions toward completion. These versatile components, which may well allow for the construction of functional materials almost unimaginable a few years ago, are clearly descendents of simple organic host molecules: intentionally designed cyclic molecules (for example, crown ethers) for the solution-phase encapsulation of shape- and size-matched molecular and atomic (ionic) guests.

Prospects for Adsorption and Membrane Separations

Sorption measurements have played an important role in establishing that MOFs can indeed be created with microporosity and that they maintain their porosity upon desorption of solvents used in their synthesis (Eddaoudi et al., 2000). These measurements also provide some first indications about possible applications in adsorption separations. For example, Eddaoudi et al. (2000) presented adsorption isotherms for Ar, N_2 , CCl_4 , CHCl_3 , benzene, and cyclohexane in IRMOF-1, and they reported that when evacuated MOF-4 is exposed to an equimolar mixture of acetonitrile and methanol, only methanol enters the pores (Eddaoudi et al., 2001). Huang et al. (2003) recently reported selectivity between p-xylene and o-xylene in a variant of IRMOF-1.

Wang et al. (2002) measured adsorption isotherms and isosteres with the explicit goal of evaluating a particular MOF for gas separation applications. The material was a crystalline framework of copper(II) benzene-1,3,5-tricarboxylate (Cu-BTC), having pore diameters of about 7 to 8 Å. From the single-component adsorption isotherms, these researchers suggest selectivity for CO_2 over methane for syngas-related processes, CO_2 and N_2O over N_2 and O_2 for air pre-purification, and ethylene over ethane, which is a “holy grail” of separations. Break-through curves suggest that molecular transport is rapid in these systems. Fletcher et al. (2001) combined sorption

measurements with X-ray diffraction studies to examine host structural changes during adsorption of guest molecules in a $\text{Ni}_2(4,4\text{-bipyridine})_3(\text{NO}_3)_4$ MOF. (Related studies have been described by Soldatov et al. (2003) and Birahda and Fujita (2002)). They report adsorption isotherms and kinetics for N_2 , Ar, CO_2 , N_2O , methanol, and ethanol in the narrow 1-D pores of this material. Some of the isotherms exhibit steps, which are explained by structural rearrangements of the host. Kitaura et al. (2003) recently showed how the flexibility of a related metal-organic framework compound based on $\text{Cu}(\text{II}), 4,4\text{-bipyridine}$ and 2,5-dihydroxybenzoate could be used to engender a gating effect. Above a critical “gate-opening pressure” (Li and Kaneko, 2001) the material suddenly becomes highly porous to nitrogen.

In 2002 Kosal et al. (2002) synthesized a microporous MOF from metalloporphyrin building blocks and trinuclear cobalt(II)-carboxylate vertices. The structure, named PIZA-1, is stable to heat treatment and many solvents, acids, and bases. It is hydrophilic and takes up nearly 4 times as much water as a given mass of zeolite 4A, a standard desiccant, and the uptake rate is faster (Stein, 2003). Kosal et al. exposed the material to various guests and then monitored their desorption under heating. Although they do not present adsorption isotherms or quantitative results, they report qualitative trends for adsorption of water, linear alkyl amines of varying chain length, aromatic amines of varying size, alcohols from methanol to hexanol, branched alcohols, and functionalized n-alkanes. Because of the catalytic functionality of many metalloporphyrins, this material and similar ones with other metals may lead to new catalytic applications.

Earlier this year Dybtsev et al. (2004) reported remarkable sorption selectivity for a manganese formate MOF. This material, which features permanent porosity with pore aperture diameters of about 4.5 Å, reversibly sorbs carbon dioxide but essentially completely excludes methane and nitrogen. At low-temperature it also reversibly sorbs hydrogen, with uptake significantly exceeding full monolayer coverage. In other words, a substantial fraction of the H_2 uptake (about a third) is achieved without direct contact with the walls of the MOF.

On the basis of these preliminary adsorption measurements, one can imagine adsorption separations with MOFs in processes such as pressure-swing adsorption. Separations with discrete molecular squares, however, are more likely to emerge as membrane processes. Czaplewski et al. (2001) fabricated membranes from the porphyrin and pyrazine molecular squares shown in Figure 1. Thin-film membranes were prepared by casting suspensions or solutions of molecular squares from a solvent onto commercially available, permeable polyester membranes. Film thickness, morphology, and crystallinity were characterized by microscopy, atomic-force microscopy (AFM), and X-ray diffraction, respectively. Tapping-mode AFM images of different film morphologies are shown in Figure 2. Simple U-tube measurements were performed for transport from a solution of given initial concentration, through the membrane, into a reservoir initially of pure water. Film transport was monitored via ultraviolet-visible (UV-vis) absorption in both chambers. UV-absorbing probe species of differing diameters were chosen: 5.7 Å (phenol), 13 Å ($\text{Fe}(1,10\text{-phenanthroline})_3^{2+}$) and 24 Å ($\text{Fe}(4,7\text{-phenylsulfonate-1,10-phenanthroline})_3^{4-}$). These investigations revealed that probes of up to 13 Å in diameter can permeate through the

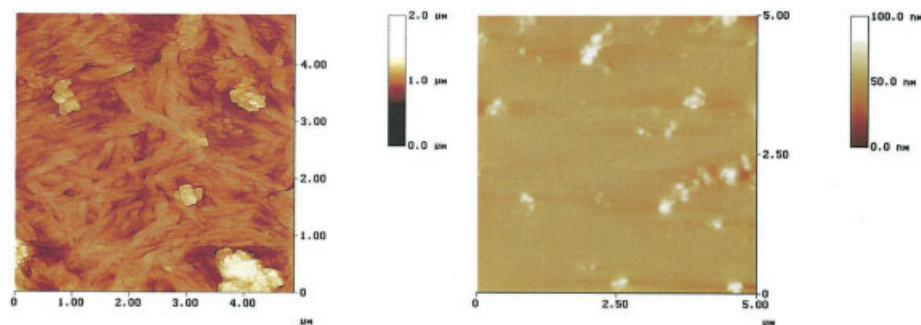


Figure 2. AFM images of molecular square membranes (Czaplewski et al., 2001).

Pyrazine molecular square membranes have rough surfaces and consist of closely packed, elongated particles (left). Porphyrin molecular square films, however, form continuous, smooth membranes (right).

porphyrin molecular squares, but only the small phenol probe permeates through films of the pyrazine molecular squares. Modification of the porphyrin molecular squares with an encapsulated tetrapyrrolyl porphyrin (Figure 1d) makes the membranes permeable only to the smallest of the probes (phenol). This is strong support for the notion that transport *through* individual cavities of the molecular squares is important.

These experiments were extended to permeation of single components and mixtures in the vapor phase (Czaplewski et al. 2003). Transport of cyclohexane, benzene, toluene, and their mixtures was measured through pyrazine square membranes on polyester supports. Steady-state permeabilities of the volatile organics were calculated from the measured fluxes

$$J_i = \frac{PD_m \Delta p_i}{L}$$

where J_i is the flux, L is the film thickness, Δp_i is the partial pressure drop across the membrane, and PD_m is the permeability, the product of the diffusion coefficient in the membrane D_m and the sorption coefficient P . The permeation selectivity in a binary mixture is then defined as the ratio of the permeabilities. The measurements revealed that the single-component permeabilities for benzene and cyclohexane are similar, whereas that of toluene is over an order of magnitude larger. Single-component sorption experiments were also performed. Interestingly, the selectivities measured in the benzene-cyclohexane and benzene-toluene binary mixtures agreed with the selectivities predicted from the single-component sorption data, whereas the toluene-cyclohexane selectivity agreed with the single-component permeation data. The authors cited diffusion effects as a possible explanation, but further research is needed to understand this behavior.

For a larger square with porphyrin walls, vapor-phase mixture selectivities for 4-picoline over toluene were observed to be around 7 to 9 (Czaplewski et al., 2003). Separate single-component adsorption and diffusion measurements showed that the mixture permeation selectivity comes from both preferential adsorption (a five-fold advantage for picoline over toluene) and preferential transport (ca. two-fold difference in diffusivities). Several experiments were dedicated to the functionalized porphyrin molecular squares. In particular, functionalization of the square cavity with tetrapyrrolyl porphyrin (Figure 1d) led to a mixture selectivity of 7 for benzene over cyclohexane.

Finally, some interesting second- and third-generation molecular-square materials have recently been described. One makes use of layer-by-layer assembly methods, and the strong propensity of square-appended phosphonate functionalities to react with Zr(IV) to form ultrathin (~ 6 nm and up), pinhole-free, supported films. These films have good porosity and reasonable molecular sieving ability (Massari et al., 2004). Initial applications focus on solar energy conversion (Splan et al., 2004) and catalytic chemical transformations. Because the phosphonated squares also have high affinities for porous alumina, tailored alumina/square composite membranes, suitable for chemical separations, can be envisioned.

Another assembly strategy involves reactive-linker/square polymerization at the interface between a pair of immiscible liquids. Reminiscent of nylon synthesis, the polymerization process is self-limiting and, during the synthesis phase, self-repairing. The resulting membranes show striking molecular sieving behavior, with a sharp permeant size cutoff at 22 Å, the nominal diameter of the component square cavities as shown in Figure 3. The sieving behavior, along with quantification of transport parameters, was tracked electrochemically. By plac-

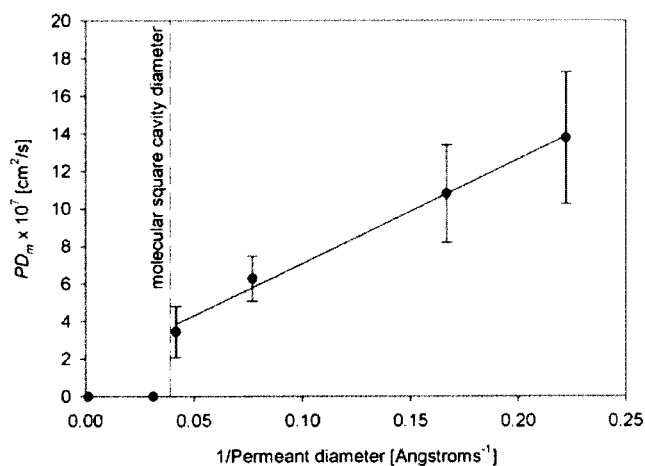


Figure 3. Dependence of the permeability on permeant diameter through thin, polymeric membranes made from molecular squares and reactive linkers as described by Keefe et al., (2003).

The permeability decreases as the probe size increases, and beyond a critical size drops to essentially zero.

ing the membrane on an electrode, permeation of redox-active probes in a solution environment could be followed by monitoring the resulting current. Size-selective membrane separation was observed by configuring the membrane in a standard U-tube and monitoring transport spectrally.

The Role of Molecular Modeling

Because of the predictability of the synthetic routes to metal-organic materials and the nearly infinite number of variations possible, molecular modeling is a particularly attractive tool for screening new structures before they are synthesized. Modeling can, as in other systems, also provide insight into molecular-level details that lead to observed macroscopic properties. Several molecular modeling studies have already appeared, and it seems that modeling will play an important role in the on-going development of metal-organic materials and their applications.

Vishnyakov et al. (2003) used an atomistic model and grand canonical Monte Carlo (GCMC) simulations to calculate adsorption isotherms for argon in Cu-BTC. They also reported experimental isotherms with high resolution in the low-pressure regime. They adjusted the force field to match the Henry's constant, but even without adjustment, the literature UFF force field gave reasonable ball-park agreement with experiment. In addition, the GCMC simulations allowed the authors to identify the adsorption sites and the sequence of pore filling. Düren et al. (2004) used GCMC simulations to predict methane adsorption in IRMOF-1 and IRMOF-6 (Figure 1). Agreement between simulation and experiment was excellent with the standard DREIDING force field from the literature. This result strongly suggests that the high methane uptake observed experimentally is because of physical adsorption. By comparing adsorption in different materials (3 IRMOFs, 4 molecular squares, 2 zeolites, MCM-41, and 4 carbon nanotubes) and calculating different properties that characterize these materials, these workers were able to identify the complex interplay of factors that influence adsorption. As expected, an ideal material for methane storage should have a large accessible surface area, a high free volume, a low framework density, and strong energetic interactions between the framework and the methane molecules. Yet, changing the linker molecules to improve one of these parameters might worsen the others. Düren et al. showed that simulation allows one to evaluate complex material topologies even if simple rules of thumb are unavailable or in conflict. They also proposed new IRMOF materials that are predicted to show substantially higher uptake of methane. The quantitative agreement between simulation and experiments for IRMOF-1 and IRMOF-6 provides support for the power of the simulation method, and the study underlines the usefulness of molecular simulations as a screening tool to identify new candidates for adsorption applications and to guide the design of new materials.

Skoulidas (2004) recently reported molecular dynamics (MD) simulations of argon diffusion in CuBTC, and Sarkisov et al. (2004) performed MD simulations of methane, several n-alkanes, cyclohexane, and benzene in IRMOF-1 and crystalline bipyridine molecular squares. Both studies conclude that diffusion in these systems is an activated process and that the diffusion coefficients are generally similar in magnitude to those found in silica zeolites. Of course, as with zeolites, the

tight fit of the molecules means that small differences in pore size can lead to large differences in diffusion coefficients.

The Future

Metal-organic materials open a vast potential for new developments in adsorption and membrane separations, as well as catalysis and energy storage. Predictable synthesis from libraries of building blocks is allowing materials scientists and engineers to truly design new materials and synthesize them in a short time. With this strategy, one can envision nanoporous materials with optimally placed functional groups to bind guest molecules or chiral cavities for enantioselective separations and catalysis — and, indeed, examples based on MOFs are beginning to appear (Kensanli and Lin, 2003). These materials open up the possibility of engineering heterogeneous catalysts with the atomic-level precision of current homogeneous catalysts. The nature of this new synthetic strategy is making the field of nanoporous materials more interdisciplinary. For example, the tools of organic chemistry create the diversity of linker molecules, but most organic chemists are not experts in the characterization of porous materials or their uses in separations. Thus, teams of researchers will be required with expertise in organic chemistry, materials synthesis and characterization, separations (or other applications), and molecular modeling. Tightly-coupled feedback within such teams will usher in true molecular engineering of nanoporous materials and exciting technological developments.

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