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Sandia National Laboratories

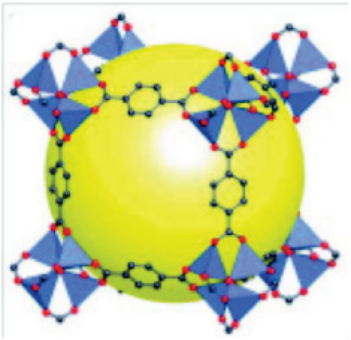
Metal Organic Frameworks

LDRD-Funded Chemical Engineering Fundamental Research Presages Numerous Technological Applications

Beginning with LDRD funding in 2006, Sandia chemists and chemical engineers have been studying metal organic framework molecules, largely because of their controllable nanoporous properties. What this means is that a bonded combination of a metal atom or metal salt together with organic molecules can form a diversity of molecular structures with controllable nanopores — nano-cages, usually of very low density because the pores (cavities) formed by the 3D molecular geometry render the molecules more space than substance. By varying the specific chemical constituents, the molecular geometry of the cavities can be controlled, leading to nanoscale cages of different sizes and shapes — that can trap or sequester a variety of other substances within their nanocavities. MOFs offer unique opportunities to control pore size, surface area, and chemical properties not readily accessible in other material classes. This gives MOFs potential applications in

- molecular trapping/ion exchange elements for water or waste stream cleanup and chemical weapons detection;
- gas sorption, including the problems of carbon dioxide sequestration and reversible storage of reactive gases in microdevices;
- next-generation electro-optical-chemical sensors;
- separation methods, such as size-exclusion chromatography, where small molecules are removed from streams containing larger biological compounds; and
- permeable membranes for fuel cells.

A simple exemplary MOF is shown at right — ZnO_4 (the metal salt) tetrahedra (blue polyhedra) joined by benzene dicarboxylate (the organic portion) linkers (oxygen, red and carbon, black) to give an extended 3D cubic framework with interconnected pores of 80-nm aperture width and 120-nm pore (yellow sphere) diameter. As a size comparison, to get a feeling for the tiny scale of these molecular cages, it may help to recognize that the size of an average bacteria is about 1 µm (or 1000 nm), the thickness of an average human hair perhaps about 70µm (or 70,000 nm).



Since 2006, the LDRD program has subsequently supported several other MOF developmental projects, all of which improved the ability of Sandia staff to manipulate MOF structures, ultimately aiming at specific applications, such as neutron detection. Recently, an important application has been discovered in the nuclear energy sector—namely, design and utilization of an MOF capable of trapping radioactive iodine from spent nuclear fuel. Applications for this MOF include nuclear fuel reprocessing or cleanup of nuclear reactor accidents. A key DOE initiative is the reprocessing of spent nuclear fuel to provide fresh fuel for nuclear power plants. This processing is critical to both derive the optimal energy from fuel rods and to reduce the volume and potential

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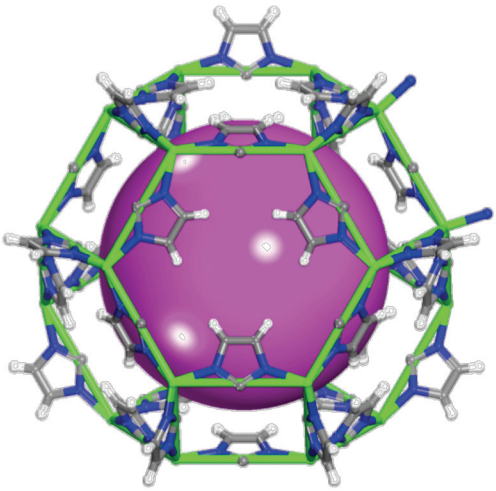
environmental toxicity from spent fuel sent to repositories. One method of doing so is to remove the radioactive isotopes in spent fuel with especially long half lives (essentially the time that the material remains radioactive). A very long half-life component in spent fuel are two isotopes of iodine — I-129 and I-131— with a half-life of 16 million years, and that are also volatile gases, capable of readily spreading through the environment if not trapped.

The trapping MOF was modeled after a silver-loaded zeolite, which although capable of binding iodine to form the nonvolatile salt silver iodide, is far too expensive for widespread use. But the pores of that inorganic structure provided the molecular template that Sandia chemical engineers were able to mimic in a newly synthesized MOF known as ZIF-8, whose exact structure is proprietary. Sandia chemist Tina Nenoff (right) heads the research team.

This technical success is illustrative of important aspects of Sandia research initiatives. First is the role of LDRD-funded research, which allowed Sandia chemists to understand the bonding and molecular geometry parameters for a range of MOFs, fundamental knowledge acquired in LDRD projects that has begun to bear fruit in this first important application. This success suggests that the fundamental understanding obtained through LDRD basic science research will continue to find pathways to important MOF applications in the security, defense, and energy arenas.



Exemplary structure of an MOF.