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TABLE OF CONTENTS

Innovative crystal's got plenty o' nuthin'

For years, chemists have fantasized about molecular scaffolds that would catalyze the tricky chemistry that enzymes foster. The structures would provide a framework for assembling and dissecting organic molecules. Toward this goal, researchers have attempted to make gauzy crystals that are themselves organic.

Scientists repeatedly succeeded in precipitating porous crystals from carboniferous broths, but when removed and dried, the crystals always collapsed.

Now, research teams at the University of Michigan in Ann Arbor and Arizona State University in Tempe have engineered a new crystal architecture, which they describe in the Nov. 18 NATURE. Their prototype material, called MOF-5, remains steady as a rock even when bone dry and heated to 300°C.

"I think many people wouldn't even have believed this was possible," comments Stephen Lee, a materials scientist at Cornell University.

The innovation is in the joinery. Earlier organic scaffolds obliged solitary atoms to hold several struts at once, a situation that stretched their capabilities.

For MOF-5, however, Arizona's Hailian Li and his coworkers joined struts using a rugged, 23-atom cluster borrowed from the toolshed of inorganic chemistry. Around an internal structure of zinc and oxygen atoms, each cluster presents six exposed carbon atoms—four in a plane, with one above and one below. The carbons serve as fastening points for organic struts—in this case, benzene molecules.

Chemists know the value of porous crystals from the many uses of zeolites, naturally occurring minerals that scientists have reproduced and improvised upon in the lab (SN: 3/2/96, p. 135). These inorganic molecular sieves figure centrally in oil refining and in the separation of gases like nitrogen and oxygen.

By constraining the orientations with which two molecules can combine, the myriad identical pockets in these crystals can coax a pool of pure product from a reaction that would otherwise produce a stew or nothing at all.

Engineering such sieves for specific uses poses a challenge: It's hard to predict how inorganic elements will link up. However, fashioning carbon structures is a snap, Lee says. The properties of MOF-5's cavities will be easy to adapt by ornamenting its braces. "You can put anything on a benzene ring," says Lee. Longer struts should be possible, too.

Chemists eagerly anticipate creating such frameworks to order. MOF-5 and its progeny promise other advantages over their inorganic forebears, as well. MOF-5 is lighter and more porous than any inorganic sieve yet made, its inventors say, and has about six times the interior surface area of its closest competitor.

Porous materials can swallow voluminous quantities of gases like methane and hydrogen, potentially making them into easily transportable alternatives to gasoline. Since the amount of methane that fits into different zeolites is proportional to their internal surface area, MOF-5 or related materials may make such fuels more practical, the researchers say.

Although 60 percent of MOF-5 is empty space, there seems little risk that chemists' enthusiasm is much ado about nothing.

—O. Baker