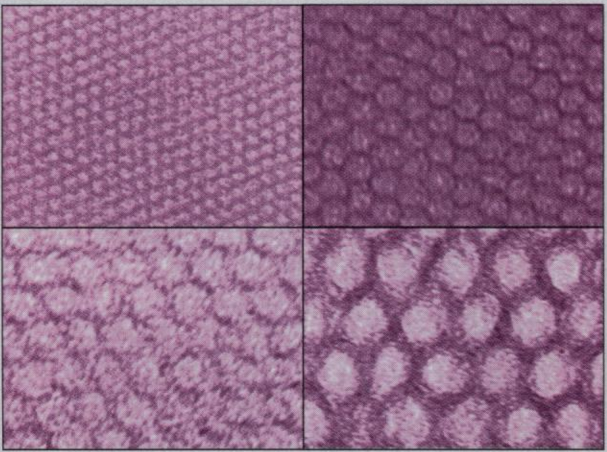
Chemists Work Their Way From Pores to Riches

Molecular sieves don't make it into a whole lot of dinner conversations. Yet the labyrinthine interiors of these natural and synthetic materials can play host to so much important chemistry that they are among the hottest industrial materials around. Now, a team of scientists from the Mobil Research and Development Corp. in New Jersey hopes to marry two hot fields by using molecular self-assembly (key to the rapidly emerging field of supramolecular chemistry) to enter the big-bucks molecular sieve market.

That market already includes oil companies, which use tons of zeolites—the most commercially successful class of molecular sieves—to "crack" larger petroleum molecules into gasoline and make petrochemicals for paints and polymers. Detergent manufacturers use piles of the stuff as water softening and lathering agents. Molecular sieves are also used to clean up hazardous nuclear sites, including Chernobyl and Three Mile Island.



Holy ground. Electron micrographs showing MCM-41 sieves with pore sizes of *(beginning at upper left and going clockwise)* 20, 40, 65, and 100 angstroms.

The key to this variety is that molecular sieves are highly selective. By choosing a sieve with the right pore size, investigators can target their chemistry to a specific substance. Most commmercially available sieves—whether from naturally occurring clays or from chemical engineers' vats—have pore sizes of less than 10 angstroms—enough for several water molecules to squeeze through. But the Mobil team is exploiting self-assembly to come up with a strategy for making "mesoporous" molecular sieves with pores ranging from 15 angstroms to 100 angstroms or more. "It is the first time I am aware of where we have materials in which we can continuously tune the pore diameter over wide ranges," remarks David Olson, a group leader at Mobil's Central Research Laboratory in Princeton. He and his Mobil colleagues aren't willing to say much about specific uses of the new materials, but other researchers say the more capacious pores should enable these materials to play host to biological molecules, broadening the molecular sieve market even further.

Others are impressed. A poster from the Mobil team was the talk of the International Zeolite Conference in Montreal last summer. The researchers went on to publish a brief account of the work last October in *Nature* and a more extended write-up in the 30 December *Journal of the American Chemical Society*. Because the Mobil researchers can tune both the size and geometry of the pores, their work is "a tour de force," says molecular sieve chemist Galen Stucky of the University of California, Santa Barbara.

The new design-to-order sieves have been designated MCM-41, with MCM standing for Mobil Composition of Matter. The crucial strategy for making MCM-41 sieves—as in supramolecular chemistry generally—is finding molecular subunits that will construct the desired form without much external intervention. A typical MCM-41 synthesis starts with a solution containing alumina and silicate molecules (which network into the sieves' hard skeleton) and surfactant molecules (which the researchers believe serve as an organic scaffolding).

Frequently in supramolecular chemistry, it's easier to see the result than to understand the process that led there. But the Mobil team has gathered evidence leading them to the following scenario: The surfactant molecules, with their long, water-avoiding hydrocarbon tails and polar, water-soluble heads, huddle into rosette-like assemblies with the polar heads on the outside. The rosettes then stack up like coins to form rods, which arrange in hexagonal honeycombs.

And that isn't the end of the self-construction. The honeycomb-like organic structures serve as templates on which the inorganic silicate and/or alumina adhere and bond into sieves. A final heating step burns off the surfactant, leaving hard, three-dimensional frameworks. The Mobil researchers can easily tailor the pore sizes and overall sieve structures since changes in the solution temperature, surfactant concentration, additives, and other factors influence the architecture of the templates. In addition to the honeycomb structures, the researchers have also made cubic sieves and lamellar ones made up of sheets that pile up like paper.

In spite of the Mobil researchers' tight lips about applications, Stucky predicts: "The main theme will be doing biotechnology in these pores." MCM-41 has spaces large enough to host enzymes that could do chemistry on other biomolecules, perhaps drug precursors. MCM-41 sieves might also serve as selective filters that let through or exclude only specific molecules, such as those found in blood and other biological fluids. It took a while for Stucky to finish his litany of possibilities. But his summation was short and sweet: "This is a major breakthrough."

–Ivan Amato

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forming a rotaxane ring on a polyether string. Completing the picture are two bulky groups attached to the ends of the string, which function to prevent the system from falling apart. "That these molecules self-assemble is quite amazing," enthuses team member Neil Spencer. Indeed it is. But, in fact, the components of the rotaxane molecule are chosen so that they have no choice: They cannot fit together any other way.

The self-assembly of the rotaxane ring on the polyether string inspires a kind of awe at the natural world—and the ingenuity of Stoddart's team. But that isn't the property that endows the system with its potential use. The possible utility of the supermolecule stems from the fact that the positively charged ring has equal affinity for the two negatively charged hydroquinol groups on the string and shuttles back and forth between these "stations" several hundred times per second at room temperature.

Stoddart's team reasoned that if the shuttling could be controlled using an external input, such as a light source or an applied voltage, then the rotaxane structure could be used to store information—with each position of the ring corresponding to a unique information state. Furthermore, if there were two chemically different stations on the thread, the affinity of the ring for each station might be induced to change under varying conditions. And if the conditions could be manipulated efficiently, the ring would then be forced to shuttle between stations on command, making the information-