Exploiting Molecular Self-Assembly

FEATURE

by Jennifer Ouellette

Molecular self-assembly (MSA) is a powerful method for assembling atomically precise materials and devices (e.g., see Figure 1). Biological organisms are composed of molecular building blocks, such as nucleic acids, proteins, and phospholipids, and are equipped to assemble these components into extremely well-organized structures—themselves. Harnessing MSA will provide a critical component in the fabrication of nanoscale machinery and microelectronics, among other applications.

"Much of nature is a product of hierarchical self-assembly, and humans are the examples par excellence," according to Samson Jenekhe, a researcher at the University of Washington. Jenekhe recently created "smart plastics"—plastic materials that assemble themselves into photonic crystals using hierarchical self-assembly. "Each of us starts as a single cell encoded with the information to guide our growth into a large structure—a complete human being," he says. "Making materials that on their own are smart and able to orchestrate their own growth marks the chemistry and polymer science of the future."

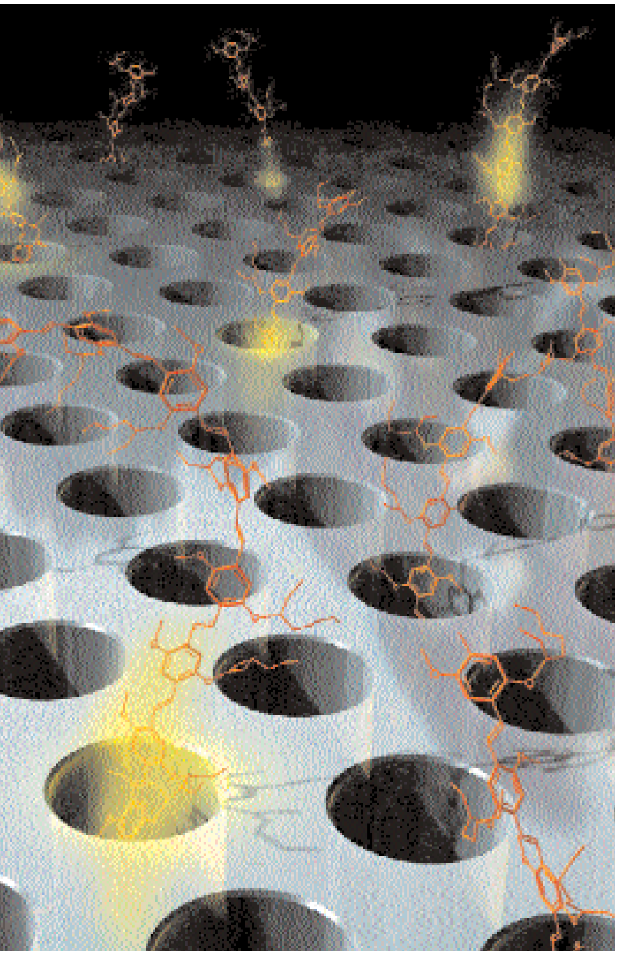

Daniel Schwartz, Digital Interactive Services Corp

Figure 1. The geometry and properties of this composite material can be controlled by threading single semiconducting polymer chains into the pores of an oriented, nanoporous silica framework.

Self-assembly on a macroscale exists throughout the natural world, and self-assembled monolayers are found in a handful of industries, says George Whitesides of Harvard University, who helped pioneer the field (see Figure 4). For example, the mining industry has long used froth flotation to separate desired minerals from surrounding material, and 3M markets a silver polish that uses a self-assembling monolayer system to prevent silver from tarnishing.

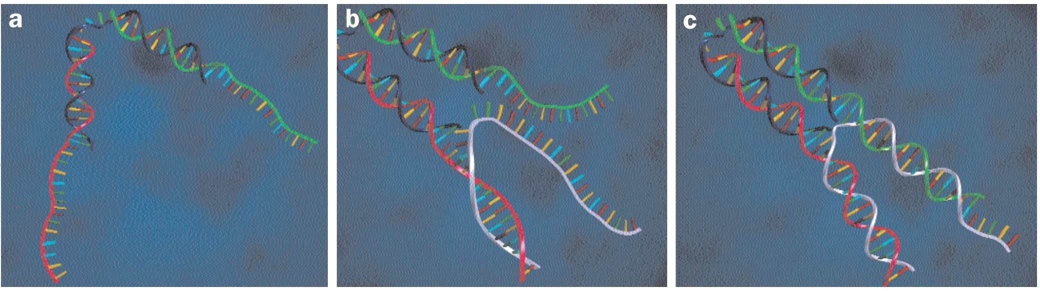
"In a sense, self-assembly has always been an integral part of science," says Whitesides. "What is new is the idea of looking at these systems as a discrete set of processes that, at the molecular level, will become an important tool for things such as nanotechnology. But self-assembly is also integral to understanding how biological systems achieve their order and, hence, it is a wonderfully fertile area for discovery."

Fluid self-assembly

Alien Technology (Morgan Hill, CA), a small start-up firm, exploits fluid self-assembly (FSA) to deposit integrated circuits across a large plastic substrate (Figure 3). In the FSA process, transistors are made on standard silicon wafers and etched to separate them. They are then floated into place across a large surface area covered with holes shaped like the transistors, according to Alien spokesman Stan Drobac. "Once a circuit lands in a hole, it lines itself up perfectly, because it only fits one way," he says. The process makes the fabrication of pixel transistors on large sheets of glass unnecessary. Using a thin, light, flexible, low-cost plastic film instead of glass allows continuous flow, roll-to-roll (web) processing.

The company's first product is a small, flexible five-digit monochrome display for smart cards. In July, Alien announced it would supply its displays to Gemplus, the world's leading provider of smart-card-based security, wireless, and e-business applications. Widely used in Europe and Asia, the cards contain an embedded microchip that electronically stores data. Although relatively new, smart cards already consume more microcontroller-based devices than any other commercial market. In fact, the consulting firm DataQuest (San Jose, CA) estimates that more than 650 million microcontroller-based cards will be shipped worldwide in 2000, and twice as many in 2002. Yet, the difficulty and cost of producing a robust and inexpensive flexible display using conventional techniques has limited their use. The low-cost FSA process enables lower consumer pricing and the early development of a high-volume production infrastructure.

Alien will start production of the smart-card displays next year, Drobac says, and the company expects unit volume to reach millions per month by 2002. Eventually, Alien plans to extend its product range to more complex



Lucent Technologies' Bell Labs

Figure 2. These two hinged DNA arms (a) act as self-assembling tweezers when a third "fuel" strand is added (b) and pulls the two arms together (c).

displays for portable devices, such as mobile telephones, and larger flat-panel displays for computers and televisions.

In addition, the Defense Advanced Research Projects Agency (DARPA) has contracted with Alien to develop a series of complex displays, culminating in a 15-in. full-color version. "Our manufacturing process is truly dual use," says Drobac. "We will be able to build the highest-volume commercial displays and complex, short-run military displays on the same equipment." Northrop Grumman plans to test Alien's displays in its military systems to study their reliability.

Labs-on-a-chip

Self-assembly is also useful for so-called labs-on-a-chip, commercial sensor arrays for high-throughput screening in genomics and drug discovery. Nanogen (San Diego, CA) markets NanoChip, a system that enables users to array and analyze DNA in a single day. The company's most recent patent takes the technology further by combining electronic concentration, focusing, transport, and analysis of a biological sample on an integrated device. "We believe the ability to concentrate and move sample DNA may ultimately lead to far more sensitive tests," says Elizabeth Mather, one inventor of the new technology. "The ability to manipulate DNA sequences electronically may aid in the improved selection of target sequences from complex DNA samples."

Benjamin Miller, of the University of Rochester, has developed a technique that shifts the burden of searching for potent new drugs from today's combinatorial screening assays to the molecules themselves. In it, molecules self-assemble into countless combinations and use a process akin to Darwinian natural selection to find the best compound. "With our technique, we try to find molecules that bind to receptors in much the same way as nature has for millions of years," says Miller. "We take a receptor we want to target, add little molecules to it, and see which ones are best at binding to the receptor."

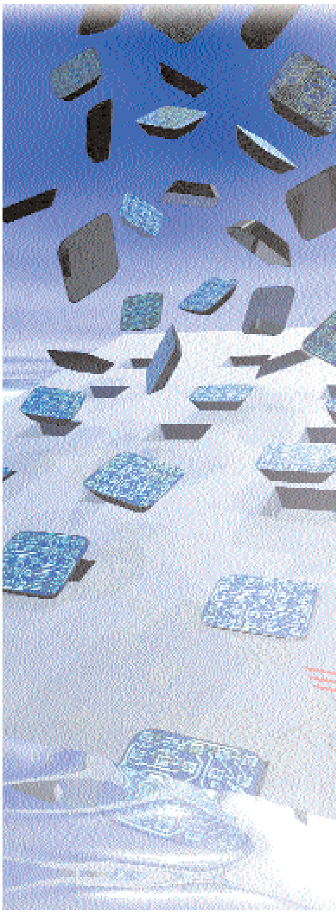
Miller's concept might also find application in the production of next-generation chemicals other than drugs, according to Paul Wender of Stanford University. "Basically, all one needs to do is develop a group of molecules that can self-assemble and a selection system to pull out the molecules that are desirable," says Wender. "It's easy to imagine producing a variety of superior materials using molecular self assembly," he adds.

Sandia National Laboratories has a strong R&D focus on the next generation of labs-on-a-chip, says project leader David Rakestraw. "There's a huge amount of information in chemical signatures that the world is not using because it is too costly," he says. "It is also very difficult to extract out all of this information using traditional analytical chemistry." In the next three years, he hopes to demonstrate a device about the size of a palm-top computer that detects explosives and chemical-warfare agents. The ultimate goal is building labs-on-a-chip that simultaneously identify hundreds of liquids and gases.

Self-assembling new materials

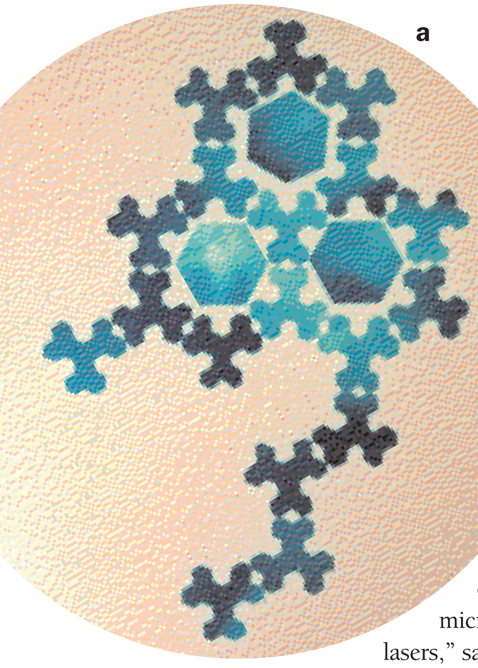
The technological success and commercial promise of labs-on-a-chip and fluidic self-assembly techniques have led to more ambitious undertakings that seek to exploit MSA to construct new materials and control their properties. The ability to directly monitor self-assembly and self-organizing processes, probe single particles and nanoscale architectures, and perform sophisticated physical measurements with high spatial resolution is central to the development of such advanced materials, says David Adams of Columbia University. These materials could, in turn, have important applications in light-emitting diodes (LEDs), optical memories, switching devices, and better chemosensors.

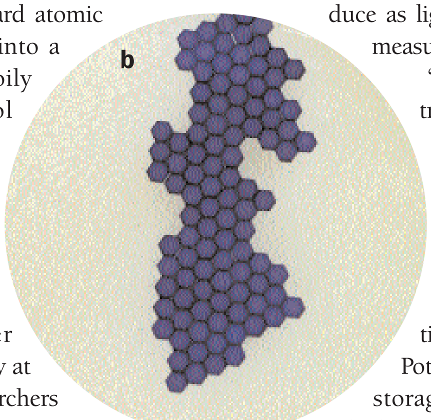
Jeff Brinker, also at Sandia, has developed what he calls surfactant-templated silica mesophases, building on work first reported by Galen Stucky and his colleagues at the University of California, Santa Barbara, in 1994. Brinker describes these mesophases as "intelligent spray-on materials that assemble themselves into circuits," a new, quicker way to build sensor chips for handheld chemical analyzers. Brinker adds ligands—in this case, surfactant molecules that both repel and dissolve in water and have binding capabilities—to standard semiconductor materials. This combination allows researchers to spray sensor arrays onto a silicon substrate using an ink-jet printer. Sprayed in a line on the substrate, the pores spontaneously form a waveguide measuring about 25 Å in diameter and become solid when heated. The technique may also prove useful for molecular filters, nanocomposite materials, and passive circuits for devices with dielectric constants lower than those made using conventional lithography, all of which are



Alien Technology

Figure 3. Transistors, made on standard silicon wafers and separated, are floated into place across a large surface area into holes shaped just like themselves.





Dept. of Chemistry and Chemical Biology, Harvard University

Figure 4. In templated self-assembly (a), weak (capillary) interactions between the template (hexagons) and self-assembling objects (trefoils) direct the trefoils into a cyclic hexamer. The regular array of floating, millimeter-scale, close-packed hexagons (b) was self-assembled by minimization of the interfacial free energy.

critical to realizing molecular-scale electronic devices. “The unique aspect of the acid polymerization synthesis approach to make these mesophases is that it greatly facilitates processing, so that the chemistry is easily used to create, for example, hierarchical structures patterned simultaneously on three length scales, patterned nanostructures for use as optical waveguides, laser/waveguide microarrays, and optical fiber micro-ring lasers,” says Stucky.

At Northwestern University, Chad Mirkin and his colleagues have developed a dip-pen nanolithography (DPN) technique, which he describes as “the world’s smallest pen.” They have transformed a standard atomic force microscope (AFM) into a writing instrument. An oily “ink” of octadecanethiol (ODT) is applied to the AFM’s tip. The tip is brought into contact with a thin sheet of gold, which transfers the ODT molecules to the gold’s surface via a tiny water droplet that forms naturally at the tip. This enables researchers to draw fine lines one molecule high and a few dozen molecules wide.

Mirkin’s team has developed a nanoplotter, which lays down a series of molecular lines with unprecedented precision and can form lines only 15 nm wide, with 5 nm separating each line. This accuracy could dramatically affect molecule-based electronics as well as molecular diagnostics and catalysis, and create new applications in nanotechnology. “In a sense, we have transitioned DPN from a single-ink process to a four-color printing process on a nanometer scale,” says Mirkin.

Although the microfabrication of electronic circuits currently uses solid-state or inorganic materials, Mirkin believes that innovations such as the nanoplotter will direct future technologies toward the use of organic and biological materials for electronic purposes. “Nature gives us a limited number of materials, but in the lab, there are an infinite number of organic molecules a chemist can make,” he says. “And by designing molecules carefully, one can use them as inks in DPN to custom-design nanostructures for science and technology.” For example, the conductivity, thermal stability, and chemical reactivity of circuits drawn using DPN could be controlled through the choice of inks used to generate structures.

Smart plastics

Self-assembling photonic crystals are another application with enormous potential. Research groups worldwide have built photonic crystals, but their efforts usually involve laborious and expensive fabrication processes. Jenekhe believes his “smart plastics” are the first photonic crystals to grow themselves. The process begins with a solution of polymer molecules—polyphenylquiniline-*block*-polystyrene, similar to the material used in Styrofoam cups—in a solution that self-organize into hollow spheres, a feat similar to bricks stacking themselves into a wall. The alternating spheres and plastic framework built into new materials manipulate light in predictable, precise ways, much like the dazzling, sharp colors that opals produce as light travels through them. The devices measure about 1 cm^2 and are 30 μm thick.

“What we’re able to do now with electrons led to the microelectronics revolution. We would like to do the same with photons,” says Jenekhe. “For that, you need materials like these photonic crystals that allow you to trap light and control the way it propagates. Light can carry thousands of times more information than electrons.”

Potential applications include optical data storage and telecommunications, both of which rely on transmission and detection of specific wavelengths, and eventually holographic data storage. The plastics might also prove ideal for improved LEDs and paints that change color under different light conditions. And Jenekhe envisions a highly efficient plastic laser that produces intense beams of light with a fraction of the energy now required.

At Oak Ridge National Laboratory, Elias Greenbaum heads a team using self-assembly to create spinach-based optoelectronic circuits that have potential applications in superhigh-resolution video imaging, ultrafast switching, logic devices, and solar power generation. The self-assembly process is used to isolate and orient spinach-leaf proteins, which convert the sun’s electromagnetic energy into stored chemical energy, onto a gold substrate. The isolated protein centers are naturally occurring photovoltaic and diode structures, and they can be used to generate electrical current when provided with an electrical contact. The researchers make the contact by depositing platinum, a good electrical conductor, on one end of the protein and anchoring it to a gold surface.

The ability to arrange proteins so that the same ends all point in the same direction is critical to their potential for biomolecular electronic applications, says Greenbaum. His team accomplishes this by chemically treating the atomically flat gold surface on a mica substrate with mercaptoacetic acid or mercaptoethanol. The sulfur atom in each chemical binds strongly to gold, and the negatively charged ends selectively bind to the positively charged ends of the protein centers.

"We're hoping we can pre-format, pre-design, and pre-ink the substrates onto which molecular components can be assembled, so that the natural interactions of these molecules—the positions they want to assume when they self-assemble on surfaces—will be those that assemble them into functional devices," says Greenbaum. "This would be less expensive and less energy-intensive than conventional lithography."

At Lucent Technologies' Bell Laboratories, Paul Kolodner seeks to exploit the natural electrochromatic properties of the protein bacteriorhodopsin for reflective flat-panel displays. "Natural materials have been optimized for these functions by billions of years of evolution and often perform them better than any human-designed material could," says Kolodner. "Furthermore, organisms manufacture biological materials all by themselves—all we have to do is feed them and harvest the products."

With Dan Morse and Brad Chmelka, Stucky heads an effort at UCSB to use biosystem models to create complex self-assembled materials for optoelectronic arrays, chemical and biosensors, optical limiters, and three-dimensional arrays for holographic data storage (Figure 5). "The challenge is to transfer the essence of one or more optimized components of a biosystem into a network with all the proper interconnects and response parameters," says Stucky. "We try to 'biomimetic' only a part of an energy dispersive biosystem and retain the desired functionality."

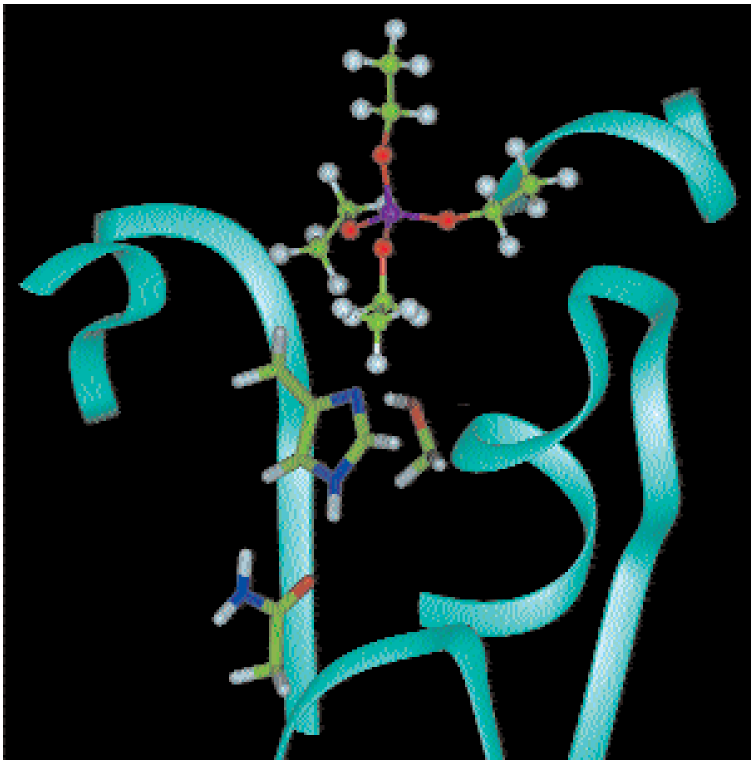
IBM researchers are using MSA to make a radically new class of magnetic materials that might allow computer hard disks and other storage systems to store 100 times more data than today's standard products. "With self-assembly, we let nature do most of the work," says Dieter Weller of IBM. "This process opens up new options for thinking about how we might make future high-density storage media." In fact, because each of the nanoparticles is already magnetically stable at room temperature, this new process may facilitate storing one data bit in a single grain of magnetic material rather than the several hundred grains used today.

Putting it all together

Of course, researchers are just beginning to understand the intricacies of MSA, and more research is needed simply to improve control of the process. This is one reason that biomotors are receiving increased attention for studying molecular-level transport. For example, scientists at Bell Laboratories recently created the first DNA motors, which resemble motorized tweezers (Figure 2). According to Bernard Yurke, the device is an important initial exercise in learning how molecules recognize one another for self-assembly. The technology also has the potential to replace existing manufacturing methods for integrated circuits, particularly for manufacturing nanodevices. "Given the size scale, no other approach appears to be practical," he says. "This may lead to a test-tube-based nanofabrication technology that assembles complex structures, such as electronic circuits, through the orderly addition of molecules."

Another challenge is achieving the self-assembly of multiple materials. Brinker's self-assembled nanocomposite materials could prove useful in developing devices such as a nanobattery, in which three materials—serving separately as electrode, anode, and electrolyte—would organize into an appropriate nanostructure.

Scientists will need to find appropriate interconnects between the self-assembled components to fully realize molecular and nanoscale electronics that mimic nature's biological membranes, where molecules "talk" to each other and transfer electrons to do useful functions. "Nature's mechanisms are much more complex and much more highly evolved" than the self-assembly currently used in laboratories, says Whitesides. "The ultimate goal is to look at these mechanisms, abstract the principles from them, and then embed those principles in nonbiological systems to make functional, very sophisticated small machines."



Dan Morse and coworkers at UCSB

Figure 5. Glassy structures can be assembled from silicon-containing molecules such as the one shown at the top approaching active sites in the enzyme-like protein silicatein, which catalyzes polymerization.