

'pumping' and 'flexing' dynamics. We should have expected this from MOF structures especially as they are constructed from well-defined molecular units that are in themselves capable of dynamic behaviour, which they should largely maintain even when held together in a crystal structure.

Could the ideas illustrated by these two entangled frameworks be the basis for designing crystals capable of responding to a stimulus (light, pressure or pH) by shifting their components to release a drug molecule or trap a harmful contaminant? I believe this will be achieved in due course, as the tale of such entanglements is as endless as they are.

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RESPONSIVE MATERIALS

Soft answers for hard problems

Soft matter has the remarkable ability to respond to stimuli in a variety of ways. Not only does this enable its application to existing scientific problems, but it also allows previously unimagined technological directions to be explored.

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It is becoming increasingly clear that novel approaches to applications such as biomimetic sensing and actuation demand the synthesis and manipulation of 'soft' materials, with their unique capacity to respond to external stimuli. Indeed, research on soft materials has recently increased dramatically, and is attracting equal attention from chemists, physicists and engineers. Hundreds of researchers convened at a symposium* devoted to the topic as part of the 2006 Fall Meeting of the Materials Research Society in Boston, Massachusetts, USA, to explore new functionalities of responsive soft materials, highlighting the timeliness of this area and revealing surprising versatility among materials formerly dismissed as 'weak'. Indeed, ordinarily disparate fields ranging from robotics to hydrogels and from peptides to nanofabrication were brought together by the common feature of responsiveness. Sessions focused on artificial muscles, controlled release of drugs, dynamic surfaces, photonic and phonic materials, and assembly of soft material structures.

In the area of stimuli-driven actuation — artificial muscles — Tim Swager (MIT, USA) presented exciting molecular-level

approaches, where rigid polymer molecules contained 'hinges' in the form of multiple-ring aromatic moieties that change conformation on electrical reduction or oxidation. These conformational changes are amplified mechanically to measurable strains, although it was pointed out that significant effort is still needed to scale-up the

phenomena to yield functioning actuators. In contrast, Ray Baughman (UT, Dallas) explained the inner workings of his group's recently reported chemical actuation system (Ebron, V. H. *et al. Science* **311**, 1580–1583; 2006), which combines exothermic chemical reactions with heat-driven two-way shape-memory alloys (SMAs). In an inspirational

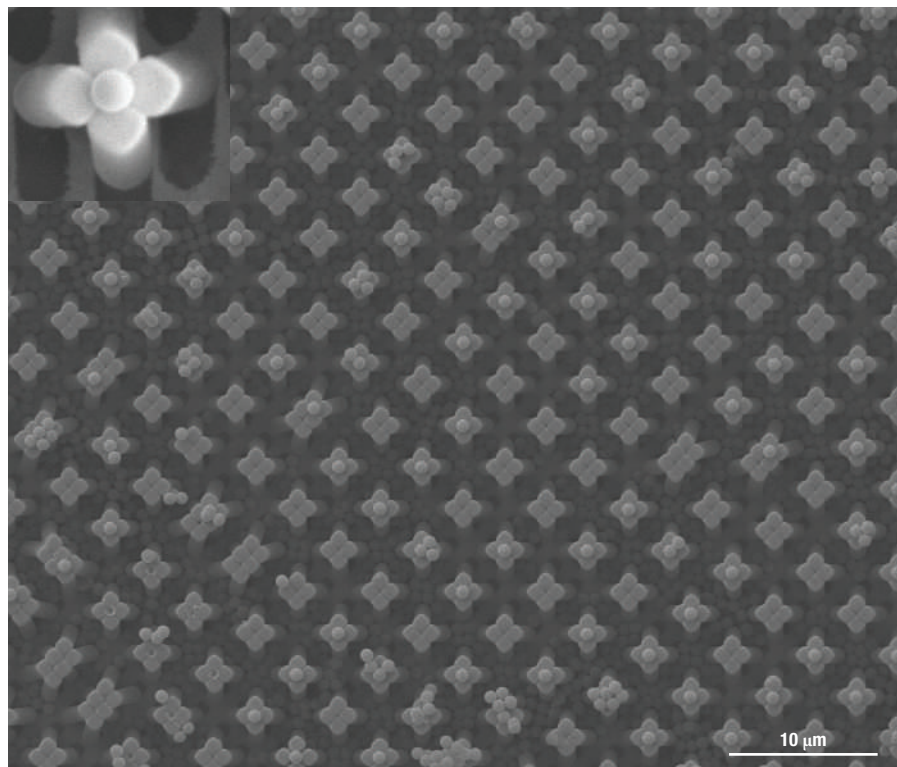


Figure 1 Selective assembly of particles on the top of polymer superlattices, where the surface of individual micropillars was coated with thermoresponsive polymer brushes. Trapped microspheres can be seen on some groups of pillars, and one is shown magnified in the inset.

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lecture, Baughman revealed dramatically fast reversible actuation that can achieve large strains using a simple design: platinum-coated SMA coils that allow catalytic and exothermic reaction of hydrogen and oxygen, the heat of which is transferred efficiently to the SMA wire to stimulate contraction — like a muscle — while heat removal allows expansion.

Not only were electroactuation and chemical actuation in evidence, advances in photoactuation were reported, too. Casper van Oosten (Eindhoven University, The Netherlands) revealed micrometre-scale cantilevers fabricated from liquid-crystalline (LC) networks, which featured exceptional photo- and chemical responsiveness. These phenomena allowed rapid and reversible cantilever curvature producing movement of 10 μm or so. By incorporating azobenzene moieties in an LC network, and then illuminating with UV light, the authors isomerized the azobenzene. This reduced the local LC order, causing shrinking of the LC on one surface and fast (0.25 s) curvature of the cantilevers towards the light. Subsequent illumination with visible light reversed the curvature with a similar speed. Similarly, Nelson Tabiryan (Beam Engineering, Winter Park, Florida, USA), with Air Force Research Lab scientists, revealed rapid photoactuation using their own LC networks — so fast it was challenging for the researchers to quantify.

But the action was not exclusive to bulk phenomena — responsive surfaces received equal attention. Benjamin Fletcher (Oak Ridge National Lab, USA) unveiled two-dimensional micrometre-scale ‘membranes’ built from surface-anchored

carbon nanotube forests that displayed tunable permeability. The forests were grown in closed loops, forming the membrane structure. By coating the membrane with electrically conductive poly(pyrrole), the researchers could switch its permeability, as electrochemical reduction of the polymer causes it to swell, reducing pore size.

In a similar vein, Shu Yang (Univ. Pennsylvania) constructed micrometre-scale high-aspect-ratio polymeric pillars that, despite their high elastic modulus, were susceptible to controlled toppling when the capillary force exerted by a solvent exceeded their critical elastic strain energy, that is, the force holding them up. When they collapsed into each other, they formed a beautiful superlattice pattern (Fig. 1). Thermoresponsive polymer brushes — which exhibited a temperature-driven transition between a hydrated and dehydrated state — were grafted onto the micropillars, thus enabling dynamic tuning of the capillary force between the micropillars. On the superlattice pattern, particles were reversibly trapped and released at different temperatures; the inset in the figure shows a trapped microsphere at 25 °C. It was suggested these structures would be useful for their superhydrophobicity, a topic also pursued with vigour by Tom Krupenkin (Bell Labs) who constructed ‘nano-nails’. The nail-head geometry offered a topography that amplified the wetting or non-wetting characteristics of straight pillars.

Research into responsive materials also holds promise in the area of photonic and phononic ‘bandgap’ materials. Those materials’ spatial modulation in refractive

index or acoustic impedance yields forbidden wavevectors — thus ‘bandgaps’ — so certain wavelengths cannot propagate and they are therefore selective reflectors of light or sound. Research in this field seems to be taking inspiration from nature, as shown by Roger Hanlon (Marine Biology Lab, Woods Hole, Massachusetts, USA). In a lecture enhanced with stunning video clips, he revealed the dramatic combination of shape malleability and optical transformation found in the octopus and cuttlefish species. With the goal of empowering materials scientists with bioinspiration for synthetic responsive materials, Hanlon reviewed mechanisms for rapid, dramatic transformation as they are currently understood — even the ability of the cuttlefish to change colour to match its environment despite being colourblind itself. It was revealed that multifunctionality in constituent materials is needed, with optical transformations deriving from multiple effects: from surface texture alteration to photonic crystal dimension changes (also known as structural colour change) and pigment cloaking. Building on this, Ryan Kramer (Air Force Research Lab) reported that ‘reflectins’ — proteins based on those found in cephalods with responsive structural colouration — can self-assemble into diffraction gratings with spacing, and thus colour, that is tunable and responsive.

The above are just a few of many contributions from around the world and across many disciplines, and I came away from the symposium with a clear belief that the biggest breakthroughs in materials science will come from formerly disregarded soft stuff.

NANOCOMPOSITES

Economy at the nanoscale

Exploiting the interplay between entropic and enthalpic contributions in block copolymer-nanoparticle blends permits construction of composites with specified structures. Disassembly can then provide well-defined structural units as building blocks for future applications.

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Nature is parsimonious in its use of ingredients and design principles. Even using them sparingly, however, it achieves a tremendously diverse

assortment of materials. For example, twenty amino acids are sufficient to create a large array of complex macromolecules, which interact to perform a stunning variety of functions. Applying this approach to the fabrication of synthetic materials could have significant benefits; for example, being able to fashion a host of structures from a small set of building blocks would be both economical and efficient. On page 156 of

this issue, Ulrich Wiesner and colleagues¹ take a step in this direction, by creating a range of hybrid materials using just diblock copolymers and a high volume fraction of nanoparticles. The self-assembling diblocks permit access to various architectures, including lamellar, cylindrical, bicontinuous and spherical forms. The diblocks, however, do not simply template the ordering of the particles. Rather, the final morphology is