

The gels were cut up into small cubes and these fragments were suspended in water to enable them to move around freely. Shaking a suspension of the little cubes of any one type doesn't result in their sticking together. However, if a mixture of the β -cyclodextrin and adamantyl cubes is agitated the result is a self-assembled chain of alternating red and green cubes as the β -cyclodextrin surfaces on the red cubes bind to the adamantyl-derivatized surfaces on the green cubes. The effect is similar for the α -cyclodextrin/*n*-butyl pair of gel cubes. The recognition process is fully reversible and the aggregates can be separated again either by heating them up, or by saturating the binding sites on the gels by adding an excess of non-polymer-attached versions of the recognition partners, such as unmodified cyclodextrins or a monomeric adamantane derivative.

One interesting facet of the work is that the strength of the molecular interactions can be gauged by measuring the force required to mechanically pull apart the coloured cubes. For the most part, the stress and strain values of the assembled gels were found to correlate with association constants measured in solution for analogous systems. In the case of the β -cyclodextrin and

adamantyl cubes, however, the binding between the different gel cubes was so strong that pulling on each end of the assembly led to individual gel cubes breaking, rather than separation of the assembly at the interfaces between the different gels.

A particularly appealing experiment that demonstrates the selectivity of the molecular recognition operating in these systems entails taking a mixture of four of the different types of gel — two host gels and two guest gels. On agitation the hosts selectively bind with the best-fitting guests to give two quite separate aggregates based on the two different complementary pairings. No unfavourable cross-pairing occurs (Fig. 1b). It is possible to watch delightful videos of these experiments in real time as part of the Supplementary Information provided with the Article. The kinds of host-guest interactions used in these gels are well known and have been studied extensively using conventional means³. Nevertheless, there is still something remarkable about actually seeing molecular recognition in action.

The total difference in interaction energy between a particular guest binding to the two different cyclodextrin hosts is very small, and yet is sufficient to bring

about complete macroscopic molecular recognition because of the multitude of such interactions occurring on the gel surface. It could be argued that this proof-of-principle demonstration is not just a colourful way of visualizing molecular recognition. It points the way to the fabrication of smart objects capable of bearing programmed information in their very structure that can self-assemble into complex structures. The selectivity bonus gained on scale-up from single molecules to macroscopic surfaces augurs well for a fascinating new field of smart surface recognition. These simple experiments also force us to think about molecular recognition as a phenomenon in real-world materials and not just limited to samples in test tubes. □

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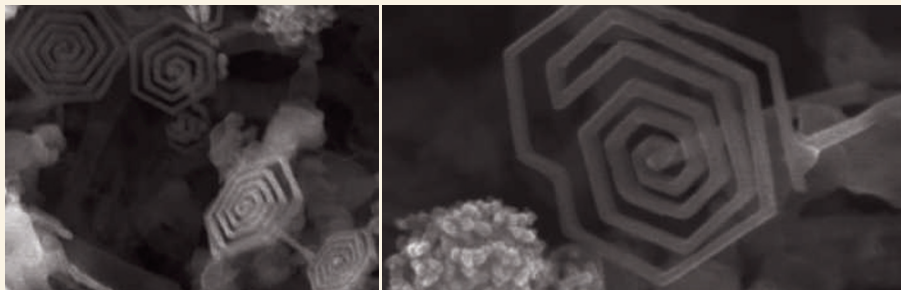
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SILICIDE NANOSTRUCTURES

Spiralling into control

The increasing importance of crystalline nanomaterials in nanotechnology has sparked much research towards controlling their structures and morphologies — which in turn determine their properties. Chromium silicide, a narrow-bandgap semiconductor with high melting point and resistance to oxidation, has attracted interest in a wide range of areas, including electronics and energy materials. Now, Tom Wu and co-workers from Nanyang Technological University in Singapore have prepared a chromium silicide single crystal that adopts an unusual hexagonal structure resembling a spider-web (pictured; *J. Am. Chem. Soc.* **132**, 15875–15877; 2010).

Chromium silicide crystalline nanowires can be prepared by a vapour diffusion method under a flow of argon. By suddenly increasing the gas flow and adjusting vapour concentrations of the components during the crystallization, Wu and co-workers induced a change of direction in the nanowire growth, giving rise to two-dimensional hexagonal



structures (nanoweb). These grew to be around 150–200 nm in diameter and 10–30 nm thick and were found to be highly crystalline, even at the corners between each nanowire segment.

Opposite sides of the nanowire segments are oppositely charged, which the researchers suggest is what induces the nanoweb's formation. This would also mean that the walls of the nanowires form charged planes perpendicular to that of the nanoweb, which is in good agreement with the structures observed, and is supported by

calculations of the electrostatic energies for different bending possibilities. At most corners, depending on the distance between the walls, the nanowires either grow into a continuous nanoweb or reverse their direction — linear or zig-zag nanowires are only rarely observed.

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