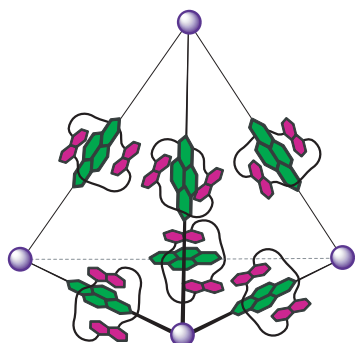


INTERLOCKED MOLECULES

Tangled tetrahedra

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The challenge of making molecules with non-trivial topologies has proved to be a popular one over the past 50 years or so. Two archetypal examples of such systems are catenanes — compounds made up of two or more macrocycles that are held together simply by being mechanically interlocked

with one another — and knots (molecular trefoils being the most common). Weaving and tying molecular strands into complex architectures not only produces eye-catching structures, but has also been used to make nanoscale machines and motors.

Now, a team based in Cambridge and Berlin, headed up by Christoph Schalley, Jonathan Nitschke and Jeremy Sanders, have studied a system in which six crown ethers can thread on to the edges of a metal–organic tetrahedron to produce an unusual [7]catenane — one member of a new class of mechanically interlocked molecules. The central tetrahedral cage is pieced together from four Fe(II) ions (these are the corners) and six identical rigid-rod organic ligands (the edges) that have an electron-poor aromatic group in the middle. The glue that holds these pieces together comes from 12 formylpyridine molecules — the aldehydes react with amines at the ends of the edges to form imines and the pyridine rings coordinate to the metal ions. The structure is dynamic because the metal–pyridine bonds are reversible, and when one of the corners opens

up, an electron-rich macrocycle (a dinaphtho crown ether) can slip on to an edge to bind the electron-deficient region.

It is shown that each edge can accommodate a threaded macrocycle, resulting in the formation of a [7]catenane if a large enough excess of the crown ether is present in solution. After a mixture containing a 10:1 ratio of crown ether (C) to tetrahedron (T) was allowed to reach equilibrium, six catenated compounds (TC_{1-6} — [2]catenane through to [7]catenane and all those in between) were observed by mass spectrometry. The next step is to explore whether catenation of the edges of the tetrahedron can be used to control the capture and release of guest molecules from the inside of the metal–organic cage. SC

SELF-ASSEMBLY

A SAGE design

Science <http://doi.org/md6> (2013)

A virus capsid is a natural example of a hollow encapsulating structure that can form through the self-assembly of modules — a process

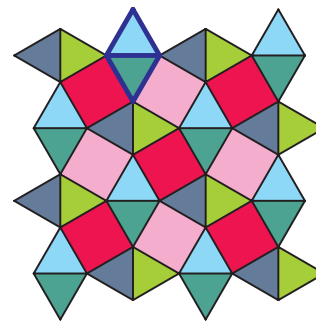
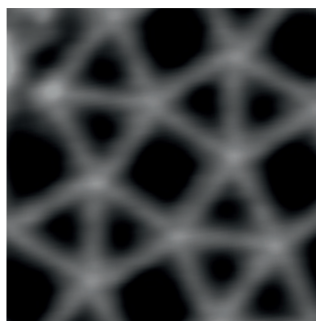
PERIODIC PATTERNS

Snub square tiling

Proc. Natl Acad. Sci. USA **110**, 6678–6681 (2013)

The organization of molecules into periodic patterns is not only intriguing from mathematic and aesthetic perspectives, it also determines the properties of the resulting materials. Among the 11 possible ways to tessellate a surface with symmetric polygonal units, eight are semi-regular Archimedean tilings comprising two or more building units. These patterns can give rise to unusual properties, such as geometrically frustrated magnetism. The best-known example is perhaps the kagome lattice, which consists of triangles and hexagons.

The self-assembly of small molecules at a surface has emerged as a convenient tool for generating interesting surface tilings for study, and although a variety of patterns have been created previously, five-vertex motifs have remained elusive. David Ćija and Johannes Barth from the Technical University, Munich, have led a team that have now observed that cerium centres and ditopic linear ligands (L) — polyphenyl segments featuring a binding carbonitrile group at each end — assemble on a Ag(111) surface into five-fold planar $\{CeL_5\}$ coordination complexes that can act as the vertices of a semi-regular tessellation. Although this ligand had previously been



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observed to form coordination polymers at surfaces with other metal centres, it had not spontaneously arranged in this manner. The unusual five-fold motif observed with cerium is likely to arise from a balance between the surface confinement of the ligands, the coordination at the lanthanide centre and steric hindrance. The patterns were characterized by scanning tunnelling microscopy, and supported by calculations.

The researchers first obtained discrete star-shaped molecules in which each cerium centre coordinates to five different ligands through a carbonitrile group. Adjusting the

concentration and the ligand:lanthanide ratio to 5:2 led to each ligand coordinating to two cerium centres. The cerium coordination sphere was flexible enough to accommodate the formation of a continuous 'snub square tiling' (pictured) up to a size of $300 \text{ \AA} \times 300 \text{ \AA}$. This extended motif is made up of triangles and squares, with the ligands acting as edges and the cerium centres as vertices. The same motif was generated with both a 3- and a 4-phenyl-ring ligand, pointing to the generality of this lanthanide-directed approach for surface tessellation. AP