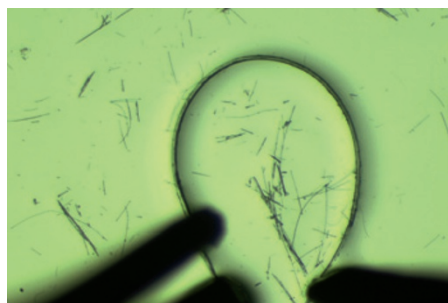


MATERIALS CHEMISTRY

Compliant crystals

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Crystalline materials are notoriously brittle, and this is particularly true for organic crystals. Although metal–organic frameworks, which are held together by coordination bonds, can display structural flexibility — such as a ‘breathing’ behaviour that allows for their lattices’ expansion and compression — organic crystals rely on

weaker non-covalent interactions and are easily broken. Only a handful of flexible organic crystals have been described and in those cases, the irreversible bending arises from the concerted movements of molecular sheets.

Soumyajit Ghosh and C. Malla Reddy from the the Indian Institute of Science Education and Research, Kolkata, have now prepared a co-crystal that is surprisingly, and reversibly, flexible, even at temperatures as low as $-100\text{ }^{\circ}\text{C}$. Slow evaporation of an equimolar solution of caffeine (CAF) and 4-chloro-3-nitrobenzoic acid (CNB) in methanol produced needle-like crystals. Using tweezers and a metal pin, Ghosh and Reddy were able to bend a 5-mm-long and 0.1-mm-thick crystal into a loop — although thicker ones were less flexible. On removal of the pressure, the needles promptly returned to their original straight shape.

X-ray diffraction studies revealed that the co-crystals comprise CAF and CNB molecules in a 1:1 ratio, arranged into

comb-like one-dimensional tapes. These tapes further stack together into two-dimensional sheets with a double-sided comb-like structure, which in turn pack into a zipper-like assembly. The lattice also features channels that are partially occupied by disordered methanol molecules. It is thought that the even distribution of weak interactions in all three dimensions, together with the mobile solvent channels, serve as release pathways for mechanical stress.

The material undergoes a reversible elastic bending process (in which the central part of the curved rod is stretched on one side and compressed on the other) in contrast to an irreversible plastic deformation. When dried, the crystals lost their elasticity; they became brittle and could not be resolvated. These findings show that small organic molecules can assemble into architectures with mechanical properties that have traditionally been observed with more complex materials.

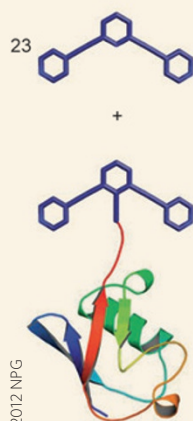
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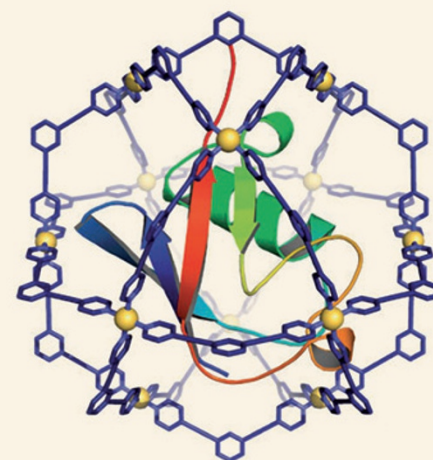
A protein gets framed

Encapsulating molecules within synthetic cages offers the potential to tailor the surrounding environment for chemical reactions in a manner similar to that used by enzymes. Small molecules have been enclosed inside a variety of hollow structures. These cages are typically formed by coordinating organic ligands around metal centres or using hydrogen bonding to hold together supramolecular structures. The interior of these synthetic structures can direct unusual regioselective or stereoselective reactions or speed up reactions in dilute solutions; however, due to their large size, proteins have resisted attempts to confine them inside discrete synthetic cages — until now.

To crack this problem, a team led by Makoto Fujita at The University of Tokyo and Koichi Kato at Nagoya City University covalently tethered a protein (ubiquitin) to an organic bidentate ligand containing two pyridine rings. The addition of Pd(II) along with more ligand (this time without a protein attached) resulted in a hollow spherical framework self-assembling around ubiquitin (pictured). The framework skeleton is made from 12 Pd(II) atoms bridged by 24 ligands, with each Pd atom bound to 4 pyridine



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groups. The internal diameter of the sphere (up to 7.3 nm) could be altered by tailoring the size of the organic bridge. The cavity was only large enough, however, to accommodate one ubiquitin molecule, preventing the inclusion of more than one protein-bound ligand in each spherical frame. Diffusion and ultrafiltration experiments proved that the protein was bound to the spherical frame and X-ray crystallography confirmed that it was located inside the cage. NMR spectra showed that ubiquitin remained in its three-dimensional

fully folded structure while inside the sphere, indicating that proteins encapsulated in synthetic cages might retain properties related to their tertiary structure.

Constructing a cage around a protein is only the first step towards harnessing the unique chemistry these systems can offer. The team explain that their ultimate goal is to match the conformational control that coordination cages offer to the functional control that proteins and enzymes provide.

RJ

Correction

In the version of the Research Highlight 'Materials Chemistry: Compliant crystals' originally published (*Nature Chem.* **4**, 866; 2012), the wrong affiliation was given. Corrected after print 23 October 2012.