NANOMATERIALS

Tools for Sherlock Holmes

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When a finger, palm or foot comes into contact with a smooth surface, the ridged surface on the skin leaves a mark known in forensic science as the friction ridge pattern or, if it is not visible to the naked eye, a latent fingermark. These fingermarks contain a complex mixture of secretions from pores on the ridges of the skin and can be detected using various optical, physical and chemical techniques. Adding to this toolbox of methods, two independent research teams have now developed two techniques for visualizing latent fingermarks.

Philip Maynard and colleagues at the University of Technology, Sydney and the University of Canberra used DNA aptamers that can recognize lysozymes (a component found in human sweat) to bind to fingermarks and produce marks with well-defined features. Fingermarks imprinted on a polyvinylidene difluoride substrate were aged for 24 h and then treated with a solution of fluorescently labelled DNA aptamers for 1 to 4 h. The marks were then imaged with a 505 nm light source, which revealed fingermarks with strongly fluorescent ridges and dark valleys.

Alternatively, Joseph Almog and colleagues at the Hebrew University of Jerusalem used gold nanoparticles modified with a bifunctional molecule to produce 'negative' fingermarks on cellulose paper. The gold nanoparticles bind to the cellulose paper but not to the fingerprint. On development in a silver solution, dark silver precipitates formed on the gold-coated areas giving rise to uncoloured fingermarks against a dark background. The process requires only 5 min of treatment with the nanoparticles, followed by 40 to 60 s of development. *ALC*

METAL DICHALCOGENIDES

The hotter the brighter

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Photoluminescence emission following excitation with laser radiation is an optoelectronic process that occurs in most semiconductors. The laser excitation provides energy for electrons to be promoted from the valence to the conduction band. After a short time the electrons relax back to the valence band and in doing so they emit light (photoluminescence). In common semiconductors, the photoluminescence intensity is higher at lower temperatures, as thermal energy induces ways for the electrons to relax other than by photoluminescence emission. Stefaattin Tongay, Junqiao Wu and colleagues at the University of California, Berkeley, MIT and the Chinese Academy of Sciences have now shown that the photoluminescence intensity of few-layer $MoSe_2$ can increase with temperature.

The bulk form of $MoSe_2$ has an indirect bandgap, which means that it is relatively difficult for electrons to relax by light emission, leading to weak photoluminescence emission. In single-layer form, the material has a direct bandgap and its photoluminescence can be very bright. For few-layer $MoSe_2$, electronic structure calculations show that it is almost equivalent for electrons to relax directly or indirectly. However, an increase in temperature decouples the neighbouring layers through interlayer thermal expansion. As a result, each layer behaves as if it was electronically isolated and with the bright photoluminescence of a direct bandgap material. *FP*

METAL–ORGANIC FRAMEWORKS

A very fine sieve

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Deuterium accounts for only a minute fraction of naturally occurring hydrogen and is used in a variety of applications from nuclear fusion to isotope tracing. It can be separated from isotope mixtures with techniques such as cryogenic distillation and thermal diffusion, but these methods can be expensive and have low selectivity. A technique known as 'quantum sieving' — in which heavier isotopes undergo preferential adsorption in nanoporous structures at low temperatures due to quantum effects — has been proposed as an alternative, and has been tested with materials such as zeolites and metal–organic frameworks (MOFs). However, the D_2/H_2 uptake ratios have typically been too low to be competitive with conventional methods.

Michael Hirscher and colleagues at the Max Planck Institute for Intelligent Systems, Jacobs University and Augsburg University have now shown that a zinc-based MOF called MFU-4 can offer significantly improved uptake ratios. The MOF has alternating large and small cavities connected by a narrow square-shaped aperture, which is formed from four chlorine atoms and whose size is similar to the kinetic diameter of hydrogen. For a molecule to reach the large pore and to be adsorbed in the framework, it must pass the small cavity and the aperture, which act as separation gates.

Using low-temperature adsorption isotherm measurements at 50 K, a D_2/H_2 uptake ratio of 4.1 was determined for the material, which the German team suggests is the highest value reported so far. *OV*

SELF-ASSEMBLY

Tied up

Science **338,** 783–785 (2012)

Knotted proteins are relatively common, but synthesizing intertwined chemical structures is extremely challenging because it requires precise synthetic steps that bypass more readily accessible macrocycles. Now, Jeremy Sanders and colleagues at the University of Cambridge and the University of Bath have created a molecule that can self-assemble into a trefoil knot.

The molecule is composed of three naphthalene diimides, which are held together by flexible alanine linkers and are terminated at both ends with a cysteine amino acid. In water, the thiol groups of the cysteine ends oxidize to form disulphide bonds. The reaction can lead to the formation of cyclic monomers, dimers and trimers, and by increasing the polarity of the solution (that is, by adding a salt) the trimer is the preferred product. The researchers found that the trimer has a short retention time in a liquid chromatography column, eluting between the cyclic monomer and the cyclic dimer. This is a clear indication that some hydrophobic parts of the molecule are buried within the structure so as to avoid contact with water and maximize hydrophobic interactions. The knotted structure was confirmed by nuclear magnetic resonance spectroscopy and the chirality of the knot can be controlled by the handedness of the peptide linkers.

The molecular structure of the precursor — three hydrophobic, electron-deficient units linked by short, flexible hydrophilic linkers — could be a general strategy for achieving knotted structures by self-assembly and might also represent a model system for studying knot formation in proteins. *AM*

Written by Ai Lin Chun, Alberto Moscatelli, Fabio Pulizzi and Owain Vaughan.