

solution, and with different alignments. Solid–liquid interfaces provide many examples of beautiful molecular tilings, but those made up from a single molecular building block are generally limited to two dimensions. To enable molecular tiles to also stack on a surface, multiple building blocks are often required to provide the additional ‘adhesive’.

Now, a team — made up of researchers from Katholieke Universiteit Leuven, Vienna University of Technology, Freiburg University and the Max Planck Institute for Polymer Research — led by Steven De Feyter and Stijn Mertens have discovered that the molecular packing of a polyaromatic cation (PQP<sup>+</sup>) at a solid–liquid interface changes reversibly in response to an applied potential — including between two- and three-dimensional packing. The cation stacks into columns in the solid state when combined with a perchlorate anion due to electrostatic interactions, yet they found that it formed a highly ordered, porous hexagonal single-layer structure on a gold surface in aqueous solution.

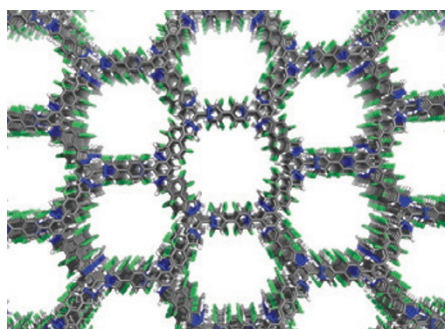
Upon applying a potential and subsequently increasing it, the packing of PQP<sup>+</sup> was altered — the increased negative charge on the gold substrate being compensated for by a higher density of PQP<sup>+</sup>. First, a new hexagonal arrangement with greater surface coverage was observed, formed by rotation and squeezing together of the molecules in the initial monolayer. More surprisingly, further increasing the potential induced a wholesale rearrangement into a bilayer of PQP<sup>+</sup> in a ‘herringbone’ pattern. The team showed that the unexpected stacking of PQP<sup>+</sup> layers is a result of a fine balance between the size of PQP<sup>+</sup> and its charge. When its charge density is not large enough to fully compensate for the substrate’s negative charge the second layer forms, but the charge is sufficiently delocalized over the whole molecule such that repulsion between adjacent layers is minimized and the bilayer remains stable. *CH*

#### MOLECULAR MATERIALS

### Persistent porosity

*Nature Commun.* **5**, 5131 (2014)

Porosity in supramolecular assemblies has attracted a great deal of attention in recent years, in particular that of metal–organic frameworks (MOFs) and their metal-free counterparts, covalent organic frameworks (COFs). The modular nature of these extended- network materials offers great opportunities in terms of pore engineering, but they are typically difficult to process



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in solution. Using discrete molecules instead can help circumvent this issue but comes with other challenges: small molecules do not tend to pack into highly porous structures, or do so in a rather unpredictable manner and usually lead to fragile materials.

Ognjen Miljanić at the University of Houston and co-workers in the USA and Taiwan have now prepared a discrete fluorinated trispyrazole molecule that assembles into a non-covalent organic framework featuring large, empty channels. The material is extrinsically porous — that is, its channels arise from the way non-porous molecules are packed, rather than intrinsic porosity from the suitable arrangement of inherently porous building blocks. The discrete molecule devised by the researchers consists of a central phenyl ring from which three ‘arms’ branch out, each of those composed of a tetrafluorobenzene ring and a terminal pyrazole group. Hydrogen bonding between the terminal pyrazole units of three adjacent molecules promotes their packing in two-dimensional layers. Those sheets are in turn held together through interlayer  $\pi$ – $\pi$  stacking interactions between the electron-rich pyrazole units and the comparatively electron-poor fluorinated aromatic rings. This arrangement results in a three-dimensional hexagonal network that features one-dimensional channels whose walls are lined with fluorine atoms.

The resulting material retained its structure not only in solution but also upon solvent removal, making the porous domain available for guest uptake. Owing to its fluorinated walls the framework is hydrophobic, and was shown to efficiently capture hydrocarbons and environmentally harmful fluorocarbons. In particular, a quick and reversible uptake — close to 75 weight percent — was observed for perfluorohexane. *AP*

Written by Gavin Armstrong, Claire Hansell, Russell Johnson and Anne Pichon.

## blogroll

### Moving on up

With the first part of the academic year in full swing for many, discussions about teaching, new jobs and prizes are rife.

The importance of educating the next generation of scientists should never be underestimated and, writing at *Endless Possibilities*, Katherine Haxton muses (<http://go.nature.com/KoKlgn>) on the start of a new year and the cyclical nature of updating and improving her teaching materials. She finds it frustrating that many lecturers are probably all trying to source the same sort of examples, such as NMR spectroscopic data or activation energies, and suggests that these resources should be pooled and shared, perhaps through a password-protected website.

More irreverently, Twitter users have been sharing their ideas on how to #explainsciencebadly, including, ‘the Earth is orbiting the Sun because it can’t find a place to park’; Vittorio Saggiomo collects a few of the best over at *Labsolutely* (<http://go.nature.com/fBuJAS>). What will your contribution be? Returning to more serious topics, after surviving the steep learning curve and challenging research, finding a job after finishing your PhD can be tough, as Tom Branson at *Chemically Cultured* writes (<http://go.nature.com/czmuy1>). He reflects on his experiences and gives some advice for other job-hunters out there, including looking at volunteering and considering what you want in the future.

And of course, who isn’t talking about this year’s Nobel Laureates in Chemistry, our celebrated scientists at the top of their game? At *Everyday Scientist*, Sam gives a nice overview (<http://go.nature.com/N1Zslm>) of the achievements of Betzig, Hell and Moerner, as well as reminding us that the *Simpsons* predicted Moerner’s Nobel recognition back in 2010! Finally, *Fluorogrol* finds ways for the rest of us to console ourselves over our lack of Nobel-worthy efforts at *Better Living Through Chemistry* (<http://go.nature.com/mkCjyt>).

Written by Jessica Frey, who blogs at <http://brightonscientist.wordpress.com>

### Correction

In the Research Highlight 'Molecular materials: Persistent porosity' (*Nature Chem.* **6**, 1028; 2014), the penultimate sentence of the second paragraph should have read: 'Those sheets are in turn held together through interlayer  $\pi$ - $\pi$  stacking interactions between the electron-rich pyrazole units and the comparatively electron-poor fluorinated aromatic rings'. This has been corrected in the online versions after print 25 November 2014.