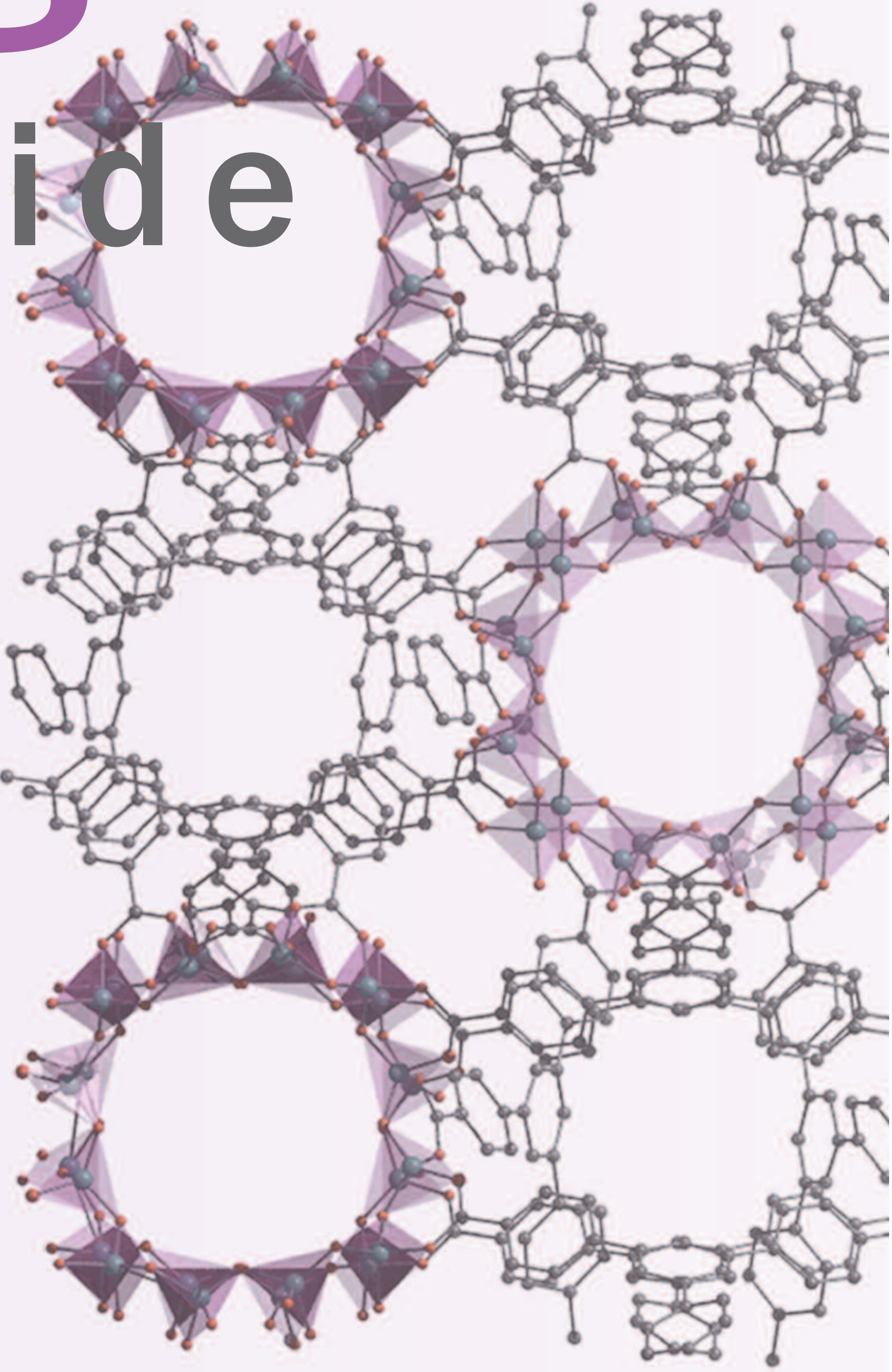
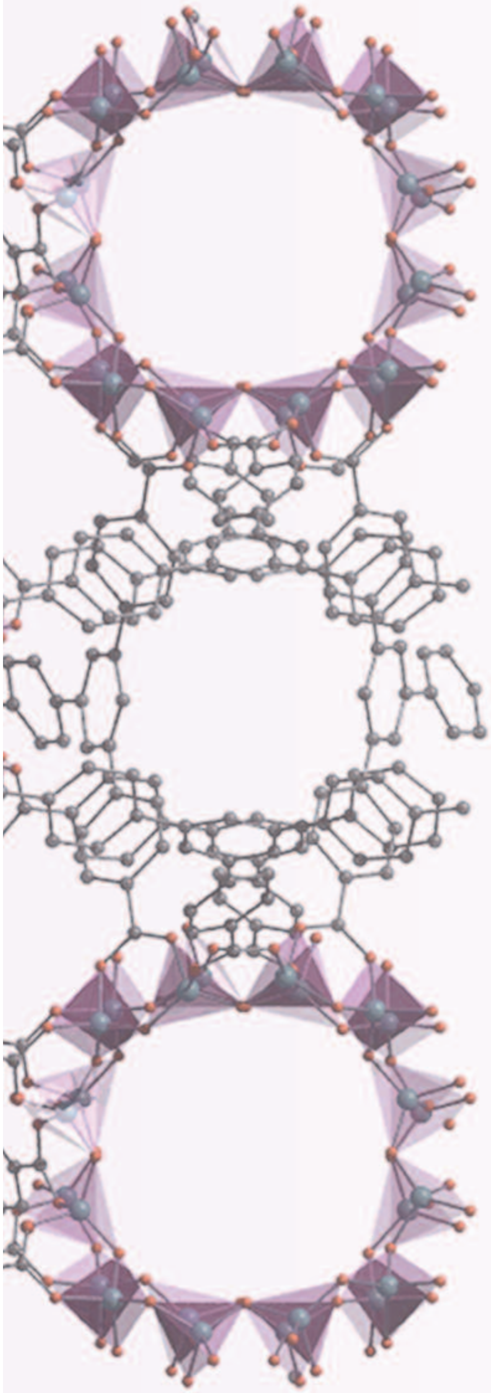
Big *on the* inside



The power of metal–organic frameworks

BY NANCY MILLS

With their spacious interiors, metal–organic frameworks offer many possibilities for research chemists and materials engineers.



This beryllium-based MOF holds the record for hydrogen storage at room temperature.
Matthew Hill, CSIRO

Talk about room to spare! With walls a single atom thick, and internal surface areas up to 10 000 square metres per gram, a metal–organic framework (MOF) can be up to 80–90% empty space. The rest of this porous material consists of metal atoms or small inorganic clusters positioned at the corners of a two- or three-dimensional framework and linked by rigid organic molecules.

MOFs, also known as porous coordination polymers, are a major growth area for research chemists and materials engineers. Their periodic sub-nanoscale porosity (0.3–5 nanometres) means big potential applications in the automotive and energy sectors, including storing hydrogen and methane to power vehicles and capturing carbon dioxide from coal-fired power stations. Using MOFs for on-board methane storage in natural gas-powered vehicles, for example, could deliver a driving range comparable to petrol-powered alternatives – with dramatically reduced greenhouse emissions and running costs.

The importance of MOFs was highlighted in January 2012 when *Chemical Reviews* dedicated a special issue to their properties and applications. The journal's editorial noted that MOFs 'epitomise the beauty of chemical structures and the power of combining organic and inorganic chemistry', and drew attention to the 'endless possibilities' afforded by manipulation of their inorganic and organic components.

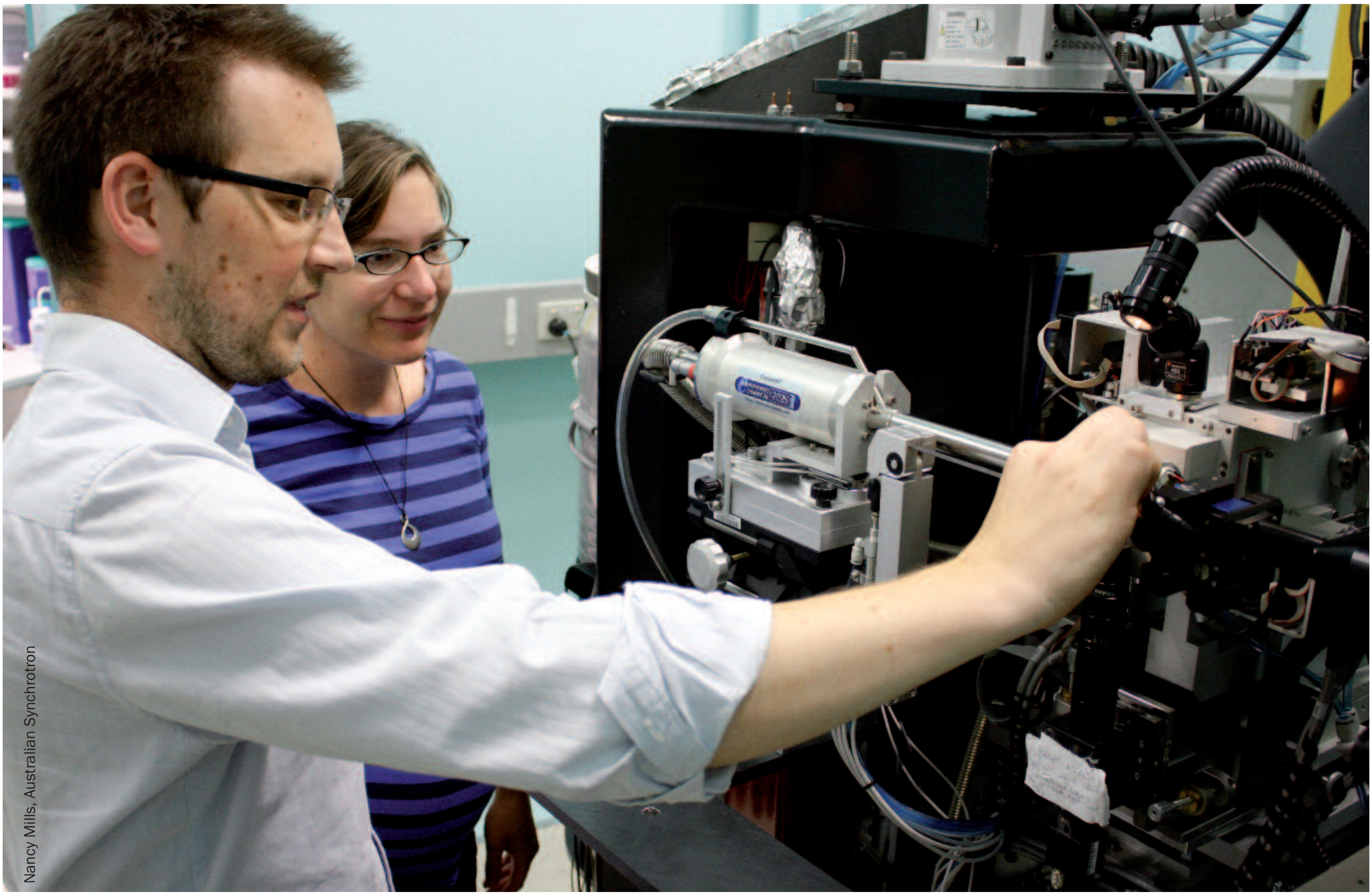
Closer to home, Victoria's six 2011 Young Tall Poppies included two early-career researchers who collaborate on MOF research at the Australian Synchrotron: Matthew Hill from CSIRO Materials Science and Engineering and David Turner from the Monash University School of Chemistry. Matthew went on to become the state's Young Tall Poppy Scientist of the Year.

Record results

Matthew's MOFs currently hold three world records for gas storage: room temperature storage of both hydrogen and methane, and zero-degree storage of carbon dioxide.

'Gases take up a lot of room, even when they're compressed,' Matthew says. 'It's one of the limiting factors in hydrogen- or methane-fuelled cars. However, if you bond a gas to a surface, the gas molecules pack in much more densely than if they were simply squashed together. MOFs have large internal surface areas because every atom is a new surface, and they can therefore store more gas in a smaller space.'

There's an old joke about fitting five giraffes into a Mini: two in the front, two in the back and one in the glovebox. How do you fit five elephants into a Mini? You can't – it's full of giraffes. In the case of MOFs, however, Matthew predicted in 2009 on the basis of earlier work with carbon and copper nanotubes that encouraging metal-substituted fullerenes to infiltrate the open framework structure would increase the attraction between methane and MOF and boost their



Nancy Mills, Australian Synchrotron

David Turner (Monash University) and Rachel Williamson (Australian Synchrotron) on the microcrystallography beamline.

methane storage capacity. His team recently validated this experimentally, smashing the storage capacity record and surpassing the USA Department of Energy target by 63%.

Similarly, in 2012, Matthew found that one gram of an MOF loaded with lithium atoms could capture as much as 170 mL of carbon dioxide near atmospheric pressure. That's equivalent to compressing the carbon dioxide to one-eighty-fifth of its original volume.

The record for hydrogen storage capacity per gram of material at room temperature was achieved in 2009, after Matthew and his CSIRO colleagues developed the first-ever MOFs made from extremely lightweight atoms.

Synthetic solutions

Synthetic methods for MOFs typically involve precipitating MOF crystals from dilute solutions of suitable precursors such as organometallic compounds with hydrocarbon ligands, under the right reaction conditions. However, the synthesis is still not well understood.

Over the past few years, CSIRO researchers have tackled several aspects of MOF production and characterisation, including the development of a high-throughput platform for preparing and screening metal–organic framework materials. The key is to use high-throughput synchrotron X-ray powder diffraction to identify crystalline materials with the large unit cells associated with a MOF's ordered porosity. Synchrotron powder diffraction offers shorter acquisition times and higher throughput, improved signal-to-noise ratios and better resolution than laboratory methods. This means researchers can assess a larger number of test reactions to determine the best conditions for producing MOFs, and map their formation in real time.

Another section of the CSIRO team has expertise in material engineering. Their aim is to grow MOFs in precise locations and on substrates with particular geometries, and prepare MOFs with embedded functional nanoparticles; both aspects are important for the fabrication of porous-based miniaturised devices such as those required for microfluidics and micro-sensing applications.

Materials engineer Paolo Falcaro and his colleagues are employing synchrotron powder diffraction to scan hundreds of samples of MOF crystals nucleated using silicon dioxide mesoporous monoliths with functionalised surfaces and mesoporous nanoparticles in solution. The group is considered one of the world's top four in the area of MOF functionalisation and patterning.

They have also used Fourier-transform IR reflectance and transmission microspectroscopy at the Australian Synchrotron to examine a new type of MOF grown on the surface of seeded substrates and patterned surfaces created using deep X-ray lithography at the Elettra synchrotron in Italy. Synchrotron Fourier-transform IR enabled detailed characterisation of seed composition as an important step towards understanding how to use these to promote MOF formation or supply compounds such as drugs for controlled release through the porous MOF structure.

Paolo and his colleagues have discovered that nano-structured polyhydrate zinc phosphate (alpha-hopeite) microparticles can act as MOF nucleation agents both in solution and on complex two- and three-dimensional surfaces. The alpha-hopeite microparticles can be used to accelerate MOF production, provide spatial control of MOF growth, or insert functional (e.g. metallic, polymeric or semiconducting) nanoparticles into MOFs for molecular size-selective applications. The importance of their findings and the beauty of their MOF nanoparticles have put them on the front covers of two major journals in the last 12 months.

'The Australia Synchrotron represents a unique facility for the control of MOF quality', Paolo says. 'Our modifications induce distortion in the MOF frameworks, and the synchrotron is essential for identifying the conditions that yield the best properties.'

Crystal chemistry and engineering

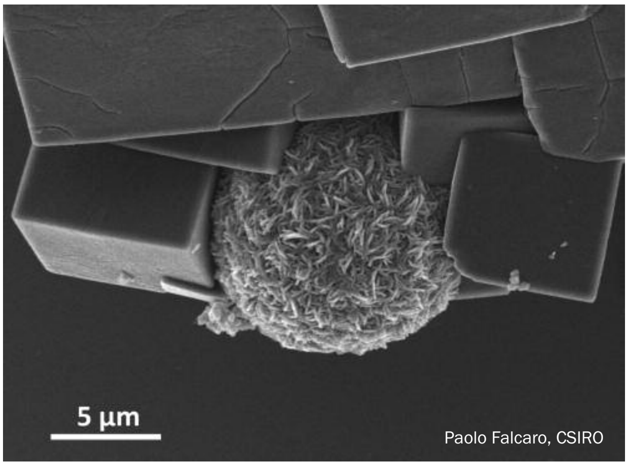
At Monash University, David Turner is interested in what he describes in simple terms as 'how best to trap or detect molecules, and how molecules pack together to form materials'. Both goals involve 'exploring intermolecular interactions that are weaker than standard chemical bonds'. His research focuses on porous materials for gas storage (such as MOFs) and more-fundamental studies of how molecules interact in the solid state. He says that the synthesis of porous systems such as MOFs is 'very challenging because the natural tendency is for materials not to contain any hollow space'.

Because MOFs have relatively few atoms per unit volume, they are unsuitable for crystallographic studies using a laboratory source. The problem is exacerbated by the fact that MOF crystals are typically around 10-30 microns.

''For crystallography, the key point is that the intensity of synchrotron radiation lets us structurally characterise materials that we would never have a hope of characterising on in-house instrumentation,'' David says. ''This has blown the field wide open. Interesting compounds that might have been discarded years ago as 'poorly diffracting, microscopic rubbish' can now be fully explored.''

David says other areas of chemistry research benefit from similar methods. For example, his group is also interested in crystals composed of discrete metal–organic cages. Crystal engineering is a key focus for another Monash group seeking to control the arrangement of molecules in the solid state: 'MOFs are really a subcategory here; we engineer them in the same way, but with porosity as the main goal.'

In 2009, while working as part of a



SEM image of a polyhydrate zinc phosphate (alpha-hopeite) microparticle seeding ultraporous cubic metal–organic crystals (MOF-5).

Monash research team led by Stuart Batten, David published the discovery of a self-assembling supramolecular complex with a complete catenane and eight associated tetrafluoroborate anions in the asymmetric unit. This remarkable catenane includes eight aromatic groups in a continuous 2.5-nanometre array of face-to-face pi interactions along its longest dimension. Not surprisingly, the researchers dubbed it an 'octapi' complex. The structure was solved on the Australian Synchrotron's MX2 microcrystallography beamline.

The quest for more

As part of the quest for even greater surface areas, Matthew and David and their colleagues made a series of MOFs with metals such as magnesium, calcium, titanium, manganese, iron, cobalt, nickel, copper, zinc, tin and lead. They used the synchrotron's crystallography beamlines to determine the crystal structures of their MOFs as part of an investigation of how the size-to-charge ratios of the metal ions affect the gas adsorption strength of MOFs. As a result, the researchers have discovered new and unexpected structures with applications not only in gas storage, but also in photocatalysis, gas separations and medical treatment.

With their diverse framework structures, extraordinary porosity and potential applications across many areas of science and industry, it is clear that MOFs will continue to fascinate.

Nancy Mills <nancy.mills@synchrotron.org.au> is the Australian Synchrotron's science writer. She says the people named in this article are just the tip of the research 'iceberg' and there are many other outstanding contributors to this work who could not be named due to limited space.