

[Join Us](#)[Member Login](#)

SEARCH



# MATERIAL OF THE MONTH: METAL ORGANIC FRAMEWORKS

**Simon Frost**

Materials World magazine, 3 Oct 2016

**Simon Frost speaks to the forefather of a class of cage-like porous materials that hold promise for some of the most hotly sought applications in science.**

Among today's most pressing technological challenges, there is the need to reduce our reliance on fossil fuels and to capture CO<sub>2</sub> – scientists are hard at work trying to produce hydrogen fuel from water, efficiently sequester and store CO<sub>2</sub>, and improve energy storage and rechargeable batteries. Add to that list the shift towards microelectronics and smart technologies, which require advances in optoelectronics, actuation and sensing. Then there is the development of public health and medicine, from finding inexpensive, benign and efficient water desalination methods, to drug encapsulation and targeted delivery technologies that could revolutionise the way we treat serious illnesses. What these problems have in common is that they could be solved in part by an exciting class of materials called metal organic frameworks (MOFs).

## What are they?

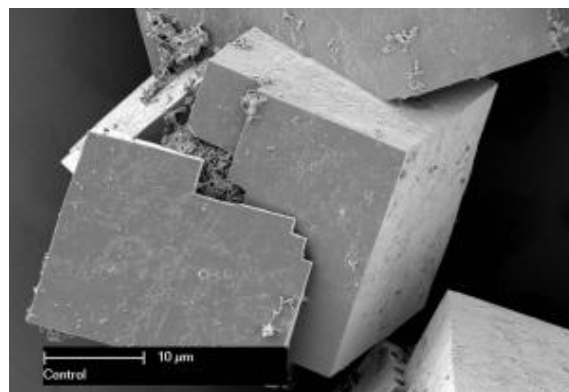
First developed in the 1990s, MOFs are crystalline hybrid materials created from both organic and inorganic molecules via molecular self-assembly. They are formed from linkers – long chains, typically of carbon and hydrogen oxides decorated with nitrogen atoms – and positively charged metal ions, which form nodes that bind the arms of the linkers together. In the most common synthesis method, the linker and metal are heated in a solvent for anything from hours to days until they settle into an orderly MOF structure. Recently, MOFs have been processed into porous fabrics, glass, flexible thin films and biocompatible membranes.

With countless combinations of metals and solvents available, MOFs offer highly diverse chemical and structural makeups that suit specific functionalities, but their key common property is high nanoporosity, which creates enormous surface areas within their 3D open-framework structures – the highest of any known materials. One pea-sized gram of MOF material can host the equivalent surface area of 40 tennis courts, and because most of their bulk is empty space, MOFs are also extremely light. They are perfectly repeating networks of functionalised, molecular-scale cages, which can be tuned in size and shape to serve a specific function by adapting their chemistry.

## The forefather

University of California, Berkley, USA, chemist Professor Omar Yaghi has pioneered research into MOFs and continues to lead the field. He authored the first published report of a MOF in 1999 and estimates that his lab alone has created in excess of 1,000 different MOF structures since. He has seen many of the major developments as they occurred.

'My group and I have been fortunate over the years to provide the conditions under which Mother Nature reveals itself to us,' he told Materials World. His group has achieved a slew of world-firsts, including the first gas adsorption isotherm (MOF-2), the record-breaking surface areas of MOF-5 and MOF-177, first open metal sites in extended structures isolated and characterised in MOF-12, the first carbon dioxide capture, methane storage and hydrogen storage, first 2D and 3D covalent organic frameworks (COF-1, 5, 102-108), the first weaving structures (COF-505), and first coordinative alignment method for crystallisation (MOF-520).

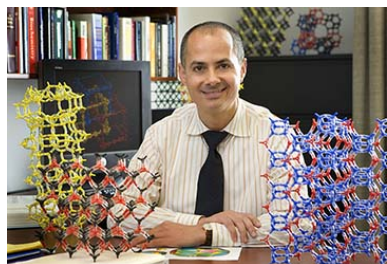


'These firsts are testament to the superb group members I have had over the years and the generosity of those who support my research. They are exciting and special, but each MOF tells its own story and reserves a place in my heart,' he said.

## Reticular synthesis

The building up of MOFs from metal-carboxyl clusters and organic linkers has enabled the formation of architecturally and chemically robust frameworks. This led to the measurement of MOFs' first gas adsorption isotherm and the determination of their internal surface area. 'It opened the way for building new frameworks from variously shaped clusters and organic linkers, which led to the current growth in the field,' said Yaghi.

The ease with which MOFs and covalent organic frameworks (all-organic frameworks) can be designed, their constituents varied and functionalised and their internal porosity used for the binding of gases, organic molecules, metal complexes and proteins has given rise to many applications. As Yaghi summarised, these include 'carbon dioxide capture and conversion, methane storage for transportation, catalysis and organic transformations, electrical conductivity, bio-imaging, and drug transport.'



On a fundamental level, MOF (and COF) chemistry is based on stitching molecules together with strong bonds into frameworks – a process known as reticular synthesis. The fact that they are crystalline and maintain their crystallinity when undergoing reactions gives rise to what Yaghi calls the 'chemistry of the framework', as opposed to the traditional focus on the molecule that organic and inorganic chemists are accustomed to. Reticular chemistry has recently been used to tailor frameworks for specific properties – notably in catalysis and separations. Meanwhile, the use of the mechanical bond to weave covalently linked threads has introduced the possibility of adding resiliency and dynamic properties to these materials.

'Frameworks with chemical stability in acids and bases, thermal stability up to 300–400°C and architectural stability (with porosity of over 10,000m<sup>2</sup>/g) can now be made dynamic by weaving their constituents,' Yaghi explained. 'Just this year, we have shown how complex organic molecules and hormones can be bound covalently into the interior of MOFs and their crystal structure determined with high resolution. This development means that the structure of organic molecules and biomolecules that defy crystallisation can be determined by this coordinative alignment method in MOFs.'

## MOF power

Sustainable, efficient and economical production of hydrogen is one of the most intense areas of research today. Not only does hydrogen offer close to three times the energy of gasoline, its exhaust product is benign water vapour, rather than the CO<sub>2</sub> and NO<sub>x</sub> that fossil fuel combustion produces. Extracting hydrogen directly from the air for use as fuel is, unsurprisingly, seen as something of a holy grail.

'We, and others, are working extensively on this objective', Yaghi said. 'It is a fantastic scientific problem, which we are slowly addressing. The current challenge is to increase the binding energy of hydrogen in MOFs and COFs to reach about 20kJ/mol. This is necessary for storage of hydrogen at room temperature.' Yaghi is optimistic – the binding energy of MOFs has already risen from 3.5kJ/mol to the current level of 12kJ/mol. 'This project is interesting and its potential is great, but it requires more work. We can currently store at 77K about 12wt% hydrogen in a MOF,' he said.

Another way to produce hydrogen is from water using photochemical reduction and, while the semiconductor titanium dioxide is currently the most effective photocatalytic material in commercial use, researchers are examining how MOFs could enhance the process. The titanium-based MIL-125 (Ti-MOF-NH<sub>2</sub>), for example, can be functionalised with an aqueous solution containing triethanolamine to create a reaction with visible light, where photons are absorbed by the MOF's linkers and transferred to its inner catalyst – clusters of titanium oxides – which then reduce the hydrogen protons to form H<sub>2</sub>. MIL-125's nanoporous scaffold can also host other catalysts such as platinum, which can further enhance the material's photocatalytic performance. MOFs, perhaps more than any class of materials, sit at the interface between chemistry and materials science.

## Proton conductivity

Once hydrogen is obtained, a fuel cell is required to generate power through electrochemical conversion. Hydrogen fuel cells rely on an electrolyte that offers high proton conductivity to regulate the charge transport between anodes and cathodes and, once again, MOFs offer an attractive solution, and their crystallinity provides new insights into molecular transport mechanisms.

In 2013, chemists at the University of Calgary, Canada, reported in the *Journal of the American Chemical Society* that they had developed a water-stable MOF with highly acidic pores that created high proton conductivity – above 10<sup>-3</sup> Siemens/cm<sup>-1</sup> at 60°C, at 98% relative humidity, retaining its structural stability in the humid conditions that would be present in a fuel cell, and resisting swelling.

Improvements can also be made to the now ubiquitous lithium ion battery, which operates on the principle of reversible lithium insertion-extraction reaction using a LiCoO<sub>2</sub> cathode and an anode made from graphite, offering respective capacities of 148 and 372mAh/g<sup>-1</sup>. In 2010, chemists at the National University of Singapore instead used a zinc-formate MOF (Zn<sub>3</sub>(HCOO)<sub>6</sub>) anode, which settled to a near-uniform capacity of 560mAh/g<sup>-1</sup> for up to 60 cycles, demonstrating that the material is both electrochemically robust and sufficiently thermomechanically stable to retain the electrode integrity over many charge-discharge cycles.

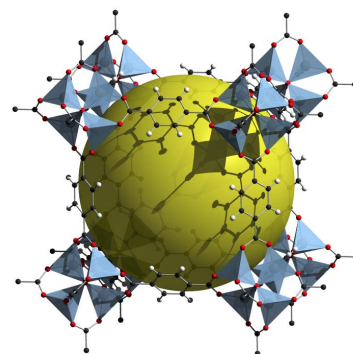
## Auspicious applications

One of the most promising features of MOFs is that they are applicable to areas of research that are growing in significance and scale – carbon capture and storage (CCS), for example, was estimated in a study by Pike Research (now part of Navigant), USA, to reach a potential market value of US\$221bln by 2030. ‘Gas storage and separations and catalysis are the very closest applications to wide implementation,’ said Yaghi. ‘MOFs are being made in multi-tonne quantities for gas separations and catalysis. They are already commercialised, and I am confident, given the diversity of this chemistry, that there will be many more applications to come.’

Yaghi notes that many companies now have their own research programmes focusing on reticular materials chemistry. ‘The question is not if, or when, but how large this chemistry and its applications will grow, and the extent to which they will solve society’s problems. I am very optimistic because of the extensive nature – its versatility, multiplicity and diversity.’

The breadth of structures that can theoretically be formed is virtually endless. Pore sizes from 3–100 Angstrom are possible and have been made. Those in the field, Yaghi believes, see no limits as they continue to surprise themselves with every new development. ‘The aim in designing pore size and shape has a lot to do with what one intends to use the framework for. Storage and separation of gases requires smaller pore sizes and more chemical crafting of the interior than the binding of organic contaminants in water, where larger pore sizes are more desirable and the shape of the pore becomes critical.’ These larger-pored MOFs have been shown to incorporate, within their interior, fully folded and functional proteins such as green fluorescent protein and myoglobin.

Despite many years working with MOFs, Yaghi’s sense of wonder for their chemistry has not dimmed. ‘We must not forget that MOFs are truly beautiful and that the way they are made has changed our way of thinking about chemical structures. They have enriched chemistry and significantly widened the scope of what we make and study.’



2016

2015

2014

2013

2012

2011

2010

2009

2008

2007

2006

2005

**Would you like to receive items like this in your inbox? [Sign up for content alerts today](#)**

[Tweet](#)

[Facebook](#)

[LinkedIn](#)

[ShareThis](#)

[Email](#)

VENUE HIRE

JOBS



JOURNALS



COMPANY MEMBERSHIP



WOMEN IN MATERIALS



---

## LATEST FROM TWITTER

[#iom3wlc](#) Finalist of the day is Li (Alan) Zhong, Singapore, Artificial Corneal Implants [t.co/7PTSBZD7t6](https://t.co/7PTSBZD7t6)