A solar panel powers a device that harvests water from the air in California's Mojave Desert.

MATERIALS SCIENCE

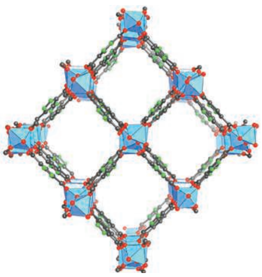
Crystalline nets snare water and make fuel from thin air

Having solved stability problems, chemists think metal-organic frameworks are ready for a commercial ascent

By **Robert F. Service**, *in San Diego, California*

When Omar Yaghi was growing up in Jordan, outside of Amman, his neighborhood received water for only about 5 hours once every 2 weeks. If Yaghi wasn't up at dawn to turn on the spigots to store water, his family, their cow, and their garden had to go without. At a meeting last week here, in another area thirsting for freshwater, Yaghi, a chemist at the University of California, Berkeley, reported that he and his colleagues have created a solar-powered device that could provide water for millions in water-stressed regions. At its heart is a porous crystalline material, known as a metal-organic framework (MOF), that acts like a sponge: It sucks water vapor out of air, even in the desert, and then releases it as liquid water.

"This is fantastic work that addresses a real problem," says Jorge Andrés Rodríguez Navarro, a MOF chemist at the University of Granada in Spain. It's also just one example of how MOFs may finally be entering their prime. Yaghi and his colleagues synthesized the first MOF in 1995, and chemists have created tens of thousands of the structures since. Each is made up of metal atoms that act like hubs in a Tinkertoy set, connected into a porous network by organic linkers designed to hold fast to the hubs and create openings to house molecular guests. By mixing and matching the metals and linkers, researchers found they could tailor the pores to capture gas molecules, such as water vapor and carbon dioxide (CO_2). "We can play games with modifying these and know exactly where every atom is," says Amanda Morris, a MOF researcher at Virginia Polytechnic Institute and State University in Blacksburg. But because many of the early MOFs were expensive to make and degraded quickly, they did not live up to initial excitement.



Pores in MOF-303, an aluminum-based metal-organic framework, can capture water vapor and release it as liquid.

In recent years, Yaghi and other MOF-makers have figured out a broad set of design rules to make MOFs more robust. More highly charged metals, for example, create stronger bonds that stand up to heat. That has opened up functions such as housing catalysts, which typically work faster at high temperatures. Another stability boost came when researchers learned to tailor the architecture to shield less-stable bonds in a MOF from attack by trapped molecules.

As a result, commercial applications are starting to take off. One recent market report predicted that sales of MOFs for applications including storing and detecting gases will balloon to $410 million annually over the next 5 years, up from $70 million this year. "Ten years ago, MOFs showed promise for a lot of applications," says Omar Farha, a MOF chemist at Northwestern University in Evanston, Illinois. "Now, that promise has become a reality."

One application is Yaghi's, which he hopes will help provide drinking water for the estimated one-third of the world's population living in water-stressed regions. Yaghi and his colleagues first developed a zirconium-based MOF in 2014 that could harvest and release water. But at $160 per kilogram, zirconium is too expensive for bulk use. So, last year, his team came up with an alternative called MOF-303, based on aluminum, which costs just $3 per kilogram. In the desert of Arizona, Yaghi and his team placed their MOF in a small, clear plastic container. They kept it open to the air at night, allowing the MOF to absorb water vapor. They then closed the container and exposed the MOF to sunlight, which drove liquid water from it—but the harvest was only about 0.2 liters per kilogram of MOF per day.

At last week's meeting of the American Chemical Society and in the 27 August issue of *ACS Central Science*, Yaghi reported that his team has devised a new and far more productive water harvester. By exploiting MOF-303's ability to fill and empty its pores in just minutes, the team can make the new device complete dozens of cycles daily. Supported by a solar panel to power a fan and heater, which speed the cycles, the device produces up to 1.3 liters of water per kilogram of MOF per day from desert air. Yaghi expects further improvements to boost that number to 8 to 10 liters per day. Last year, he formed a company called Water Harvesting that this fall plans to release a microwave-size device able to provide up to 8 liters per day. The company promises a scaled-up version next year that will pro-

IMAGES: (TOP TO BOTTOM) MATHIEU PRÉVOT; F. FATHIEH *ET AL.*, *SCI. ADV.* 4, EAAT3198, 2018 duce 22,500 liters per day, enough to supply a small village. "We're making water mobile," Yaghi says. "It's like taking a wired phone and making a wireless phone."

Other MOF applications are showing promise as well. In the 25 January issue of *ACS Applied Nano Materials*, Farha and his colleagues reported using a MOF to detoxify chemical weapons. The MOF consists of a lanthanum-based framework linked to ring-shaped organic compounds. The compounds, called porphyrins, had previously been shown to be adept at absorbing light and using that energy to convert oxygen molecules in the air to a reactive form known as singlet oxygen. In the study, the singlet oxygen in turn could break down molecules of a lab-safe molecular cousin of mustard gas both inside and outside the pores. At the meeting here, Farha's Northwestern colleague Joseph Hupp reported that he and his colleagues have extended the idea with a series of zirconium-, hafnium-, and cerium-based MOFs that can detoxify nerve agents such as sarin gas. A thin coating of MOFs on gas masks and uniforms could help protect soldiers from exposure to chemical weapons, Hupp says.

Farha and others have also encapsulated enzymes inside MOFs, protecting the fragile molecules from harsh environments and enabling them to carry out industrial reactions outside cells. In one example, Farha's team reported in the 26 March issue of *Angewandte Chemie* that a MOF-caged enzyme called formate dehydrogenase can convert CO_2 to formic acid, a common industrial chemical, at more than three times the rate of the uncaged enzyme, and under greener conditions than formic acid is normally made. At the meeting, Thomas Rayder, a graduate student at Boston College, reported building on the idea. He encapsulated a pair of enzymelike catalysts in a zirconium-based MOF to drive a series of reactions that convert gaseous CO_2 to methanol, a liquid fuel.

When they were unprotected by the MOFs, Rayder found, the two catalysts didn't produce any methanol because they were quickly deactivated, likely by reacting with each other. But safely ensconced in the MOFs, they could make methanol at temperatures and pressures far below those used in existing methanol plants, offering a potentially cheaper and greener way to make the fuel.

Rayder and others still need to show that these and other MOFs can be manufactured cheaply on a large scale. Each potential commercial MOF needs to prove itself in stability, efficiency, and life span. But if MOFs can pass those tests, they could offer a framework for tackling some of the world's most pressing problems. ■

SCIENCE & SECURITY

Australia targets foreign influence at universities

New task force triggered by concerns about China

By **Dennis Normile**

Growing concern about foreign influence at Australia's universities has prompted the government to launch a task force that will develop guidelines for "dealing with foreign interference." Officials did not mention China when unveiling the panel on 28 August, but it is understood to be a reaction to fears of Chinese entities gaining access to military technology through collaborations and hacking into university computer networks.

The University Foreign Interference Taskforce will have four working groups, focusing on cybersecurity, intellectual property, foreign collaborations, and raising awareness of security issues. Half of the panel's yet-to-be-determined number of members will come from universities; the remainder will come from the Department of Education and government security agencies. The guidelines are due in November.

"We must get the balance right" between pursuing "our national interest and giving universities the freedom to pursue research and collaboration," said Minister for Education Dan Tehan.

In recent years, Australia's Department of Defense and some analysts have argued that universities are lax in overseeing collaborations involving technologies that might have security applications. On 26 August, the Australian Strategic Policy Institute in Canberra published a report alleging that artificial intelligence software being used to monitor China's minority Uyghur population "may have benefited from connections with Australian universities and Australian government funding."

The vulnerability of university computer networks is another worry. In a 2017 report, the Australian Cyber Security Centre in Canberra warned that attempts to hack university networks were increasing and that they are attractive targets as gateways to information on research activities and intellectual property. In June, cybersecurity experts suggested hackers based in China were behind a computer breach at Australia National University late last year that netted records on up to 200,000 current and former students and staff. "There've been a series of miniscandals … that show there is a big problem of foreign interference in universities coming from China," says Clive Hamilton, an ethicist at Charles Sturt University in Canberra who has been outspoken on the issue.

"The government gives every impression that this is going to be a thorough-going review leading to major changes."

Clive Hamilton, Charles Sturt University

Still, some worry that officials are overreacting to concerns about China. The conversation has become "slightly hysterical," University of Sydney Vice-Chancellor and Principal Michael Spence said in a 26 August radio interview. Despite the tensions, China is on track this year to become Australia's leading international collaborator, surpassing the United States. That forecast, in a July report from the Australia-China Relations Institute at the University of Technology Sydney (UTS), is based on the number of peer-reviewed papers co-authored by scientists in the two countries.

Spence approves of the new panel, saying it is a promising "forum for dialogue." And Universities Australia, which represents 39 schools, pledged cooperation.

Michael Zhou, an international relations researcher at UTS who co-authored the recent report on scientific cooperation, says that in Australia problems with collaborations have been viewed as an institutional oversight issue. So far, no Chinese or Chinese Australian researchers have been subject to disciplinary measures. In stark contrast, academic researchers in the United States have faced dismissal and criminal prosecution for failing to disclose ties to Chinese institutions (*Science*, 26 April, p. 314; 31 May, p. 811).

Hamilton believes the effort could lead to tougher policies. "The government gives every impression," he says, "that this is going to be a thorough-going review leading to major changes." ■

Science

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Science **365** (6457), 964-965.
DOI: 10.1126/science.365.6457.964