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

Crystalline nets harvest water from desert air, turn carbon dioxide into liquid fuel

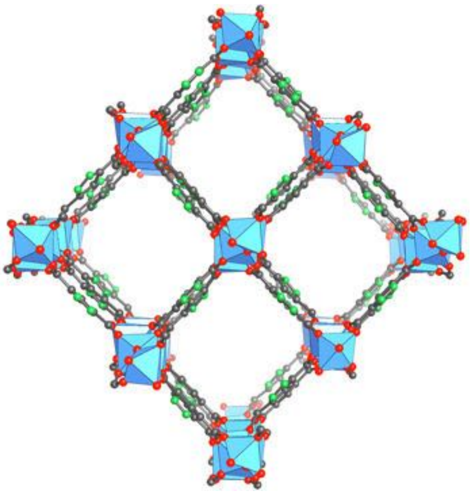
By **Robert F. Service**Sep. 3, 2019 , 6:05 PM

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 an-other 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.

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."



Pores in MOF-303, an aluminum-based metal-organic framework, can capture water vapor and release it as liquid. F. FATHIEH, *ET AL.*, *SCI. ADV.* 4, EAAT3198 (2018)

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 produce 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.