

NEW SORBENTS FOR GREENER COOLING

ACS MEETING NEWS: Custom porous materials give eco-friendly adsorption chillers a boost

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THE POSTDOC STANDING in the back of the hot, crowded room fanned herself repeatedly. So did the national lab researcher sitting in the front row, and the well-known academic sitting next to him. Apparently the air-conditioning wasn't reaching the tiny meeting room at the far end of a hard-to-find corridor in San Francisco's Moscone Center during last month's American Chemical Society meeting.

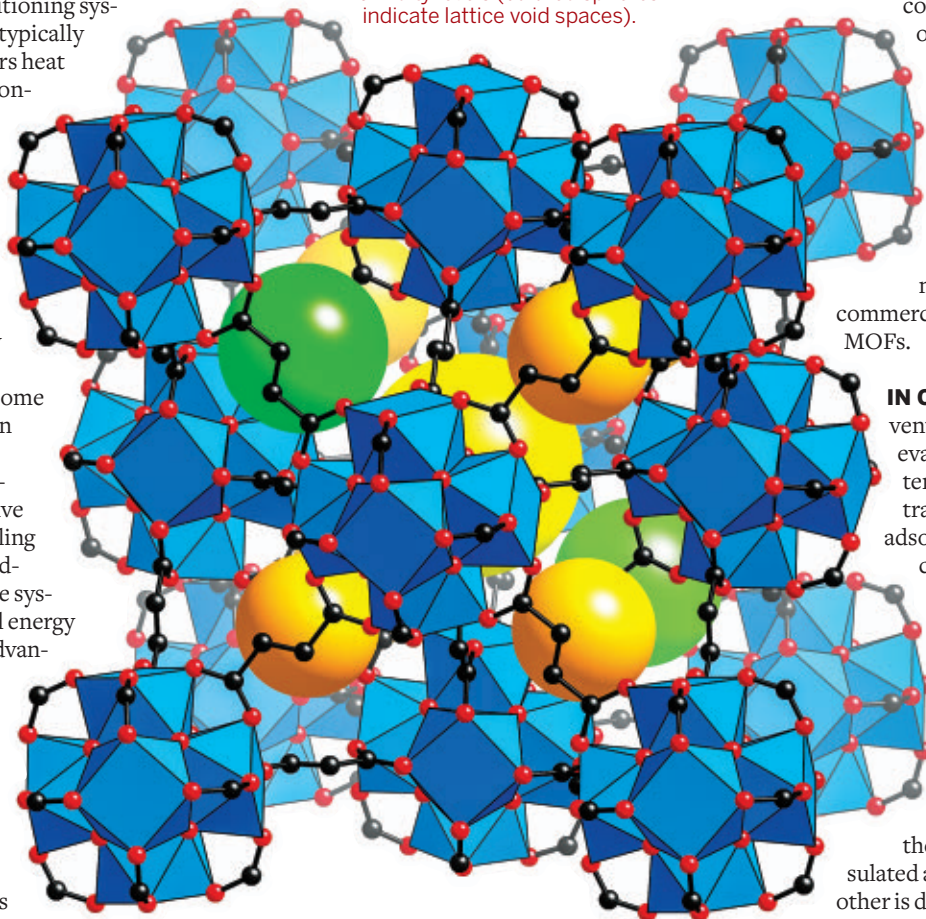
Had the system been working properly, as it was in the rest of the giant convention center, the room would have been cooled by a heat-transfer process driven by cycling a refrigerant between gas and liquid states. This kind of air-conditioning system, in which a fluid, typically a halocarbon, transfers heat by repeatedly being condensed and evaporated, is ubiquitous. It's found in residential, commercial, and industrial settings and used on land and sea and in the air.

But it isn't the only game in town. Some scientists, including some of the ones gathered in that stuffy room, are investigating new materials for an alternative heat-pump or air-cooling system known as an adsorption chiller. These systems offer substantial energy and environmental advantages compared with conventional cooling systems because they require much less energy and, depending on application, can use water as the refrigerant.

Adsorption chillers

are available commercially but are used on a relatively small scale. They tend to be very large and heavy and rely on common sorbents such as silica gel and zeolites, which exhibit mediocre water-uptake properties. Implementing these devices on a much larger scale calls for far superior sorbents, such as metal-organic framework (MOF) compounds. These materials have

SUPER SPONGE Custom-made Zr-based MOFs with carboxyl linker groups, such as the one shown here, take up record quantities of water even at very low humidity levels (colored spheres indicate lattice void spaces).



shown great potential in recent years for numerous adsorption applications, such as gas storage and separation. Now, researchers are studying them for water-based adsorption cooling. They're making customized MOFs designed to maximize water-uptake capacity and cycling performance and testing them in industrial settings for long-term stability.

MOFs are porous crystalline materials composed of metal ions or metal clusters bridged by organic linking groups. They have generated intense scientific interest over the past dozen years because of their outstanding adsorption properties and numerous potential applications.

"But so far, that interest has not led to commercial application of these materials," says B. Peter McGrail, an environmental engineering specialist at Pacific Northwest National Laboratory (PNNL). He suggests that adsorption cooling is one of the most likely near-term commercial applications of MOFs.

IN CONTRAST to conventional condensation-evaporation cooling systems, adsorption chillers transfer heat through adsorption-desorption cycles. Both systems capitalize on the heat-transferring—or cooling—effect brought about by coupling an endothermic process with an exothermic one. One step is carried out inside the building or other insulated area to be cooled; the other is done outside.



PRAVEEN THALLAPALLY/PNNL



CHILLAX
PNNL's Feng Zheng prepares a MOF-filled adsorption heat pump/chiller for testing.

In the case of adsorption systems, sending the refrigerant gas from the house to a sorbent positioned outside, and adsorbing (trapping) the gas there, releases unwanted heat to the atmosphere, thereby cooling the house. Desorbing the refrigerant from the trap regenerates the sorbent and liberates the gas so it can be sent back into the house for the next cycle.

The desorption step requires heat input, but not much. The upshot is that adsorption chillers can run on very little energy. These units can tap freely available solar heat or low-temperature waste heat, contained, for example, in industrial plant exhaust gases that are normally vented to the atmosphere.

So how suitable are MOFs to this task? To date, only a handful of MOFs have been tested for water uptake and release. As expected, researchers have begun with the ones available for purchase. At the University of Birmingham, in England, for example, mechanical engineer Raya Al-Dadah and coworkers evaluated a copper benzene tricarboxylate-based MOF known as HKUST-1 and its iron analog. In terms of water uptake, they found that the iron compound isn't much better than silica gel, but HKUST-1 showed an enhancement of 93% (*Int. J. Heat Mass Transfer* 2012, DOI: 10.1016/j.ijheatmasstransfer.2012.07.068).

A similar study by Heinrich Heine University Düsseldorf chemist Christoph Janiak and coworkers found that a MOF made from chromium and benzene dicarboxylate linkers (MIL-101) can be loaded

with roughly 1.4 g of water per gram of sorbent (140% water by weight). That value is more than four times as high as the loading of conventional zeolites and silica gels.

The team finds, however, that upon repeated cycling, the water-uptake capacity of that material and all commercially available MOFs decreases. Results of these studies are summarized

in a brief review by Janiak and coworkers (*Eur. J. Inorg. Chem.* 2012, DOI: 10.1002/ejic.201101056). Despite the degradation, the team stresses that the ability to tune MOF hydrophilicity by customizing the organic linkers and metal clusters gives MOFs "a clear advantage over conventional zeolite-type sorbents," which are less amenable to customization.

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That's the approach taken by Mircea Dincă, a chemistry professor at Massachusetts Institute of Technology. His group reasoned that increasing the hydrophilicity of the interiors of MOF pores would broaden the range of atmospheric conditions, such as relative humidity and temperature, over which an adsorbent would function well in a cooling application.

A RECENT STUDY suggests they're on the right track. The team made a series of MOFs featuring pyrazolate-bridged Zn^{2+} ions and a network of channels lined with functionalized naphthalenediimide groups. Those materials adsorbed water efficiently when the relative humidity was near 50%. But when the MOFs were subsequently oxidized with dimethyldioxi-

fornia, Berkeley, stand out in this regard.

In that study, Hiroyasu Furukawa, Omar M. Yaghi, and coworkers prepared several MOFs featuring $Zr_6O_4(OH)_4$ units and variously shaped organic linkers. At just 10% relative humidity, one of the compounds, which contains fumaric acid linkers (MOF-801), can take up 20 wt % water. That value is three times as high as a commercial zeolite used in adsorption chillers. And a related compound with multiringed linker groups (MOF-841) soaks up a record-setting 40 wt % water at roughly 30% humidity. The group reports that both compounds can be regenerated at room temperature and retain their adsorption values for at least five cycles (*J. Am. Chem. Soc.* 2014, DOI: 10.1021/ja500330a).

three months and involved “many tens of thousands of cycles,” Thallapally says. The kilogram quantity of MOF loaded into the industrial-sized unit maintained its water-uptake and cooling capacities throughout the trial run, demonstrating its durability.

The PNNL team is not yet sharing many details of the MOF used in that test. The group is awaiting patent approval. But McGrail offers that the proprietary material was designed with superhydrophilic channels to provide high water capacity and rapid adsorption-desorption kinetics. He adds that using that MOF in a newly redesigned chiller led to “the most efficient, compact, and lightweight chiller demonstrated so far.”

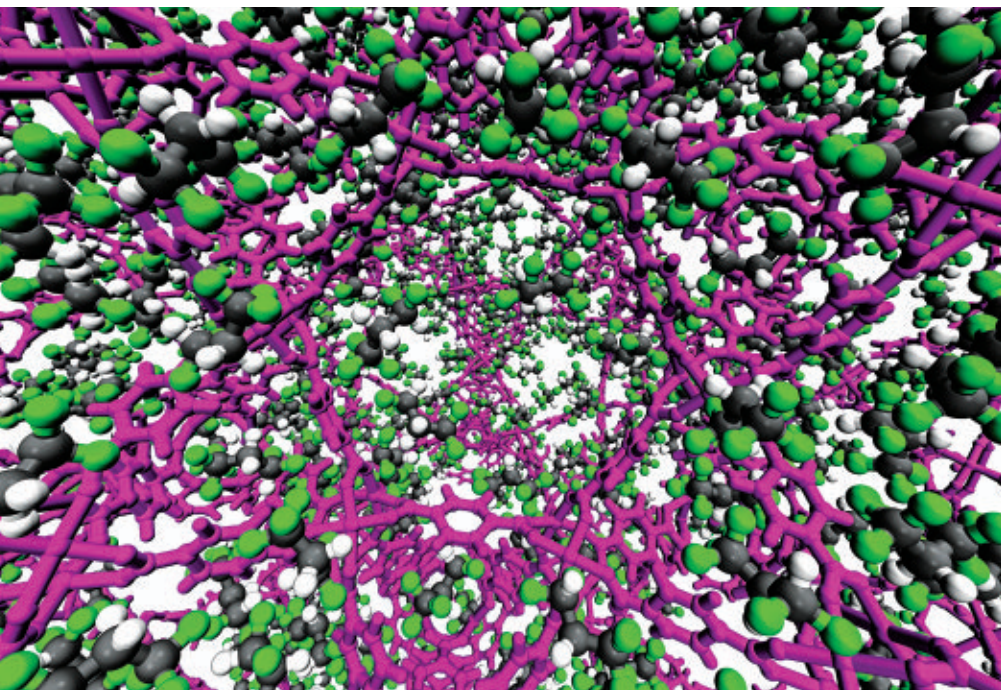
Now the PNNL team is working on a prototype unit for the Navy. Specifically, the researchers are working to design an adsorption chiller for refrigeration and freezer applications to be used aboard supply vessels that deliver goods to the fleet.

Currently, ships burn diesel to power an electric generator, to run a compressor, to cool the cabin, and to operate refrigerators and freezers for perishable cargo. “With an adsorption chiller, we can short-circuit that process and save a lot of fuel,” McGrail says.

The idea is to tap the ship's propulsion system for waste heat that's normally vented through the exhaust stack and use it to drive a fluorocarbon-charged chiller system. Fluorocarbons are far better suited than water to reaching refrigeration temperatures, so the team is evaluating these kinds of refrigerants.

To help establish guidelines for making high-performance sorbents for this unexplored application, the group just conducted a systematic study of the interactions of a series of fluorocarbon refrigerants with common MOFs. They examined the influence of fluorine-metal interactions on orienting the molecules in the MOF pores, the effects of pore size and morphology, and other factors regulating fluorocarbon uptake in MOFs (*Nat. Commun.* 2014, DOI: 10.1038/ncomms5368).

Perhaps it was the novelty of the “MOFs for green air-conditioning” idea that soon caused the scientists in the stuffy San Francisco meeting room to stop fanning themselves. More likely, it was the conventional air-conditioning finally kicking in and doing its job. Either way, fast-paced progress in customizing MOFs for refrigerant uptake is sure to help conference-goers chill out sometime soon. ■



PRAVEEN THALLAPALLY/PNNL

rane to coat the channels with sulfoxide and sulfone groups, and thereby increase the channel hydrophilicity, they soaked up water even when the humidity was as low as 30% (*Energy Environ. Sci.* 2013, DOI: 10.1039/c3ee40876k).

MOFs not only need to trap water efficiently to be useful in adsorption chillers, they must also retain their uptake capacity and release the water with little energy input. Two new MOFs reported recently in a study conducted at the University of Cali-

ORIENTATION Modeling studies reveal the influence of fluorine-metal interactions on the preferred orientation of a fluorinated refrigerant (gray, green, white) in a Cl-containing MOF (purple).

Five adsorption-desorption cycles in lab-sized test equipment is a good start. But far longer tests in an industrial rig are needed to learn about the long-term stability of MOFs. That need prompted McGrail, Praveen K. Thallapally, and other

PNNL scientists to team up with Power Partners Inc., an Athens, Ga.-based manufacturer of adsorption chillers for hospitals and other institution-sized buildings.

In the summer of 2013, the team conducted a test that ran continuously for