

## WATER CAPTURE

# An improved water-harvesting cycle

Tuning metal-organic frameworks at the atomic level helps release trapped water molecules

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The importance of the phase transformations of water cannot be overstated. The steam engine was a leap in engineering as well as a major inspiration for thermodynamics. Cloud seeding using silver iodide is arguably one starting point of crystal engineering. On page 454 of this issue, Hanikel *et al.* (1) tackle the goal of harvesting water from desert air using water-catching channels inside porous metal-organic frameworks (MOFs). This technique may become important as fresh, potable water is turning scarce in many regions. The authors' design was guided by single-crystal x-ray diffraction studies of water assembly, molecule by molecule, inside a prototype MOF. This MOF was then tuned at the atomic level to achieve better water-harvesting properties.

Over 2 billion people live in water-stressed countries (2), and almost two-thirds of the global population experience water scarcity every year (3). Air contains a lot of water, even over deserts and semi-deserts. Plucking the water out of the air is relatively easy, but the great challenge is inventing a system that can also release water without a high energy cost.

Although zeolites, aluminosilicate minerals, can sorb water easily, liberating the water molecules may require temperatures of 250°C. Molecular-level interactions are the key to unlocking the water, with two areas of importance. One occurs between the

water molecules and the channel surface of the material, and the other between the water molecules inside the channels.

Coordination bonds exist where the water binds to a metal ion with one of its free electron pairs. Hydrogen bonds between free electron pairs on nitrogen (N) or oxygen (O) atoms in the framework and water hydrogens. The reverse is also true with interactions between framework N-H and O-H groups and water oxygens. In addition, there are hydrogen bonds between the water molecules themselves.

To tune these with atomic-level control in zeolites, micro-, and mesoporous carbon and silica, for example, is difficult. MOFs allow this sort of control because of the ability to change and mix linkers and metal ions (4). As the coordination bonds are relatively strong, sorption is easy, but this also may hinder the release. These bonds are engineered by creating, or blocking, free sites on the metal ions. The hydrogen bonds to the framework are controlled by the linkers and to some extent also the metal-ion nodes.

The interactions between the water molecules define water and any polymorphs of ice, and the closer the sorbed water structure gets to the local environment in water or ice, the tighter they will be bound. These interactions are controlled by the framework topology and the linker size.

Hanikel *et al.* started with the observation of a notch in the water sorption data of MOF-303. Some water molecules were sitting rather tight even at low relative water pressures, which the authors call “step S”, thus impeding the full water-harvesting potential. This prompted an atomic-level

study of the sequential water filling using 23 single crystal structure determinations. The authors determined all water positions and hydrogen bond interactions from the fully loaded material with 31 weight percent water to the empty MOF (see the figure) and identified “step S” as two waters strongly hydrogen bound by N-H groups in two neighboring linkers. The authors then used the multivariate approach, mixing different, but size- and shape-congruent linkers, by introducing a linker with N-H replaced by C-H in 50% of the sites to eliminate “step S.”

Not only the structures but also the energies are important, as revealed by quantum chemistry and thermodynamics. This method has implications for other devices that use water phase transformations. Air conditioning, for example, accounts for nearly 20% of the electricity used in buildings around the world (5). MOF-based water-adsorption-driven chillers could potentially improve the efficiency (6, 7).

Other applications are removal of trace amounts of water from natural gas or from organic solvents. Again, a lower heat of desorption makes the regeneration less energy demanding compared to commercial zeolites (8). The relative humidity for a healthy environment falls between 45 and 65%, and a different type of MOF may be designed for such uses (9, 10). Another idea is adsorption desalination to make potable water (11).

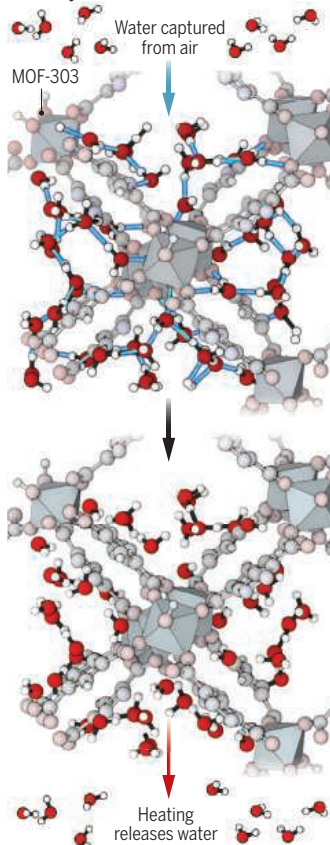
The detailed structures of the sorbed waters increase the possibilities of designing specific MOFs. However, knowing the structure alone is only a part of the puzzle. Determining the mass and heat transfer is also important for improving MOFs for applications, and these are less obvious properties to derive directly from the structure. ■

## REFERENCES AND NOTES

1. N. Hanikel *et al.*, *Science* **374**, 454 (2021).
2. U. N. Water, Summary Progress Update 2021: SDG 6, United Nations (2021).
3. M. M. Mekonnen, A. Y. Hoekstra, *Sci. Adv.* **2**, e1500323 (2016).
4. L. Öhrström, F. M. Amombo Noa, *Metal-Organic Frameworks* (American Chemical Society, 2021).
5. IEA, “The future of cooling,” Paris (2018); [www.iea.org/reports/the-future-of-cooling](http://www.iea.org/reports/the-future-of-cooling).
6. S. Cui *et al.*, *Sci. Rep.* **8**, 15284 (2018).
7. K. H. Cho *et al.*, *Nat. Commun.* **11**, 5112 (2020).
8. X. Liu, X. Wang, F. Kapteijn, *Chem. Rev.* **120**, 8303 (2020).
9. R. G. AbdulHalim *et al.*, *J. Am. Chem. Soc.* **139**, 10715 (2017).
10. P. K. Tsobnang *et al.*, *Cryst. Growth Des.* **19**, 2869 (2019).
11. E. Elsayed, R. Al-Dadah, S. Mahmoud, P. Anderson, A. Elsayed, *Desalination* **475**, 114170 (2020).

## Catch and release

The molecular evolution of the water capture in metal-organic framework (MOF)-303 was determined on an atomic level using single-crystal diffraction. After molecular fine-tuning of the cavities was carried out, a material that more easily desorbs water was created.



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