

And for MOFs' Next Trick: Pulling Water out of Thin Air

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Record-breaking water adsorption in metal–organic frameworks may help pave the way to the energy efficient harvesting of fresh water from air and the development of new systems for heating and cooling.

A team led by Mircea Dincă at MIT recently revealed in *ACS Central Science* that one approach to supplying fresh water to some of the most parched regions of the globe could be achieved through the design of new porous materials that are capable of adsorbing water vapor from air.¹ This work is highly important as limited access to clean, potable water plagues nearly 11% of the global population² and, as a result, is considered to be one of the world's leading causes of death. With continued climate change, this problem is expected to escalate: a recent United Nations report projects that the world could face a 40% water deficit in as little as 15 years.³ While a problem of this scale requires a multilevel approach, the development of new materials capable of adsorbing and/or purifying large quantities of water are imperative for environmental, human, and economic well-being.

The materials of choice developed by Dincă et al., known as metal–organic frameworks (MOFs), are expected to pave the way to the development of adsorbent-based atmospheric water generators (AWGs), a technology that is anticipated to be more energetically efficient than existing water delivery systems, such as distillation and air chillers. The main idea of the work is to take advantage of natural temperature and humidity swing processes to deliver this precious life sustaining resource to global desert regions. In this work, the MOF, known as CoCl_2BTDD (Figure 1), can adsorb large quantities of water vapor at night ($\sim 25^\circ\text{C}$ and at a relative humidity greater than 28%) and subsequently desorb the water during the warm part of the day ($\sim 45^\circ\text{C}$ and at a relative humidity less than 28%). While the idea of adsorption-based AWGs is not a new one, the material developed by MIT currently holds the record for adsorption

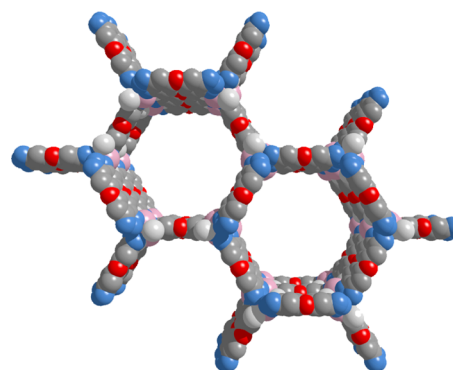


Figure 1. Structure of $\text{Co}_2\text{Cl}_2\text{BTDD}$ projected along the c -axis where pink, blue, gray, white, and red spheres represent Co, N, C, Cl, and O, respectively. BTDD represents the organic ligand, bis(1*H*-1,2,3-triazolo[4,5-*b*],[4',5'-*i*])dibenzo[1,4]dioxin).

in the pressure regime of interest for water capture from air (10 to 30% relative humidity). With a working capacity of 0.82 g of water per gram of adsorbent,¹ a value that is remarkably two times better than the current state of the art,⁴ only 1.2 kg of this MOF could deliver of as much as 1 L of water per cycle.¹ Only days before the report of Dincă et al., Wang and co-workers published a report in *Science* focused on the development of an AWG prototype using a MOF-based adsorbent; while the chosen MOF is one of the best performing materials in the field, it offers a deliverable capacity that is 4 times less than the one described here.⁵

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Despite that water adsorption in CoCl_2BTDD occurs on the upper end of the desired pressure range for AWGs, at 28% relative humidity—a limitation for some regions with consistently low humidity levels—this material still functions at significantly lower relative humidity values than

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most current AWGs. Further, the modular features of MOF structures (tunable pore shape/size and surface functionality) can be used to optimize a material's performance toward controlled capture and release and under a variety of application relevant conditions. Such flexibility sets MOFs apart from other classes of porous adsorbents. As an example, the team shows, by engineering the building blocks in the appropriate size regime, that a MOF with a ~ 2 nm pore size inhibits irreversible capillary condensation that otherwise significantly limits the material's deliverable capacity. Further, using pyrazolate struts renders CoCl_2BTDD more hydrolytically stable than many other carboxylate-containing MOFs, a feature necessary for long-term use.

When compared to benchmark adsorbents, MOFs have reportedly higher thermodynamic efficiencies and record-breaking volumetric water adsorption capacities, implying that these materials can also help address other environmental issues through the development of adsorption driven heat pumps (AHPs).⁶ Currently the building sector alone consumes 20.1% of the global energy demand, most of which involves heating and cooling residential and commercial structures.⁷ With continued climate change and as developing countries around the world adopt air conditioning, it is projected that worldwide power consumption for cooling could increase by a factor of 50 by 2100.⁸ In this work, Dinca et al. demonstrate that the high gravimetric capacity of CoCl_2BTDD helps minimize the amount of energy required for regeneration and hence produces an optimized cold energy output relative to other water adsorbents. The cooling capacity of this material is on the order of 400 kWh/m^3 , a value that is over 10% higher than that of any other known material.

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Despite the promising nature of the work, there are some future considerations that should be taken with regard to AHGs and AWGs. For instance, studies that assess the level of purity of the water produced and whether it is truly

consumable are still required. Further, considering that both aforementioned applications will require large quantities of MOFs, on the kilogram scale, it is necessary to have a thorough cost assessment of materials involved, particularly those incorporating expensive metals, such as cobalt. Last, the material should be proven stable over hundreds or even thousands of cycles and under variable environmental conditions. Despite this, the study is a nice demonstration of the strong potential impact that metal–organic frameworks can have in an impending global water shortage and gives critical insight into the structural features necessary to promote reversible adsorption of large quantities of water. This study and others consistently demonstrate the bright future that MOFs may have in various environmentally relevant applications. Their rich host–guest chemistry combined with the competitive nature of the field is quickly bringing these materials to the cusp of industry.

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REFERENCES

- (1) Rieth, A. J.; Yang, S.; Wang, E. N.; Dinca, M. Record Atmospheric Fresh Water Capture and Heat Transfer with a Material Operating at the Water Uptake Reversibility Limit. *ACS Cent. Sci.* **2017**, DOI: [10.1021/acscentsci.7b00186](https://doi.org/10.1021/acscentsci.7b00186).
- (2) World Health Organization and UNICEF Joint Monitoring Programme (JMP). *Progress on Drinking Water and Sanitation—2015 Update and MDG Assessment*; UNICEF and World Health Organization: 2015.
- (3) *The United Nations World Water Development Report 2015: Water for a Sustainable World*; UNESCO: Paris, 2015. <http://unesdoc.unesco.org/images/0023/002318/231823E.pdf>.
- (4) Furukawa, H.; Gándara, F.; Zhang, Y. B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Pore Metal–Organic Frameworks and Related Materials. *J. Am. Chem. Soc.* **2014**, *136*, 4369–4381.
- (5) Kim, H.; Yang, S.; Rao, S. R.; Narayanan, S.; Kapustin, E. A.; Furukawa, H.; Umans, A. S.; Yaghi, O. M.; Wang, E. N. Water harvesting from air with metal–organic frameworks powered by natural sunlight. *Science* **2017**, *356*, 430.
- (6) De Lange, M. F.; Verouden, K. J. F. M.; Vlugt, T. J. H.; Gascon, J.; Kapteijn, F. Adsorption-Driven Heat Pumps: The Potential of Metal–Organic Frameworks. *Chem. Rev.* **2015**, *115*, 12205–12250.
- (7) U.S. Energy Information Administration (EIA). *International Energy Outlook 2016*; 2016.
- (8) Sivak, M. Will AC Put a Chill on the Global Energy Supply? *Am. Sci.* **2013**, *100*, 330.