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Metal–Organic Frameworks for Water Harvesting from Air, Anywhere, Anytime

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Authors

Xu, Wentao
Yaghi, Omar M

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Outlook

Metal–Organic Frameworks for Water Harvesting from Air, Anywhere, Anytime

Wentao Xu and Omar M. Yaghi*

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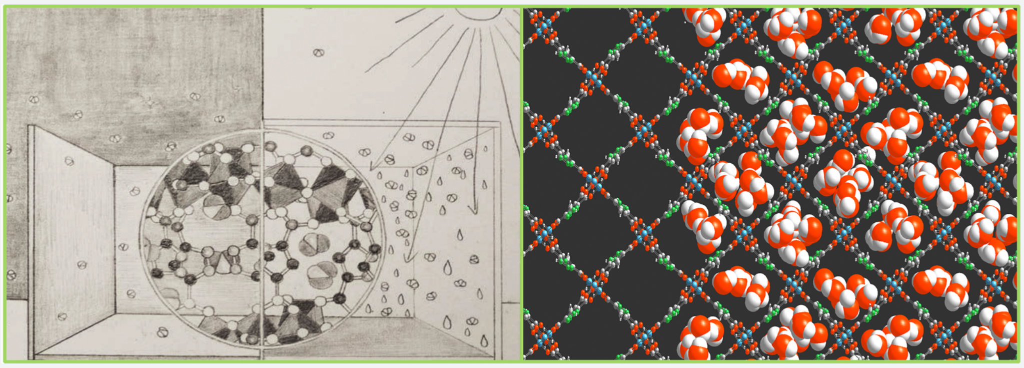

ABSTRACT: Water is essential to life. It is estimated that by 2050 nearly half of the world population will live in water stressed regions, due to either arid conditions or lack of access to clean water. This Outlook, written for the general readers, outlines the parameters of this vexing societal problem and presents a solution to the global water challenge. There is plenty of water in the air that potentially can be harvested not only from the desert atmosphere where the humidity is low but also from more humid regions of the world where clean water is needed. In principle, the materials used to harvest water from air in these climates should be applicable to deployment anywhere in the world to extract atmospheric water at any time of the year. Metal–organic frameworks (MOFs) have emerged as a unique class of porous materials capable of trapping water at relative humidity levels as low as 10%, and doing so with facile uptake and release kinetics. From laboratory testing to field trials in the driest deserts, kilogram quantities of MOFs have been tested in several generations of devices. The initial results of these experiments showed that MOFs could capture water from desert climates and deliver over one liter per kilogram of MOF per day. More than an order of magnitude increase in water productivity could be achieved with members of the MOF family when employed in an electrified device operating at many cycles per day. We show that the vision of having clean water from air anywhere in the world at any time of the year is potentially realizable with MOFs and so is the idea of giving "water independence" to the citizens of the world.

INTRODUCTION

Water is the molecule separating life and death, yet more than half of the world will experience a shortage of this important substance by the year 2050.[1] In the desert regions, water is scarce because of lack of rain, and in those more watered regions, either the lack of clean drinking water or the nagging sense of uncertainty about its purity continue to be a challenge. Additional factors exacerbating this "global water challenge" are the diminishing underground water resources in agricultural regions of the world, security issues related to the fact that 160 countries are importing their water, increasing salinity of large bodies of water next to desalination plants, and the environmental impact on weather patterns due to continued burning of fossil fuels. There is also of course the rising demand for clean water because of the increasing world population, and the adverse health implications on societies where clean water is not widely available. Fortunately, there is a potential solution: namely, the extraction of water from the atmosphere where, at any one time, there is much more water than in all the rivers on our planet. In principle, if we can directly harvest water from air efficiently, anywhere in the world and at any time of the day, month, or year, it should be possible to provide humanity with an additional supply of clean water and help solve the global water challenge. However, the concentration of water in the air is low (ca. 0–30 g per cubic meter, Figure 1), and therefore, finding a way to trap this water

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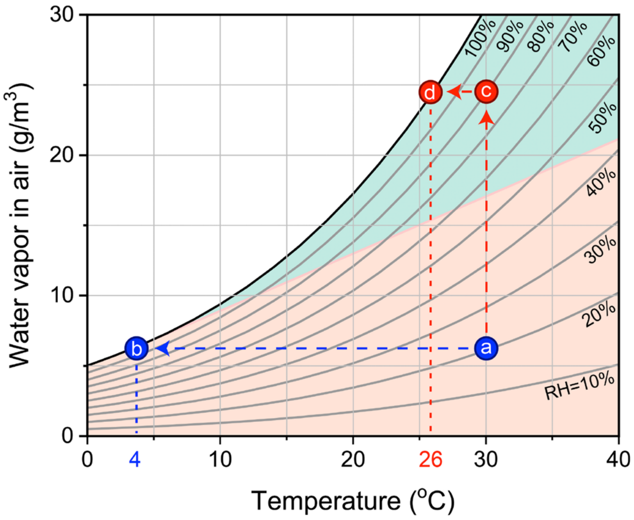

Figure 1. Modified psychrometric chart illustrating how air of low relative humidity, RH (a), must be cooled to low temperature (b) to be saturated with water (i.e., dew point), while at high RH (c) such cooling is minimal (d). The use of MOFs essentially takes low RH air (a) and makes it high RH (c) and thus saturates desert air with water more efficiently than direct cooling. The green region is where direct cooling may be used to generate water from air, but not in the pink region where MOFs are ideally suited to turn desert air of lower levels of moisture into "tropical air". Such MOFs also work in the green region.

in an energy efficient manner is challenging: that is, until the recent discoveries and developments in the field of reticular chemistry[2] (defined as linking molecular building units by strong bonds into crystalline extended structures) and the impact they have made on this important problem, as we will discuss in this contribution.

The principal difficulty in harvesting water from air is that, in the arid regions of the world, where more than a billion people live, there is little moisture in the atmosphere (typically <50% relative humidity, RH, pink region of Figure 1), and therefore, the dew point (the temperature required to saturated the air with water) is very low. For example, moisture in the air of a city experiencing a 20% RH at 30 °C has a dew point of around 4 °C (Figure 1a→b), which means that the air temperature must be cooled down to this low temperature in order to turn water moisture into liquid. This makes harvesting water by direct cooling of desert air energy intensive and impractical. In contrast, at 80% RH and 30 °C the dew point is 26 °C, making it easier and requiring much less energy to condense water in humid climates (Figure 1c→d). Thus, in order to solve the problem of harvesting water from lower-moisture air, a method must be found that is not reliant on direct cooling to extract water from air. We note that a material designed to take up water at low humidity (pink, Figure 1) will also work at higher humidity (green, Figure 1), but that the opposite is not true. Indeed, if the difficult problem of trapping water under arid conditions is solved, these same materials will also operate in regions of higher humidity, thereby realizing the vision of harvesting water from air anywhere, anytime.

The use of a porous material capable of trapping water from the desert air could have the effect of increasing the humidity level in a closed system and therefore allowing for a much higher dew point as illustrated by going from a → c → d of Figure 1. In this way, one can "bring the tropics to the desert" by using such a material to humidify an otherwise dry desert air. The potential here is great for harvesting water provided that the adsorbed water in the pores of the material can be removed without applying too much heat so that the process becomes inefficient and uneconomical. However, finding a porous material that is capable of capturing water at low RH and releasing it under practical conditions has been a major quest over the many years of trying to achieve this vision for dry or humid air.

In this contribution, we outline how metal−organic frameworks (MOFs), porous crystalline solids resulting from reticular chemistry,[2−4] have emerged at the forefront of chemical structures for harvesting water from the desert air and indeed any air,[5−11] at any time of the year, anywhere in the world. We describe the basic science discovery that water can be taken up at low RH by MOFs, the mechanism of how MOFs carry out this process, and how this discovery led to the design of devices and their testing in the desert. Through several desert field experiments, these MOF devices were demonstrated to harvest significant amounts of water and have shown that reticular chemistry is poised to solve the vexing water problem.

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We show that, since our discovery of water harvesting by MOFs and the development of the MOF water harvester devices, we have succeeded in increasing the water production (per unit weight of MOF) several orders of magnitude in the span of less than five years. Based on these results, we put forward the proposition of "water independence" for allowing individuals worldwide to make clean water independently of the water grid and also have the ability to personalize it to their needs, be it for drinking, household, agriculture, or industrial use. This Outlook is largely intended for general readers as more technical reviews have already been published.[8,11] It is focused on our experience in taking MOF water harvesting from a laboratory discovery to field demonstrations of working devices—aspects unique to our efforts.

■ SYSTEMS AND MATERIALS FOR HARVESTING WATER FROM AIR

The idea of harvesting water from air has been around since time immemorial. Almost all the materials and technologies explored, developed, and commercialized along these lines work at more humid conditions (green, Figure 1). These commercial systems are based on the principles of direct cooling of air using the condensation cycle. Despite their claims in the advertising literature, they do not work at lower RH (pink, Figure 1) because of the dew point issue stated above. Attempts to develop materials intended to work at low RH involved using simple inorganic salts, zeolites, porous silica, or other such matrices.[12−15] All these suffer greatly from either having slow kinetics of uptake and release cycles (and therefore it takes a long time to carry out the water harvesting cycle), low water uptake capacity at low RH, or high water adsorption energy. The earlier two are detrimental to water productivity, and the latter requires extensive energy to remove the adsorbed water, casting doubt over the practical use of such materials for harvesting water from air.

In 2014, while studying MOFs for the separation of carbon dioxide from flue gas, where water is present in appreciable amounts, we were also examining the uptake of water into the interior of those MOFs to understand the dichotomy in behavior of these two molecules within the pores. We discovered that certain members of the MOF family exhibited unprecedented water uptake and release properties.[5] Specifically, a series of porous, crystalline zirconium MOFs made from $Zr_6O_4(OH)_4(-CO_2)_n$ (n = 6, 8, 10, or 12) secondary building units (SBUs) and carboxylate organic linkers were investigated. A member of the series, MOF-841 $[Zr_6O_4(OH)_4(\text{methane-tribenzoate})_2(\text{formate})_4(H_2O)_2]$, showed the highest water uptake capacity (Figure 2), which was maintained over at least 80 adsorption−desorption cycles.[5] More significantly, this MOF exhibited a water uptake step-shaped isotherm at 25 °C, indicative of a cooperative mechanism for water binding into the pores. The discovery was that this step uptake occurred at around 20% RH and that the release of water can be effected at only 45 °C. This meant that perhaps such a MOF can be deployed in the desert where it can trap water from the atmosphere at night and release it during the day upon exposure to ambient sunlight, which may very well be at around the desorption temperature observed in the isotherm measurements. If successful in taking the experiment outside the laboratory, it would demonstrate (*vide infra*) for the first time that a material could harvest water from the desert air without energy input aside from ambient sunlight.

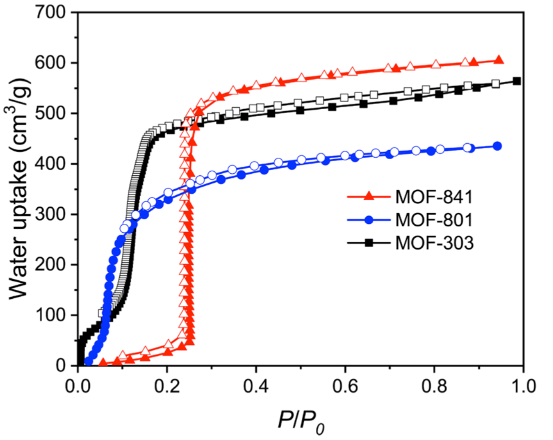

Figure 2. Water adsorption isotherms of three MOFs for capturing water from air of low RH. MOF-801 and MOF-303 have been used in kilogram quantities to build MOF water harvesters demonstrated to deliver water in the desert. Uptake and release of water are indicated in solid and open shapes, respectively.

WATER HARVESTING MECHANISM AND OBSERVATION OF “SEEDS” IN MOF PORES

We observed a similar water isotherm profile in other zirconium MOFs, most distinctly, that of MOF-801 $[Zr_6O_4(OH)_4(\text{fumarate})_6]$, where we found the step uptake behavior at 10% RH, much lower than that of MOF-841 (Figure 2).[5] Since MOF-801 showed a spectacular binding of water at such a low RH, we studied its crystal structure by X-ray and neutron diffraction techniques to determine the location of water molecules in the pores.

There are two different kinds of micropores in the structure of MOF-801 that have the shapes of tetrahedra and octahedra. Fortunately, we were able to dose the crystals with small amounts of water and characterize their location and geometry in the pores. We observed in those pores the formation of tetrahedrally and cubically arranged water aggregates, respectively, each held together by hydrogen bonds.[5] These aggregates were found to be bound to the zirconium SBU with water interacting with the −OH and carboxyl units of the SBU. We considered these to be seeds onto which additional water molecules are attracted to further aggregate in the pores. This followed a cooperative mechanism as the step isotherm behavior indicated. Indeed, the step behavior observed in the isotherm is potentially attributable to the enhancement of water binding, being driven by the formation of these seeds. The fact that the pores are made from polar SBUs and nonpolar organic linkers provided a means of lowering the water binding energy (strength) to the pores and thus allowed for the release of water under mild conditions.

> This [water harvesting] followed a cooperative mechanism as the step isotherm behavior indicated.

PROOF-OF-CONCEPT WATER CAPTURE DEVICE

Equipped with the idea of harvesting water from the desert air and the probable seeding effects of water uptake as well as the step isotherm profile at very low RH, we and collaborators designed a proof-of-concept device. The objective was to show that the MOF can trap water from low-RH air outside the laboratory setting and ultimately make liquid water.[6,16] The device was quite simple in that it can be likened to a glass “jar” with a lid containing the MOF (Figure 3a). It worked by exposing the MOF to the atmosphere to be saturated with water, and upon closing the device and exposing it to ambient

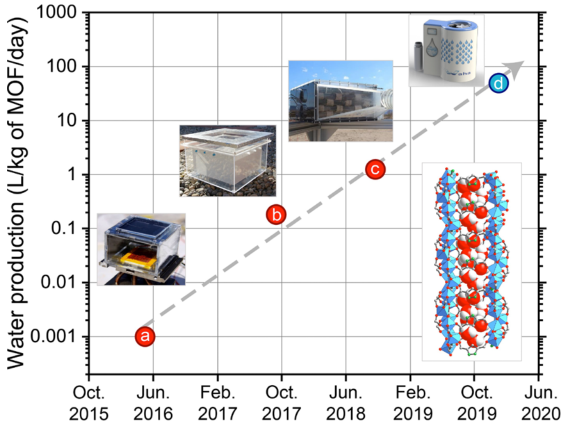

Figure 3. Progression from a (a) proof-of-concept to (b) first generation, (c) second generation, and to (d) near commercialization device for water harvesting from air including the advances in water production levels based on MOF-801 (a, b) and MOF-303 in the inset (c, d). MOF-303 is shown with rod SBUs in blue polyhedra for aluminum and small red spheres for oxygen, and with the pores filled with water shown in space-filling style.

sunlight, water is released from the MOF and condensed. The device was tested on the roof of a building under conditions of <20% RH and 25 °C using only 2 g of MOF-801. Working as expected, droplets of water were observed to form on a cooled surface in the interior of the device. This setup was successfully tested in the Arizona desert.[7] It was a proof-of-concept device, and although water droplets were observed, no water was actually collected from it.

[At this juncture, O.M.Y. wishes to take the liberty to comment that we were all excited by these results, and no one was more so than him. As a child growing up in one of the most water stressed regions of the world (Amman, Jordan), he had firsthand experience with water shortages. Water from the municipality usually came once every week, or sometimes every 2 weeks, for only up to 6 h, during which time the storage water tanks in his house had to be filled. Sometimes this water was sufficient for his family's, needs and other times it was not, especially on hot days when the garden and livestock animals added to the watering load of the household. The discovery of water harvesting MOFs and the feasibility of harvesting water from air (especially from the desert air) were tantalizing to him for what he could see in the potential in addressing one of the most pressing problems of our day.]

FIRST GENERATION MOF WATER HARVESTER

Motivated by these results, we built a device equipped with kilogram quantities of MOF-801 in the hope of collecting drinking water from air in the desert. Our design of the MOF water harvester was composed of two boxes fitting within each other (Figure 3b).[9] The inner box is open and holds the MOF powder, and the outer box has a lid. The lid is open at night to expose the MOF to air and to allow water from the air to fill the pores of the MOF, and then, it is closed during the day when the water harvester device is exposed to sunlight. This device was tested in the Arizona desert (33°N, 111°W) where initially we observed as expected the uptake of water into the MOF and its release into the outer box. However, to our surprise, initially we observed that no condensation was taking place on the inside walls of the outer box. This was addressed by covering part of the device with soil to create a sufficient temperature differential between the interior and exterior of the outer box, thereby successfully condensing the released water. The experiment was concluded after 7.5 h, and the liquid water was collected. This device delivered 200−300 mL of water per kilogram of MOF per day at 5−40% RH and 20−40 °C, with the temperature rising inside the closed device to almost 80 °C. This result is powerful in that it constituted the first device in the history of humanity to deliver drinkable amounts of water from the desert air and to do so using nothing more complicated than two plexiglass boxes and no energy input aside from ambient sunlight. The key is the MOF structure and its ability to trap water from low humidity and to readily release it at relatively mild temperatures, properties unmet by any other class of materials.

> It [MOF harvester] constituted the first device in the history of humanity to deliver drinkable amounts of water from the desert air.

The Arizona desert experiment was also fruitful in identifying the parameters (e.g., air flow and heat, mass transfer) we needed to further optimize the efficiency of the MOF and for building a highly productive device. We found that the bed form of the MOF employed in the device was not ideal because it did not allow maximum exposure of the MOF to air. Therefore, most of the MOF was inaccessible to air in the water uptake experiments and consequently giving lower than expected water productivity. In addition, the low heat conductivity of MOF led to slower kinetics for release of water relative to what we expected from the very open structure of the MOF. Nevertheless, it was remarkable that significant amounts of water could be harvested under arid conditions, and that the water harvested was found to be ultrapure, showing no detectable amounts of metals, organics, or air impurities.[9] It is worth noting that the MOF itself is a natural filter in that it only stores water into its pores. The fact that water binds to the pores stronger than any possible air contaminants, such as carbon dioxide or even hydrocarbons, makes it an effective competitor for occupying the adsorptive sites within the porous structure of the MOF.

RAPID CYCLING IN SECOND GENERATION MOF WATER HARVESTER

The stage was set for propelling the MOF water harvester project to the next level. This was greatly aided by the discovery of MOF-303 [Al(OH)(1*H*-pyrazole-3,5-dicarboxylate)], a porous, crystalline structure (Figure 3, inset).[9,10] It is composed of rod SBUs linked by organic units to make a 3D structure supporting a 1D pore system. We showed that this MOF is capable of taking up water at very low RH (Figure 2) and also exhibiting adsorption−desorption cycles each on the scale of minutes under mild temperatures (<10 min at 85 °C). Thus, with an external power source, one is able to pull air into the MOF to harvest the water, heat the MOF to release it, and then repeat this cycle several times a day, giving significantly higher water productivity. A device was designed in which several cartridges were each loaded with 1 in. of MOF-303 powder and arranged so as to allow incoming air to pass, while simultaneously water is removed by heating (Figure 3c). This device was initially tested in our laboratory at University of California, Berkeley, and found to deliver 1.3 L water/kg of MOF/day (at 32% RH, 27 °C) and later in the Mojave Desert (east Twenty Nine Palms: 34°N, 115°W) under conditions as extreme as 10% RH and 27 °C to give 0.7−1.0 L water/kg of MOF/day.[10] This advance represents an order of magnitude improvement over our previous devices.

The main findings from our research and development of the MOF water harvesters are listed here. First, MOF structures can be designed to have the right balance between a hydrophobic and hydrophilic pore environment to allow both the capture of water from the desert air and its release with minimal energy requirements. Second, the MOFs are stable in water to hundreds of cycling experiments due to the thermal and chemical stability of their structures. Third, the MOF powder is not entirely being used in the water harvesting cycle, and accordingly the MOF harvesters still have the potential to multiply their water output, provided that the MOF material is maximally exposed to air. Fourth, the ability to design MOFs and the facility with which they can be modified coupled with our success in making MOF water harvesters can only indicate a promising future in the design of even better systems.

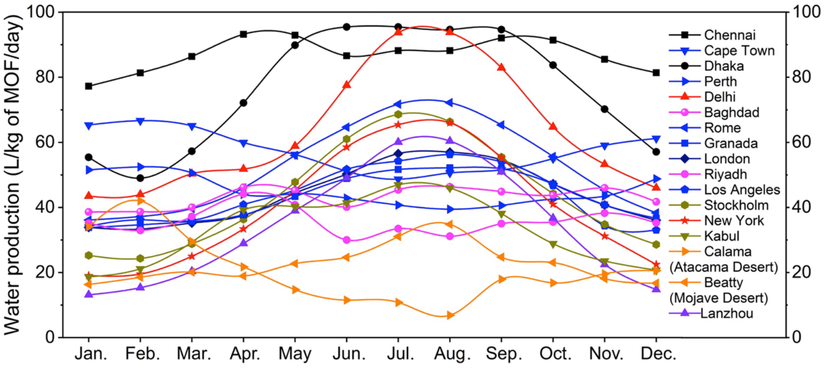

Figure 4. Productivity of MOF-303 expected in various climates around the world. Daily rates as high as 90 L of water per kilogram of MOF can be achieved in the regions where the air is rich in water (Chennai, India), while a remarkable 7−20 L of water per kilogram of MOF can be achieved in some of the driest deserts of the world (Mojave and Atacama).

Several research groups have already been propelled to design reticular structures capable of exceptional water uptake.[17−27] These materials have been screened and studied for their water uptake properties. However, as yet they have not undergone the field device testing to demonstrate their viability in harvesting water from air.

■ SCIENTIFIC PLANS FOR WATER HARVESTING

In the remainder of this contribution and to appreciate how far we could advance in the engineering of MOF water harvesters, we wish to consider further the performance of MOF-303. This MOF is composed of an inexpensive metal (aluminum). Already we have demonstrated in our laboratory its synthesis at the kilogram scale, and with BASF's ability to scale up MOFs to multiton quantities, it should not be prohibitive to make this MOF (and related ones) at scale.[28] The key features of MOF-303 are its (a) rod SBU, which make it water stable over many cycles, principally due to the hindered Al−O bonds preventing its hydrolysis, and (b) highly open structure allowing passage of water molecules freely and facilely such that it is possible to load and unload water from air within a short time. The first feature gives the MOF the ability to be cycled over hundreds and potentially even thousands of adsorption−desorption cycles, and the second allows multiple cycles to be carried out daily (especially when a power supply is available to manage the air flow and heating for water desorption).

MOF-303 uptake capacity is 40% by weight at 20−40% RH and ambient temperature, and this amount potentially can be delivered for each water harvesting cycle.[10] If one opts for the passive device design where only ambient sunlight is used with no additional power input, a construct permitting the exposure of MOF in the box within a box design (Figure 3b) should be capable of delivering 0.4 L water/kg of MOF/day. It is entirely possible to perform multiple cycles a day with this passive device provided that the temperature differential can be achieved. However, if an external power source is available, with a simple calculation taking into account the 10 min per cycle, the MOF should give about 57 L water/kg of MOF/day. To achieve this amount it is necessary to access all the MOF particles, and accordingly we should move away from using the bed MOF design. A need exists to develop a MOF formulation that would maximally expose the MOF and facilitates application and conduction of heat through the MOF. In terms of energy requirements, initial calculations taking into account the heat of adsorption of water in the MOF (ca. 50 kJ/mol) give a requirement of less than 1 kW h per liter of water produced. This energy could be dramatically reduced by using heat exchange mechanisms in the water harvesting cycle. A latest MOF water harvester running on electricity is expected to be released from Water Harvesting Inc. This model is capable of realizing a significant percent of the water harvesting capability of the MOF (Figure 3d).

■ WATER HARVESTING FROM AIR ANYWHERE, ANYTIME

We used the parameters of MOF-303 stated above to calculate the expected water production for cities with different climates around the world (Figure 4). The water production rate was calculated as a monthly average by using monthly average temperatures and RH data of the cities, which were classified according to the Köppen climate classification system.[29] It is assumed that the air flows through the MOF at a constant flow rate while a steady portion of moisture (10%) in the incoming air is taken up by the MOF. The desorption of water, which takes 150 s, is carried out once the MOF becomes saturated with water vapor.[10]

Cities with tropical savanna climate (Chennai and Dhaka) have distinct wet and dry seasons. Although the precipitation is low during the dry months (less than 60 mm), the RH and temperature are always high. As a result, the water production rates of these cities are among the highest even during the dry months. A city with humid subtropical climate (Delhi) with high RH during the year, provides a high rate of water production during the summer. However, the rate will decrease as the temperature drops during the winter.

Cities with Mediterranean climate (Cape Town, Perth, Rome, Granada, and Los Angeles) are characterized by their dry summers and humid, mild winters. The water vapor content during the summer (December to February for cities in the Southern Hemisphere) is not significantly higher than that during the winter. A city with marine west coast climate (London) also shows a similar trend of water vapor content due to its cool summer. For cities with these types of climates, the water production rate during the summer is slightly higher than that during the winter. Cities with warm summer continental climate (Kabul, Stockholm, and New York) and semiarid climate (Lanzhou) have distinct seasons and large seasonal temperature differences. The warm weather during the summer allows the water to be harvested with good efficiency. However, the water production drops dramatically and becomes unsuitable as the temperature goes below 0 °C during the winter.

The water production in desert areas is distinct based on the temperature. For cities with hot desert climate (Baghdad, Riyadh), although the RH is extremely low (14% for Riyadh in August) during the hot summer, MOF-303 will be capable of collecting water from air with a moderate rate of 30 L water/kg of MOF/day in August. The water production is relatively stable during the year and sometimes even comparable to cities with Mediterranean climate. Although, the water production is lower for cities with cold desert climates such as Calama (Atacama Desert) and Beatty (Mojave Desert), the rates during the most severe conditions of Calama (August) are remarkably 7 L water/kg of MOF/day at low RH (10%) and low temperature (13 °C) while the annual average can achieve 20 L water/kg of MOF/day.

MOF WATER HARVESTERS IN SOCIETY

It is clear from the forgoing discussion that MOFs constitute an important advance for making water harvesting from air a reality. Our success in the incorporation of MOFs in water harvesters not only takes the science beyond the laboratory but also demonstrates the power of reticular chemistry in controlling matter on the atomic, molecular, and framework levels to achieve useful properties. It is a matter of time that the engineering of these systems will catch up with the MOF design, in terms of producing setups that fully achieve the expected water productivity for the passive (ambient sunlight) and active (electrified) harvesters. It will be necessary to balance the air flow, thermal conduction, and mass transport to obtain optimal water productivity promised in Figure 4.

Plans are currently underway to engineer MOF water harvesters using progressively larger amounts of MOF and correspondingly higher amounts of water produced: for consumers (4−5 L water/day), household (500 L water/day), and the so-called village scale (20 000 L/day). We note that for such systems the engineering aspects are extremely important and require further development. The lower thermal conductivity of MOF solids makes scaling up the water productivity by direct stacking of the MOF bed more challenging, calling for new engineering designs of MOF formulation. Long-term studies will be needed to assess the possibility of bioaccumulation for devices with high water productivity. Nevertheless, as these studies are ongoing, it is useful to keep in mind that the MOF has the potential to remain in the water harvester for the lifetime of the device, and therefore, it will not have any specific maintenance requirements. In essence, the MOF works well for harvesting water; the remainder relies on progress in device engineering.

To be able to see the potential of this technology in society, it is imperative that the correct comparisons be made. We discourage comparing water harvesting technologies with water desalination and other infrastructure-based water industries. The idea of MOF water harvesting is not to compete or replace these more established technologies, especially in the foreseeable future. However, the MOF water harvesters have the potential of changing our way of thinking about water use. The vision is to realize for water what was achieved with the telephone, and how we have in a short time moved from the wired to the wireless telephone. With the MOF water harvesters, we have the potential not only to provide clean water in any climate at any time of the year but also to make the water supply distributed and mobile. This mobility provides independence on a personal level and control of the individual's own water supply. Since the water harvested is clean, with mineralization it can be used for drinking, and without mineralization (as harvested) it can be used for agriculture and other societal endeavors not the least of which for resiliency planning and sustainable urban development.

We believe that the water harvesting productivity expected from these systems is one which begins to meet the current water stress facing the world. It will alleviate water issues related to national security, purity, and accessibility. In the fullness of time, MOF water harvesters will serve as an instrument to make water a human right available to everyone living in urban or rural areas as well as remote locations of the world. Accordingly, as this becomes a societal reality, so will the idea of water independence.

> MOF water harvesters will serve as an instrument to make water a human right available to everyone.

AUTHOR INFORMATION

Corresponding Author

Omar M. Yaghi − *Department of Chemistry, University of California—Berkeley, and Kavli Energy NanoSciences Institute, Berkeley, California 94720, United States; UC Berkeley−KACST Joint Center of Excellence for Nanomaterials for Clean Energy Applications, KACST, Riyadh 11442, Saudi Arabia;* orcid.org/0000-0002-5611-3325; Email: yaghi@berkeley.edu

Author

Wentao Xu − *Department of Chemistry, University of California—Berkeley, and Kavli Energy NanoSciences Institute, Berkeley, California 94720, United States;* orcid.org/0000-0002-9772-1036

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c00678

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): O.M.Y. is a co-founder of Water Harvesting Inc., a company in Silicon Valley, California, aiming to commercialize the MOF water harvesters.

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