

## Envisioning the “Air Economy” — Powered by Reticular Chemistry and Sunlight for Clean Air, Clean Energy, and Clean Water\*

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Addressing the three major stresses facing our planet, clean air, clean energy, and clean water, is within our reach. At present, new materials such as metal-organic frameworks and covalent organic frameworks, produced by reticular chemistry, are at the forefront of efforts to capture carbon dioxide from air and harvest water from air. We envision that the products of these two capture processes (carbon dioxide and water) can be fed into a conversion cycle in which they are used to produce fuels and chemicals via artificial photosynthesis. The use of air as a nonpolluting, cyclable, and sustainable resource for carbon and water can be powered by sunlight. We describe how the scientific basis for realizing this vision is either already achieved or being established, and that in the fullness of time this paradigm may lead to new global industries and a thriving “air economy.”

**Keywords:** Clean air; carbon dioxide capture; clean energy; water harvesting; metal-organic frameworks; artificial photosynthesis; reticular chemistry.

### EMERGENCE OF THE AIR ECONOMY

Our planet is facing difficult problems relating to clean air, clean energy, and clean water. Unlike any other time, the present focus on capturing carbon dioxide from air and point sources (e.g., power plants) is gaining momentum and resources, and bringing more attention to issues of energy and water for a sustainable future. Clearly, if we can capture carbon dioxide and convert it to fuels, the possibility of having a clean energy cycle becomes real. Access to clean water from air to both supply the needs of the clean energy cycle and provide potable water will help address the ever-increasing need of almost two billion people worldwide living in water-stressed regions. In this contribution, we envision that through reticular chemistry, carbon dioxide and water can be extracted from air to generate clean air and water, and that by combining these technologies with artificial photosynthesis, the captured carbon dioxide can be converted to clean

fuels and chemicals, with all these processes being powered by sunlight. We expect these new materials and processes to form the scientific and technological underpinning of what we call the “air economy.” Significant economic gains can be made by honing in on the benefits of capturing the constituents of air and using them to meet some of the United Nations sustainability goals<sup>1</sup>. Although separating nitrogen, oxygen, and noble gases from air is already a thriving industry, capturing carbon dioxide from air and converting it to fuels, and harvesting water from air have the potential to generate industries and economies with far-reaching positive impact on our society and planet.

What is needed in order to harness this great potential that air provides and address the problems of clean air, energy, and water? First and foremost, it requires new materials capable of trapping carbon dioxide at 400-ppm levels, a nontrivial task for this low (but harmful) concentration;

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furthermore, this process requires selective removal of carbon dioxide from a host of other gases present in air (e.g., nitrogen, oxygen, and water). Thus, materials designed to “pluck out” carbon dioxide from these gases would be required. Second, a process for converting the captured carbon dioxide to fuels (and/or other useful chemical products) will be needed. This also requires materials and chemistry as yet to be fully established, although as we present in the following, artificial photosynthesis is playing a vital role in converting carbon dioxide to fuels and valuable chemicals.

Also needed are materials capable of seeking and trapping water from air where its concentration is only 10 g per cubic meter of air, as it is in almost one-third of the world for most of the year. The captured water can also be used to help supply the biotechnology component. Practical implementation of this vision calls for an integrated system encompassing renewable power, the capture ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ), and conversion processes operating in a closed cycle. These are fantastic chemistry, biology, and engineering challenges demanding new advances in science and engineering. However, there is preliminary evidence that the components of the proposed closed cycle are already feasible. Achieving their successful integration, with energy efficiency and at scale, will lay the scientific and technological foundation for the air economy.

## 21ST CENTURY CHEMISTRY AND MATERIALS

**A historical perspective.** Historically, the advancement of civilizations tracked closely with innovations in materials. The materials that transformed the world and formed the basis of our current global economy such as wood, cement, glass, steel, alloys, aluminum, silicon, petroleum, plastics, woven cloth, and paper will not be sufficient to solve the new challenges. While each of these substances will continue to play an important role in society, new kinds of materials will be needed to address the challenges we face in energy, environment, sustainability, and health. Whoever can foresee the future of materials and realize new and useful compositions will not only improve our planet, create new wealth, and build new economies but also transform the standards of living for people worldwide. Thus, what are the materials of the future?

The 20th century was the age of the molecule where we witnessed the emergence of atom-by-atom synthesis of molecules and development of tools to examine matter at the atomic and molecular levels. Clearly, our masterful manipulation of molecules has transformed chemistry and biology with tremendous implications on materials (polymers) and health (pharmaceuticals). We believe that there is a foundational shift taking place today pertaining to understanding how molecules interact with each other to make larger systems spanning the angstrom to the macroscale. In these systems, molecules are linked by *strong chemical bonds*, which yield

robust materials capable of fully harnessing the power of the molecule. This is now an emerging field of science called reticular chemistry<sup>2</sup>.

Reticular chemistry is concerned with linking molecular building blocks by strong bonds into crystalline extended structures. There are three unique features highlighted in this definition: first, molecular building blocks are used to allow for making materials by design; second, the strong bonds impart thermal and chemical robustness to the materials produced such that they can operate for years in an industrial setting without being replaced; and third, the crystallinity provides means of characterizing the resulting materials on the atomic and molecular scales. These aspects lead to opportunities for understanding materials properties and open the way for pinpoint modifications to be made on reticular structures. Prior to reticular chemistry, these qualities were not achieved together by any other class of materials. This advance has contributed greatly to the current exponential growth witnessed in reticular chemistry<sup>3</sup>.

Unlike any other time in history, reticular chemistry is making available extensive classes of materials (e.g., metal-organic frameworks (MOFs) and covalent organic frameworks (COFs)) with implications on a kaleidoscope of societal priorities including clean air, clean energy, and clean water. In essence, this new field is combining Nature’s matter, minerals, and organics into an infinite number of chemical structures and materials, giving rise to a vast number of potential applications. Today, research for reticular structures and materials is being carried out in academia, industry, and government laboratories in over 100 countries. If the 20th century was the age of the molecule, the 21st century is emerging as the age of reticulating the molecule. Given the flexibility with which reticular structures can be varied and designed, it is not unreasonable to also expect new breakthroughs in combining this chemistry with biotechnology (*vide infra*) to solve the air, energy, and water challenges and realize the air economy.

In the following sections, we provide our perspective on (1) the features of reticular structures that make them especially appealing for the development of the air economy, (2) the specific scientific challenges for carbon capture and conversion, and harvesting water from air, and (3) the vision of an integrated system capable of producing fuels and chemicals from air.

**Vast Composition and Structure Space.** MOFs and COFs are typical reticular structures. In MOFs, transition metal ions are linked by anionic organic linkers (e.g., carboxylates) to make crystalline, porous, extended structures<sup>4–8</sup>. The carboxylates form strong bonding interactions with the metal ions and, due to their chelating ability, lock the metal ions into position through the formation of multimetallic secondary building blocks (SBUs). These SBUs are, therefore, rigid and directional, making them ideal building units to target

specific structures for synthesis. Since the first crystallization of carboxylate MOFs in 1995<sup>4</sup>, the strong bond, SBU approach led to MOFs with architectural, thermal, and chemical stability, permanent porosity, and ultra-high surface areas<sup>5,6</sup>. These features play a decisive role in the utility of MOFs for air economy applications. In contrast, COFs are constructed from organic building units linked by strong covalent bonds to give crystalline, porous, extended structures. COFs are entirely organic and their backbone is composed of covalent linkages between light elements (B, C, N, O, P, S). Both MOFs and COFs (commonly referred to as reticular structures) have structures extending “infinitely” into 2D and 3D<sup>7,8</sup>. Today, there are over 100,000 MOFs and 500 COF structures known.

However, far higher multiplicity and diversity is possible and available not just through variation of the building unit's geometry and composition but also via the attachment of organic functional groups on the backbone of these frameworks. It is also possible to make MOFs containing many different metal ions in one structure, and COFs to whose organic backbone metal complexes may be covalently attached. Thus, a wide range of compositional variations is possible and can be applied to precisely fashion the pores of reticular structures for specific binding of carbon dioxide or water. Metric variations through the isoreticular approach whereby the pore diameter in reticular structures can be varied incrementally and within a fraction of an ångström from 5 Å to 100 Å have already been reported<sup>9,10</sup>. In other words, if one can imagine a structure, one is able to find ways of making it using reticular chemistry. This aspect has led to proliferation of reticular structures and their applications, thereby creating what can be effectively described as infinite chemistry, materials, and applications. The control with which such structures can be synthesized and modified bodes well for realizing the air economy through carbon capture from air and conversion to clean fuels, and water harvesting from air to access drinking water.

**Crystallinity and ultra-high porosity of reticular structures.** Single crystal X-ray diffraction remains the most definitive technique for characterizing reticular structures. The reaction conditions originally established for MOFs in 1995<sup>4</sup> 1998<sup>5</sup> and 1999<sup>6</sup> are still in use today and carboxylate MOFs remain the overwhelming majority of porous metal-organic structures being studied. These reaction conditions were also determined for the crystallization of 2D and 3D COFs in 2005 and 2007, respectively<sup>7,8</sup>. The ability to overcome the “crystallization challenge” by modulating the kinetics (fast enough to make sufficiently large crystals but not too fast as to prevent error correction during the crystallization process) and thermodynamics (microscopic reversibility of linkages) of crystal formation opened up this area to become what we know today. The crystallinity of reticular structure ensures the full characterization of their atomic connectivity and significantly endows

these structures with homogenous pores and composition across the entire crystal and indeed the sample. Therefore, a reticular structure is expected to exhibit coherent, reproducible function.

Unlike other porous materials such as carbon, zeolites, and mesoporous silica, the pores of reticular structures have no walls. In other words, their framework structures are open scaffolds constructed from “joints” and “struts.” This arrangement allows for maximization of adsorption sites within the pores and facile diffusion of incoming and outgoing molecules. Typically, this scaffold-type structure endows MOFs and COFs with ultra-high surface areas of up to 7,000 meter square per gram. The high porosity observed, when coupled with the functionalization of the pores, provides ideal grounds for the design of materials capable of selective capture of carbon dioxide and water and storing them in voluminous amounts. As explained further in the following, these features, arising from molecular considerations, are directly related to creating materials that can operate with high storage capacity, energy efficiency, and high productivity.

## AIR TO CARBON DIOXIDE

In developing methods and materials for capturing carbon dioxide from air, it is important to have a medium of sufficient basicity to covalently bind carbon dioxide. A viable system must be selective, have high capacity, be stable under operating conditions so that carbon dioxide uptake and release can be cycled repeatedly over many years, have fast kinetics in taking in carbon dioxide and releasing it, consume low energy, and be inexpensive. Today, there are two broad classes of materials being studied. In the first class, a liquid absorbent such as aqueous ethanolamine or hydroxide salt solutions is used to make carbamate or carbonates, respectively. These systems, although highly selective, suffer from low capacity because of the limited diffusivity of carbon dioxide through aqueous solutions. They also require high energy consumption for release of carbon dioxide due to the high heat capacity of water.

The second class of materials is adsorbent porous structure: zeolites, polymers, silica, and MOFs. Zeolites take up considerable amounts of carbon dioxide from air (0.25–1.4 mmol/g) but have very high regeneration temperatures. The remaining three types of materials must be functionalized with primary amines to enhance their selectivity for carbon dioxide. Amine-functionalized polymers suffer from very low capacity since the amines are not all accessible to incoming carbon dioxide. The most promising silica materials are covalently functionalized with amines and have capacities of 0.1–1.8 mmol/g with favorable selectivity, kinetics, and regeneration temperatures. MOFs appear to perform well in all categories with a capacity ranging from 0.1 to 4 mmol/g<sup>11</sup>.

For these particular MOF systems, recycling over a large number of cycles is yet to be reported. Nevertheless, these results indicate that MOFs have great promise for direct air capture (DAC), especially given their amenability for functionalization and introduction of high-density amine sites enabled by their ultrahigh porosity.

COFs are an emerging class of carbon capture materials but remain in the synthesis and development stage with very little data available on their capabilities, although since their frameworks are made from strong covalent bonds, COFs are expected to rival if not surpass MOFs.

The next step for the MOF systems is to design MOF coatings for testing in DAC contactors. Indeed, integration of an MOF-binder formulation into additively manufactured, passive heat exchangers by a robust coating process will be needed. Such efforts will also require contactor process modeling, including mass–energy balancing and techno-economic assessments. Since air must be passed through the MOF formulation at high speed, it will be critical to evaluate the pressure drop across the contactor, its buildability, and its necessary scale. Thus, while the scientific challenge of trapping carbon dioxide from air is being solved, significant engineering work remains to produce devices that can operate at suitable scale.

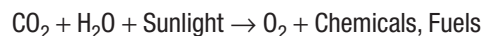
It is worth noting that the current estimate of carbon capture for DAC systems spans a range of \$100–\$1000/tCO<sub>2</sub> captured, a higher value range compared to a \$70–\$100/tCO<sub>2</sub> captured estimates for prevailing flue gas capture techniques. The immediate need is to reduce the unit cost of capture below \$100/tCO<sub>2</sub> captured with scalability to million-tonnes-per-year (DE FOA-0002402 AOI-2 TRL 6: minimal 0.1M tCO<sub>2</sub>/year net captured; X-Prize: demonstration >1000 tCO<sub>2</sub>/year, modelling >1M tCO<sub>2</sub>/year, show scalability to >1G tCO<sub>2</sub>/year). These are critical targets for increasing the feasibility of DAC for general deployment.

## AIR TO FUELS

Carbon dioxide sequestration is not an ideal solution. Not only must the carbon dioxide be captured and released in high concentration, it also must be relocated to underground sites where it will remain without any leaking at geological time-scales. Locating, providing, and filling such sites is a daunting proposition. Far more sound would be a process in which the CO<sub>2</sub> is converted into a fuel source, which could be burned to regenerate CO<sub>2</sub>, thus completing a cycle, or is transformed into a useful product with a favorable carbon footprint.

To produce fuels and chemicals from captured CO<sub>2</sub> efficiently and sustainably, a desired process has to utilize energy and resources that are naturally abundant and readily renewable. Artificial photosynthesis, which uses sunlight to convert CO<sub>2</sub> and water into valuable chemicals, is a prime

candidate: it utilizes solar power, which can provide up to 10<sup>5</sup> TW of energy, to convert water and CO<sub>2</sub> into H<sub>2</sub> and hydrocarbons; and it is a solar-to-chemical process, where solar energy is captured and stored in chemical bonds<sup>12</sup>. The net chemical reaction of artificial photosynthesis is as follows:



The success of this approach relies on efficient utilization of solar energy as well as effective catalytic conversion of water and CO<sub>2</sub> to fuels and chemicals (Figure 1).

Artificial photosynthesis promises to fundamentally transform the current economy of fossil fuels into a sustainable economy of “photons.” These renewable photons will fuel the processes driving the air economy (clean air, energy, and water). As its name suggests, artificial photosynthesis has been originated from humanity’s desire to mimic nature’s unique photosynthetic processes to store the energy from sunlight into high-energy chemical bonds.

The first direct chemical product of artificial photosynthesis is renewable green hydrogen from the direct solar-driven water-splitting process. Ever since its first demonstration<sup>13</sup>, there have been significant efforts to split water into H<sub>2</sub> and O<sub>2</sub> with high conversion efficiency using sunlight. Effective electro-catalysis coupled with high-efficiency state-of-the-art solar junctions can already deliver green hydrogen at ~30% solar-to-hydrogen efficiency<sup>14</sup>. The growing abundance of renewable sources of electricity, driven by decreases in the levelized cost of electricity (LCOE) for solar (\$0.04–0.06 kWh<sup>-1</sup>) and wind (\$0.06–0.08 kWh<sup>-1</sup>) that are approaching parity with fossil fuels, bodes well for a green hydrogen energy revolution in the very near future.

Green hydrogen is a highly valuable energy carrier and can be readily converted into electrical power without generating byproducts harmful to the environment. It can be used for the selective hydrogenation of carbon–carbon double and triple bonds for the production of many fine industrial chemicals. It can also be employed in microbial electrosynthesis to convert CO<sub>2</sub> into many different value-added chemicals. In addition to these carbon-based chemicals, ammonia (NH<sub>3</sub>), the primary nitrogen source in agricultural fertilizers and a potential H<sub>2</sub> storage material and fuel, can also be produced from renewable H<sub>2</sub> and N<sub>2</sub>.

Efforts to reduce and recycle CO<sub>2</sub> have accelerated recently with the goal of renewably generating carbon fuels and other value-added chemicals. The development of so-called “drop-in fuels” from CO<sub>2</sub> and H<sub>2</sub>O would enable use of unlimited solar energy without the need to modify our current energy infrastructure, clearing some of the financial and logistical obstacles to a fully renewable energy powered “air economy.” An efficient and highly selective catalyst that drives the CO<sub>2</sub> reduction reaction (CO<sub>2</sub> RR) is required to make this happen.

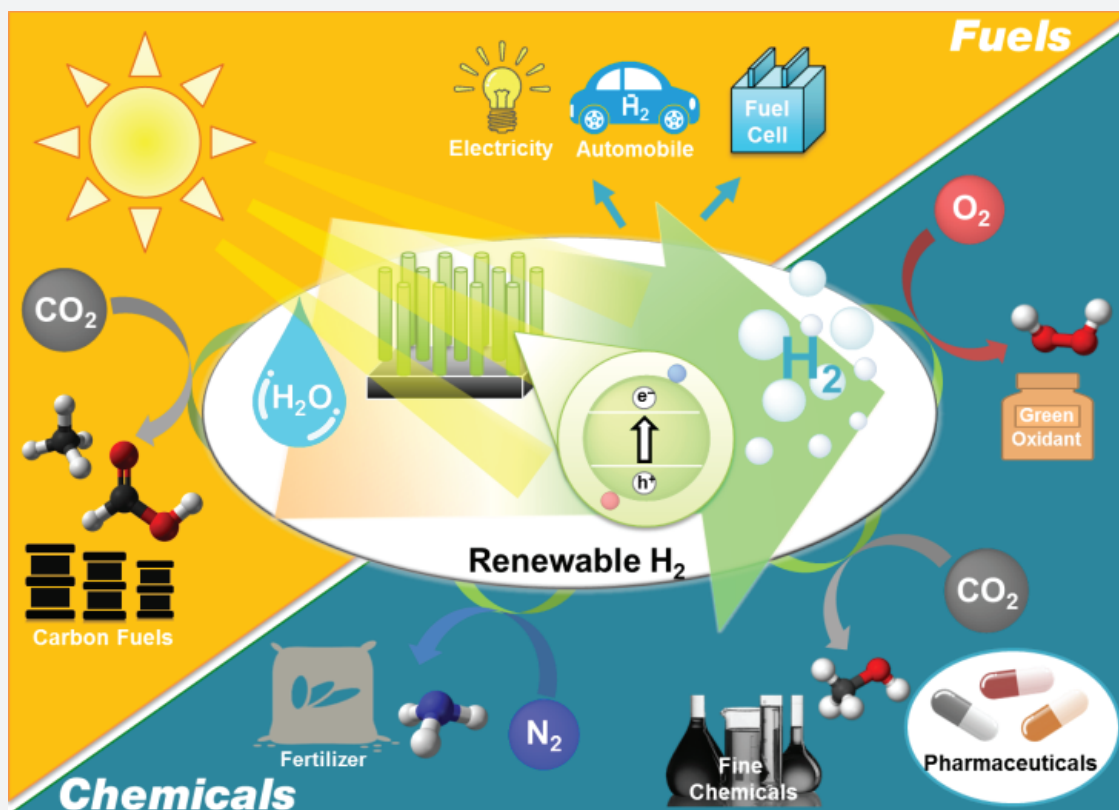


Figure 1. The role of artificial photosynthesis in the air economy, reprinted with permission from Ref. 12. Copyright 2015, Wiley.

Despite intense multidisciplinary efforts to discover such efficient and highly selective catalysts, comprehensive solutions remain elusive. For many decades now, researchers have been searching for an ideal catalyst that can carry out CO<sub>2</sub> RR with low overpotential, high production rate, high selectivity toward multicarbon products, and excellent durability<sup>15</sup>. Recent developments in heterogeneous electrocatalytic conversion of CO<sub>2</sub> have brought new opportunities and optimism in the solar-to-fuel (photovoltaics combined with CO<sub>2</sub> electrolyzers) technology. However, the status of this field, enticing as it is, is far from the relatively advanced stage of green hydrogen production from solar water-splitting. Overpotentials required for cathodic conversion of CO<sub>2</sub> are still very large because of limited success in electrocatalyst discovery. And more importantly, few synthetic electrocatalysts can compete with the high specificity, kinetic performance, and self-replicating/self-repairing properties of biological CO<sub>2</sub> fixation.

Biology achieves CO<sub>2</sub> fixation to energy-dense multicarbon compounds with impressive selectivity using its

arsenal of powerful enzymes. It can do so with relatively low overpotential and, in many cases, remarkable selectivity toward specific chemical products. Upon the interfacing of these natural CO<sub>2</sub>-reducing enzymatic systems with renewable electron sources or photons, a new generation of artificial photosynthetic systems has emerged: photosynthetic biohybrids. Unlike pure CO<sub>2</sub> electrocatalysis, photosynthetic hybrids provide a route to bridge the high catalytic activity and selectivity of enzymes in living cells with efficient solar conversion in robust solid-state devices (such as a solar cell or a powerful semiconductor light absorber)<sup>16–18</sup>.

Microorganisms engage a collection of enzymes and reductive pathways to produce multicarbon hydrocarbons from simple building blocks, including CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. It has now been demonstrated that many autotrophic acetogenic microbes serving as a CO<sub>2</sub>-reducing electrocatalyst can be coupled with different semiconductors and photovoltaic devices for direct solar-powered CO<sub>2</sub> reduction<sup>19–21</sup>. Under solar irradiation, these integrated biohybrids could effectively capture sunlight and reduce CO<sub>2</sub> into a common chemical

intermediate, acetic acid, without additional external energy input, and the energy conversion efficiency could be as high as 3.6%<sup>22</sup>. This solar-to-chemical energy conversion efficiency can be further optimized by tuning the medium pH, semiconductor bandgap, microorganism selection, the semiconductor and microbe loading density, as well as the charge transfer interface<sup>23</sup>. The acetate, as a common chemical feedstock, can then be readily upgraded into other value-added chemicals such as liquid fuels, biodegradable polymers, and pharmaceutical intermediates using existing chemical or biological processes. In addition to acetate, electrochemically derived formate, among other chemical intermediates, can serve as a feedstock for microbial production of fuels and chemicals in the air economy based on artificial photosynthesis<sup>24</sup>. A comparison of such schemes based on comprehensive multiphysics modeling is presented in Abel *et al.*<sup>25</sup>

Artificial photosynthesis, as a solar-to-chemical technology, thus offers a critical solution to seasonal-scale electrical grid-level storage, chemical feedstocks, transportation fuels, and even specialty chemicals and pharmaceuticals. It presents one of the essential solutions, if not the only one, toward net-zero carbon emission or even a negative emission society of the future.

## AIR TO WATER

There is almost as much water in the atmosphere as in rivers and lakes on our planet. Harvesting this water, especially in arid regions, would tap into a natural resource that is nonpolluting, recyclable, and sustainable. Water harvesting from air is already a commercialized technology, but with the serious

limitation that it works only in humid regions with >60% relative humidity (RH) or >10 g of water per cubic meter of air. In arid regions where the humidity in the air is typically <60% or <10 g of water per cubic meter of air, this technology fails to harvest water with suitable energy or economic efficiency.

There are at least four important criteria for developing a useful material for water harvesting from arid air: (1) water capture at low humidity where almost 2 billion people live under water-stressed conditions, (2) rapid uptake and release of water within the material to maximize the number of cycles per day, (3) high capacity of water uptake to maximize productivity per cycle, and (4) low-regeneration temperature so as to avoid high-energy requirements for device operation. In this regard, zeolites, polymers, and inorganic salts fall short of meeting all four criteria.

Our strategy has been to design MOFs capable of taking up water from arid atmosphere, concentrating it into the pores. In a closed container, such hydrated MOFs can release the water at mild conditions (45–90°C) thereby turning arid air into tropical air whose water content can be easily condensed upon mild cooling. We discuss here the Yaghi group's most recent MOF, building of a water harvester prototype, and its performance in the Mojave desert<sup>26–29</sup>.

The success in harvesting water using MOF in a simple box within a box prototype (productivity 200–300 L per kilogram of MOF-801 per day) was exciting since it was the first time that pure water was harvested from desert air with no energy input aside from ambient sunlight. Furthermore, the MOF has high stability in water and can potentially remain in the device for many years without being replenished. Once this feasibility study was completed, attention was turned

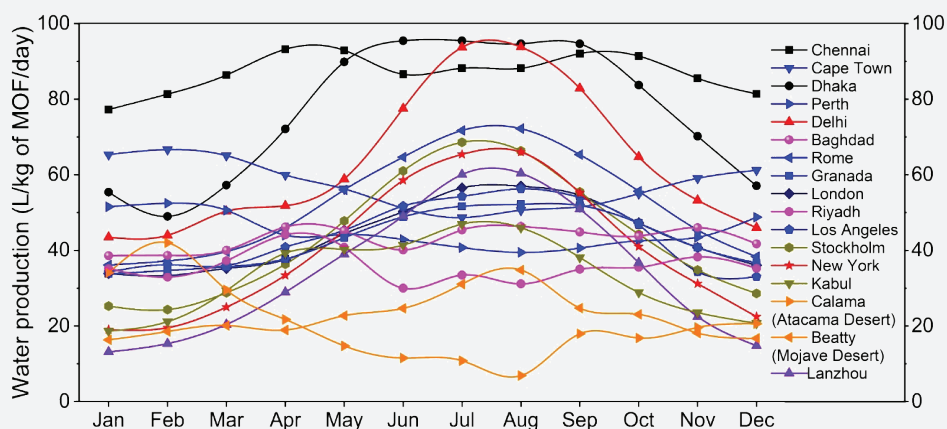


Figure 2. Expected productivity of MOF-303 in climates around the world. Up to 90 L of water per kilogram of MOF can be achieved in the regions where the air is rich in water, while 7–20 L of water per kilogram of MOF can be achieved in the driest deserts of the world. Plot extracted from Ref. 29.



Figure 3. MOF Water Harvester. A working prototype for water harvesting from air based on 100 g of MOF. It is capable of producing 4 L per day with minimum energy input. The MOF is based on aluminum and can remain in the device for the lifetime of the electronics (6 years). Image: courtesy of Water Harvesting Inc.

to developing an MOF water harvester that could carry out multiple cycles and therefore deliver larger amounts of water. The new MOF-303 [Al(OH)(1H-pyrazole-3,5-dicarboxylate)] showed exceptional water uptake characteristics. Its crystal structure is composed of rod metal-oxide units linked by pyrazole units to give a three-dimensional framework supporting one-dimensional pores. Laboratory experiments indicated that MOF-303 extracts water from very low humidity (<7% RH) and does so with fast kinetics. Indeed, our measurements showed that an adsorption–desorption of water cycle can be completed within 5 minutes at 85°C. Accordingly, much higher amounts of water per kilogram of MOF can be harvested as observed by the MOF-303 water harvester tested in the Mojave desert. Specifically, under conditions as severe as 10% RH and 27°C, the productivity of this device was 0.7–1.0 L per kilogram of MOF per day, an order of magnitude higher than the box within a box harvester. Based on the performance of this MOF, it is anticipated that it will deliver water around the world regardless of time of the year (Figure 2).

MOF-based water harvesting technology is currently being automated and commercialized by Water Harvesting Inc. Their latest device (Figure 3) employs only 200 g of MOF and can harvest water at the rate of 40 L per kilogram of MOF per day. Plans are in progress to produce larger devices with water productivities of 250 L and 20,000 L per day. It is worth noting that the MOF material is recyclable and is made in water with zero discharge. The lifetime of the MOF is equivalent to the lifetime of the electronics (6 years). At the end of the

device life, the MOF can be treated with strong acid to dissociate the linker from the metal and resynthesized in water.

## CONCLUDING REMARKS

It is clear from the foregoing discussion that the materials and processes are emerging to realize our vision of what we call the air economy. There is much to be gained scientifically and financially by our society capturing carbon dioxide from air and converting it to fuels and chemicals, with the water for the conversion processes being supplied by harvesting water from air. The latter also produces potable water. These giant steps operate with power supplied from sunlight via an artificial photosynthetic process. In this way, the carbon energy cycle is combined with the water harvesting cycle to realize a closed network producing clean air, clean energy, and clean water for what we envision would become the scientific and technological basis of the air economy.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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