Metal-Organic Frameworks for Water Vapor Adsorption

Le Shi,[1,2] Kent O. Kirlikovali,[3] Zhijie Chen,[1,2,*] and Omar K. Farha[3,4,*]

1 Stoddart Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou 310058, P. R. China

2 Zhejiang-Israel Joint Laboratory of Self-Assembling Functional Materials, ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou 311215, P. R. China

3 Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

4 Department of Chemical & Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States

*Corresponding author. Email:
zhijiechen@zju.edu.cn,
o-farha@northwestern.edu

MAIN TEXT

INTRODUCTION

Water is the most abundant and cleanest natural resource on earth, and it is the driving force of all nature. It not only affects food security, human health, and ecosystem integrity and maintenance, but is also an important driver of energy in industrial production and life. Importantly, water adsorption applications are considered to be highly energy-efficient and environmentally friendly technologies,[1] including atmospheric water harvesting,[2-4] desiccation of clean gases,[5] indoor humidity control,[6,7] and adsorptive heat transformation.[8,9] However, current water adsorption-related applications are still constrained by properties of adsorbents, such as their low water uptake capacities, poor cyclic stabilities, limited feasibilities over a range of humidity conditions, and minimal commercial availabilities. Conventional nanoporous materials (e.g., silica gels, zeolites, and clays) were the first adsorbents used in water capture applications due to their low cost, commercial availability, and favorable water adsorption kinetics. However, these materials generally suffer from either low water uptake capacities or high regeneration temperature, limiting their use in practical water absorption applications.[1,10] Metal-organic frameworks (MOFs), a class of crystalline porous materials, are assembled from inorganic nodes and organic linkers through coordination bonds.[11,12] Benefiting from their exceptional porosity and surface area, tunable pore size and geometry, and highly tailorable and designable structures and functionalities, MOFs show considerable potential for gas storage and separation, heterogeneous catalysis, and other energy and environmental sustainability applications.[13-17] In recent years, MOFs have also shown great potential for water vapor adsorption because of a growing understanding of the relationship between MOFs and water, as well as an increasing number of reports detailing MOFs that exhibit high water stability.[1,4,9] Moreover, judicious design of the MOF structures enables control over their water adsorption properties and the water uptake capacities, which make MOFs ideal candidates for water adsorption-related applications (**Figure**

1).

This review aims to provide an overview of recent advances in the development of MOFs for water adsorption, as well as to offer proposed guidelines to develop even better water adsorption materials. First, we briefly introduce the fundamentals of water adsorption, including how to ascertain key insights based on the shapes of water adsorption isotherms, descriptions of various water adsorption mechanisms, and a discussion on the stability of MOFs in water systems. Next, we discuss several recent reports have detailed how to improve water uptake capacity through the design and synthesis of MOFs. In particular, we highlight the importance of reticular chemistry in the designed synthesis of MOF-based water adsorbent materials. We then shift our focus to discussing the enormous potential of MOFs for use in selective water vapor adsorption applications with both theoretical and practical considerations considered. Finally, we offer our thoughts on the future development of this field in three aspects: chemistry and materials design, process engineering, and commercialization of MOFs for water adsorption. We hope that this review will provide fundamental insights for chemists and inspire them to synthesize MOFs with better water adsorption performance; and provide assistance to engineers researching MOF-based water adsorption devices and working towards the development of highly energy-efficient and environmentally friendly technologies with reduced carbon footprints.

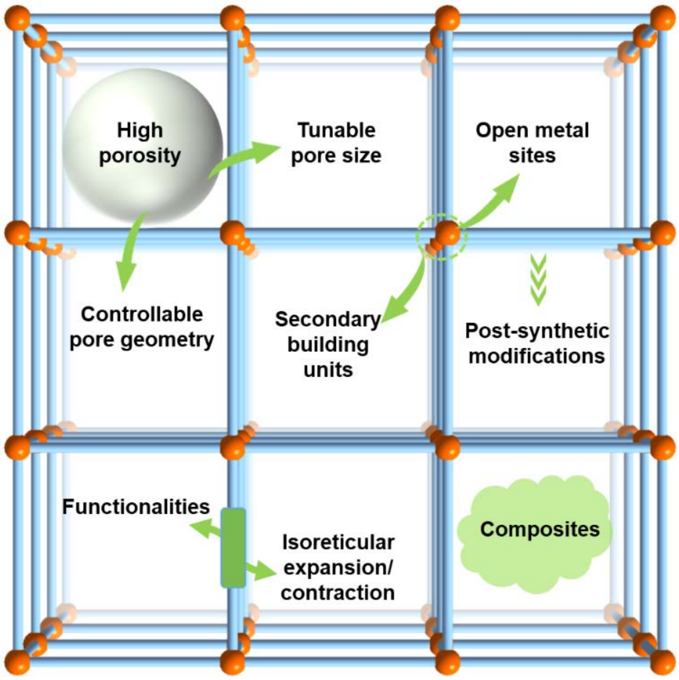

Figure 1. An overview of water adsorption using metal-organic frameworks

MOFs FOR WATER VAPOR ADSORPTION

Fundamentals of water adsorption

Kaskel and coworkers reported the water adsorption properties of series of MOFs, including HKUST-1, ZIF-8, MIL-101, which differed significantly in their water uptake capacity and isotherm shapes.[18] In this regard, the exploration of the water adsorption mechanism is of great importance for the further development of MOF water adsorbents. Three adsorption mechanisms are generally accepted: (i) chemisorption on open metal sites, (ii) cluster adsorption, and (iii) capillary condensation.[9] Adsorption and desorption of water molecules on open metal sites of MOFs are accompanied by changes in the metal coordination number and/or structural deformation.[19,20] Water adsorption in MOFs often undergoes a physical adsorption process in which water molecules are adsorbed in the pores through hydrogen bonding interactions. The adsorbed water molecules then serve as nucleation sites for the formation of water clusters, promoting water adsorption in the larger cavities that ultimately leads to water condensation in the overall framework. Both chemisorption on open metal sites and cluster adsorption in MOFs are similar to those of porous carbons and zeolites, and water adsorption proceeds through reversible pore filling, as in the case of MOF-801, UiO-66, and other hydrophilic microporous MOFs.[21] For MOFs with larger pores (~2 nm), the capillary condensation mechanism dominates the water adsorption process. Due to the irreversible nature of the capillary condensation adsorption process, water adsorption isotherms typically exhibit "*S*" shaped profiles with hysteresis loops between the adsorption and the desorption branches.

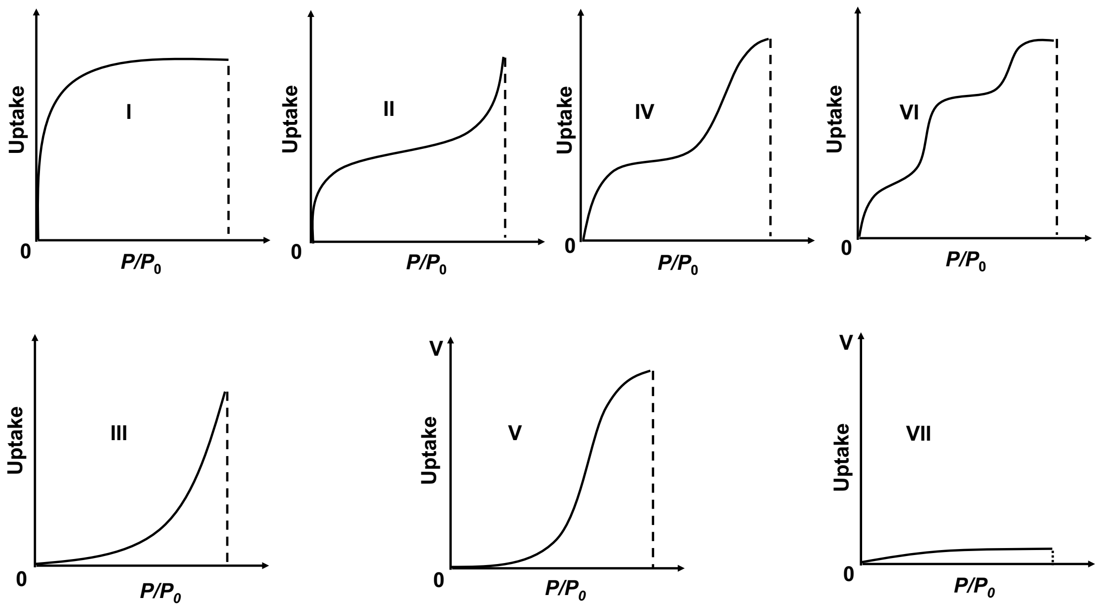

Figure 2. IUPAC classification of water vapor adsorption isotherms[10]

Based on multiple potential water adsorption mechanisms, MOFs exhibit diverse types of water adsorption isotherms. The isotherm shape not only provides important information on the water adsorption mechanism, but also offers insight into both the strength of the adsorbate-adsorbent (i.e., water-MOF) interactions and the relative hydrophilicity or hydrophobicity of the pore environments of MOFs. In this review, all water adsorption isotherms discussed were measured at 298 K unless otherwise noted. Relative pressure, P/P_0, is equivalent to relative humidity (RH, in %). Although water uptake capacity is given in a gravimetric unit (g g^{-1}) for most reported examples, volumetric uptake capacity (g cm^{-3}), which specifies the volume of sample to be occupied at a certain water uptake capacity, is more relevant for practical applications. In particular, high mass specific working capacities suggest great promise for water adsorption-related materials in the stage of industrial applications.

According to the IUPAC, the water adsorption isotherms are classified into seven types (**Figure 2**).[10] In type I, II, IV and VI, the water uptake increase steeply at very low relative pressures, indicating that the hydrophilic character of adsorbents. In type III, V and VII isotherms, very low water uptakes at low relative pressures imply the presence of moderately hydrophobic pore environments. In addition to the isotherm shape, the position of the isotherm's inflection point (α), which is defined as the point at half of the maximum adsorptive uptake, can also indicate which practical water adsorption application is best suited for each MOF, ranging from atmospheric water harvesting to autonomous indoor humidity control and adsorptive heat transformation, among others.[1] However, the poor hydrolytic stability of many MOFs limits their applications for water adsorption.

For a MOF to be hydrolytically stable, it must maintain its crystallinity and porosity upon exposure to humidity (or liquid water). A comparison of powder X-ray diffraction (PXRD) patterns collected before and after exposure to humidity should be used to assess the MOF stability.[4,22] In addition, researchers should characterize the permanent porosity of the MOFs before and after humidity exposure through analysis of adsorption-desorption isotherms, which will indicate whether the pore structure collapses or remains intact upon exposure to humidity. In general, MOFs that undergo framework collapse in the presence of water due to the breakage of coordination bonds between organic linkers and inorganic metal ions exhibit weaker PXRD diffraction peaks or increased half-peak widths, as well as reduced porosity.[22] Considerable effort has been devoted to elucidate the degradation mechanism of MOFs in the presence of water and to develop appropriate strategies to improve the water stability of MOFs.[23,24] In the context of thermodynamics, the strength of metal-linker coordination bonds is a decisive factor in predicting MOF stability in the presence of water. According to the hard/soft acid/base (HSAB) principle, hard Lewis bases form strong bonds with hard Lewis acids, while soft Lewis bases tend to form strong bonds with soft Lewis acids.[22,25,26] In this context, stable MOFs are often constructed from organic and inorganic building units following HSAB principle. For instance, MIL-101,[27] MOF-303,[28] and UiO-66,[29] which feature carboxylate linkers coordinated to high-valent Cr(III), Al(III), and Zr(IV) metal ions, respectively, exhibit excellent water stability. In addition to thermodynamic considerations, kinetic factors, including inert metal ions, hydrophobic linkers, highly connected building units, and catenated frameworks, can also improve hydrolytic stability of MOFs by preventing water from attacking metal-linker coordination bonds.

Rational design of MOFs for water adsorption

The development of MOFs with appropriate hydrolytic stability depends on the rational control of both thermodynamic and kinetic factors. In this regard, reticular chemistry has enabled the rational design and assembly of MOFs with great potential to precisely design and control the pore geometry and size, surface area and various functionalities and pore hydrophilicity or hydrophobicity.[30,31] Using a reticular chemistry approach, researchers can design a blueprint net to guide the synthesis of MOFs from preselected inorganic and organic building units that coordinate in desired geometries. A blueprint net is often referred as an edge-transitive net with one type of edge or a related minimal edge-transitive net. Alternatively, researchers can leverage isoreticular synthesis strategies, including isoreticular expansions or contractions, functionalization, and node modification, to finely tune the water adsorption properties of a MOF with a desired net.

In this part, we focus on the main achievements of reticular design of MOFs for water adsorption performances. We discuss typical and latest examples of MOFs, as well as their respective water sorption properties, that highlight the important features of reticular chemistry that render MOFs a unique class of sorbents for water vapor adsorption (**Figure 3**).

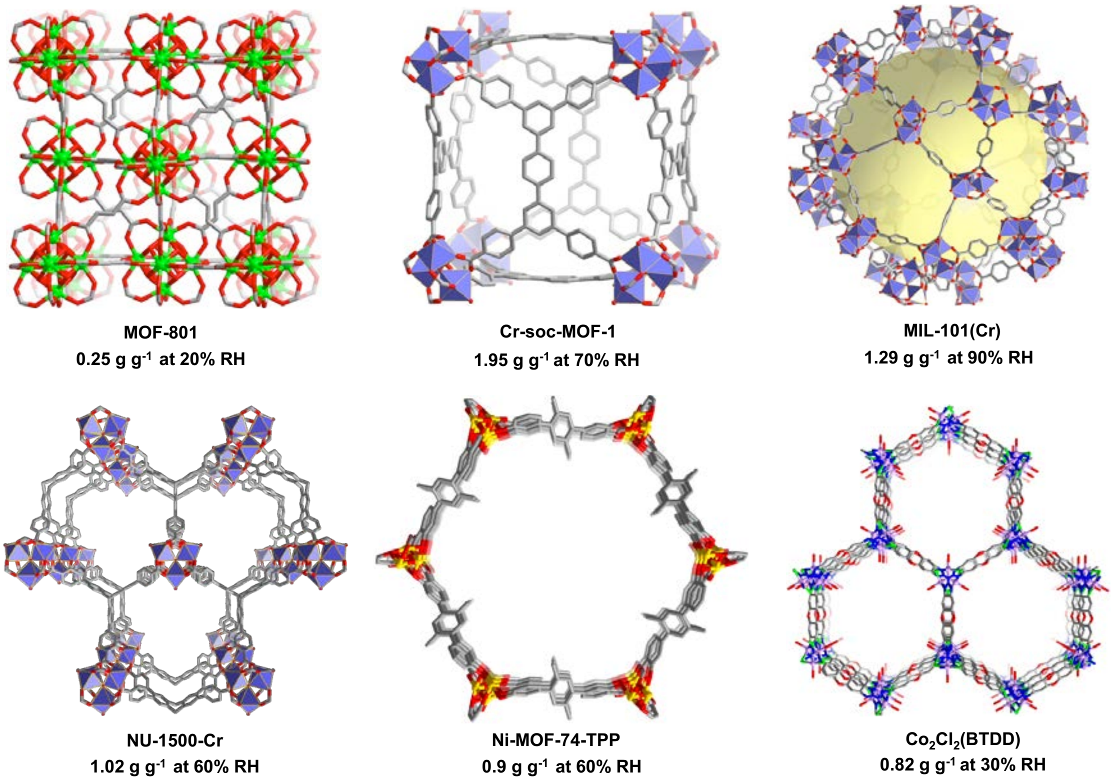

Figure 3. Crystal structures of selected MOFs and their water uptake capacities under specific operating conditions.

Designing MOFs for water adsorption with reticular chemistry

Zirconium-based MOFs have garnered considerable attention owing to their superior chemical and thermal stability, multi-functionality, and reproducibility. Of particular interest is their versatile connectivity, which can range from 3-connected to 14-connected, that allows for the rational design and synthesis of a wide set of extraordinary structures with many types of multitopic carboxylate linkers.[29,32-34] For instance, the combination of linear ditopic linkers and 12-connected Zr_6 clusters affords a series of 12-connected **fcu**-MOFs (**Figure 4**).[29,33] Among this family, MOF-801, assembled from fumarate linkers and Zr_6 nodes, exhibit the notable water stability and high uptake capacity at low relative pressures, render MOF-801 suitable for water harvesting. Recently, Serre, Chang, Maurin, and coworkers synthesized a robust large-pore zirconium MOF with **csq** net, denoted as MIP-200, from the assembly of 4-connected tetracarboxylate linker and 8-connected Zr_6 nodes.[35] MIP-200 has hexagonal channels with size of *ca.* 13 Å and triangular channels with size of *ca.* 6.8 Å, respectively. The high porosity and stability render MIP-200 with superior water-sorption properties, including an S-shaped isotherm and high uptake of water below 25% RH. Recently, Farha and coworkers explored the synthesis of Zr-MOFs with a unique [2.2]paracyclophane (PCP) scaffold.[36] Interestingly, the backbone can be easily extended to ditopic and tetratopic carboxylate linkers that can further assemble into Zr-MOFs with different topologies, including the 2D NU-700, NU-405 (**fcu**), NU-1800 (**flu)**, NU-602 (**she)** net, and NU-913 (**scu)**. These MOFs exhibit high hydrolytic stability due to the hydrophobic nature of PCP scaffold.

MOFs based on trinuclear chromium (III) (Cr_3) nodes represent an outstanding subclass of water-stable MOFs. Early examples include MIL-100 (Cr) and MIL-101 (Cr) with the **mtn** net,[27,37]which are assembled from terephthalic or trimesic acid linkers and Cr_3 nodes. The water sorption isotherm in MIL-101 (Cr) shows a unique shape, which has initial adsorption followed by hysteresis loops, that is attributed to the presence of the coordinatively unsaturated chromium sites, as well as two mesoporous cages in the structure. The outstanding water uptake capacity (1.29 g g^{-1} at 90% RH) of MIL-101(Cr) is one of the highest values ever reported for a solid adsorbent.[38] Eddaoudi and coworkers combined 4-connected 3,3',5,5'-tetrakis(4-carboxyphenyl)-p-terphenyl ligands with Cr_3 nodes to yield a hydrolytically stable chromium-based MOF with the **soc** net, Cr-**soc**-MOF-1.[39] The extraordinary high porosity affords a water vapor uptake of 1.95 g g^{-1} at 70% RH. Recently, our group reported hydrolytically stable and highly porous NU-1500-Cr with the **acs** net, which consists of rigid triptycene-based organic ligands and Cr_3 node.[40,41] NU-1500-Cr displays a high water capacity of about 1.02 g g^{-1} at 60% RH and 298 K. Both Cr-**soc**-MOF-1 and NU-1500-Cr can maintain high water vapor uptake after multiple adsorption-desorption cycles, indicating that the chromium-carboxylate coordination bonds are highly kinetically inert. The excellent chemical stability of these MOFs paved the way for the rational synthesis of MOFs used in water adsorption application devices.

MOFs made from infinite, rod-like units are often stable because of steric shielding by the binding groups.[42] The position of the inflection points in water adsorption isotherms for MOFs that contain rod-like building units are generally located in the low relative humidity range (RH < 50%), which has been proven to be a key feature in designing water harvesting materials for use in arid regions. For example, the promising water adsorbent CAU-10-H, which is assembled from chains of edge-sharing AlO_6 octahedra and 1,3-benzene dicarboxylic acid linkers, shows a water uptake capacity of 0.26 g g^{-1} at 20% RH and retains its capacity after 10000 adsorption-desorption cycles.[43] Yaghi and coworkers recently combined the polar organic linkers and alternating *cis-trans* AlO_6 octahedra to yield a MOF-303 with **xhh** topology. Due to the presence of a hydrophilic one-dimensional pore with a 6 Å diameter and a free pore volume of 0.54 cm^3 g^{-1}, MOF-303 exhibits a water uptake capacity of 0.4 g g^{-1} at 20% RH.[44]

In addition to carboxylate-based MOFs, metal-azolate frameworks comprise a class of stable MOFs that positions them as promising for use in water adsorption applications.[45] For example, Dincă and coworkers synthesized stable mesoporous triazolate-based MOFs, $M_2Cl_2(btdd)(H_2O)_2$ (M = Mn, Co, Ni), from the assembly of H_2btdd linker and related metal salts.[46-50] Among these MOFs, $Co_2Cl_2(btdd)$ with a hexagonal pores of *ca.* 22 Å displays a total water uptake of 0.82 g g^{-1} at the relative humidity of 30%.[46]

Fine-tuning pore size and pore geometry of MOFs with isoreticular chemistry

Once a MOF based on a specific topological net that exhibits favorable water adsorption properties is identified, isoreticular synthesis, including expansion or contraction, linker functionalization, and modification of the metal nodes, can be used to fine-tune the pore size and pore geometry of the MOFs. This offers a strategy to tune different water adoption properties of the MOF, such as the shape of water isotherm, the position of the inflection point, and the water uptake capacity at specific relative humidity range.

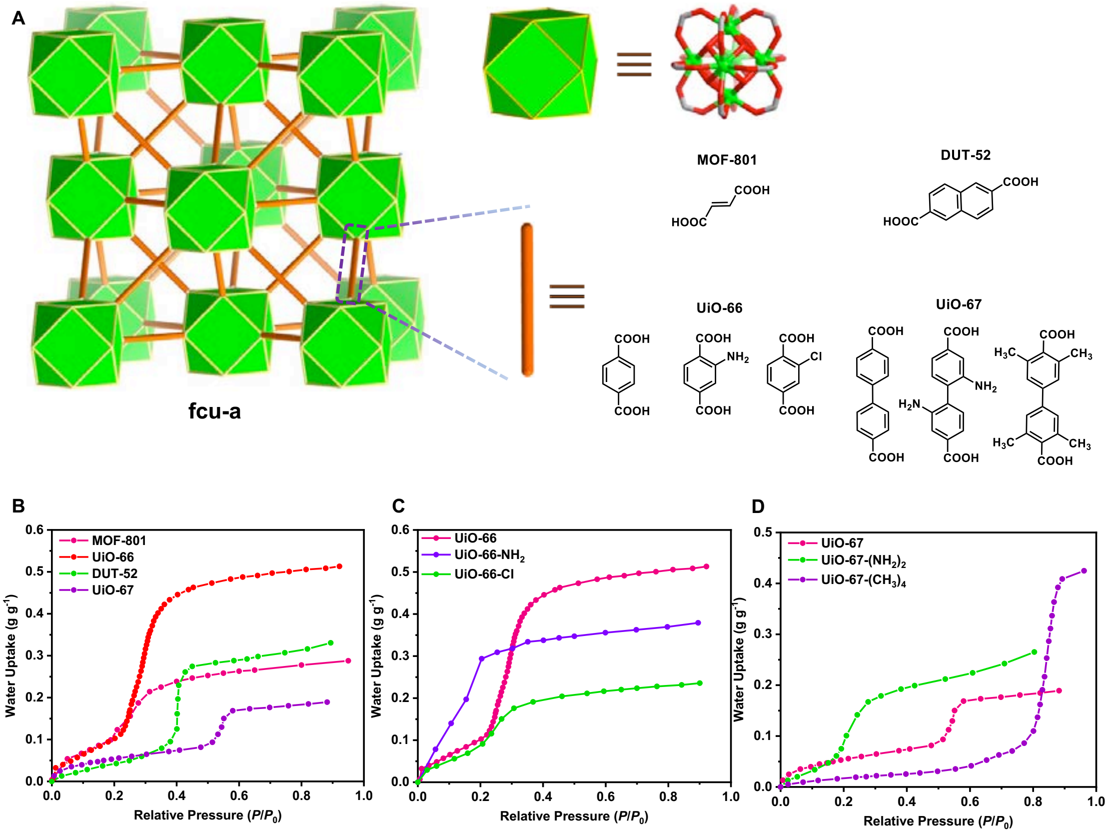

Figure 4. Isoreticular synthesis of MOFs with **fcu** topology.

(A). The linear ditopic linkers with different size and functional groups and 12-connected Zr_6 SBUs generate **fcu** topology

(B) Water adsorption isotherms of **fcu**-MOFs with different pore size. Data from ref [21,51]

(C). Water adsorption isotherms of functionalized BDC in the structure of UiO-66. Data from ref [51]

(D). Water adsorption isotherms of functionalized BPDC in the structure of UiO-67. Data from ref [4,52]

The power of isoreticular expansion lies in the ability for researchers to increase the pore volume while retaining the skeleton and topology of the initial MOF. As the water uptake capacity of MOFs is dependent on its pore volume, the water uptake capacity can be enhanced using an isoreticular linker extension strategy. For example, the **fcu** UiO-66 contains a slightly longer BDC linker compared to the isostructural fumarate linker in the **fcu** MOF-801, and as a result, exhibits a larger pore volume and thus a larger water uptake capacity (**Figure 4A**). In another example, Zheng, Motkuri and coworkers applied the isoreticular expansion strategy to study water adsorption behavior in a set of Ni-MOF-74 structures.[53] The maximally extended framework, denoted as Ni-MOF-74-TPP, exhibits the highest water uptake capacity value of 0.9 g g^{-1} at 60 % RH. However, the maximum water uptake capacity does not always follow the trend of total pore volume by isoreticular expansion strategy, which has been rationalized as a result of a partial collapse arising from capillary-force-driven forces during water adsorption.[54] Additionally, this linker extension strategy generally involves either incorporating polycyclic aromatic linkers, which increases the hydrophobicity and decreases the thermal stability of the MOF. Therefore, tools such as molecular simulations may be required to rationally enhance the water adsorption ability through the isoreticular expansion approach. Recently, Yaghi and coworkers employed an experimental-computational approach to extend MOF-303 by appending a single vinyl group to the PZDZ linker.[55] The resulting MOF featured an increase in pore volume while retaining the ability of the MOF to harvest water in arid environments.

Compared to the isoreticular expansion, linker functionalitzation not only tunes the pore geometry and size, but can also improve the stability of MOFs. For instance, Li and coworkers synthesized thirteen isoreticular UiO-type MOFs with linkers of different lengths and functional groups (**Figure 4**)[51] and found that incorporating hydrophilic groups into UiO-66 can improve both the low-pressure water uptake capacity and the water adsorption kinetics. This performance increase can be attributed to the existence of strong hydrogen-bonds between the functional groups in the MOF and the H_2O molecules. In contrast, hydrophobic groups can alter the position of the inflection point to higher relative humidities. Therefore, the precise introduction of functional groups enables control over the hydrophilic or hydrophobic of the pores to meet the requirements of different applications. For example, Su and coworkers recently introduced both hydrophobic and hydrophilic groups in proper ratios into the UiO-67 platform as a strategy to tune the overall frameworks stability and water vapor uptake capacity.[52] As a result, UiO-67-4Me-NH_2-38% exhibits S-shaped adsorption isotherms located in the optimal RH range for use in autonomous indoor humidity control applications. Although this strategy has proven most successful in shifting the isotherms of the parent MOFs, this functionalization strategy is not an effective solution for all MOFs since the introduction of new functional groups results in a significant decrease in pore volume, and subsequently, a less steep water adsorption isotherm.[56]

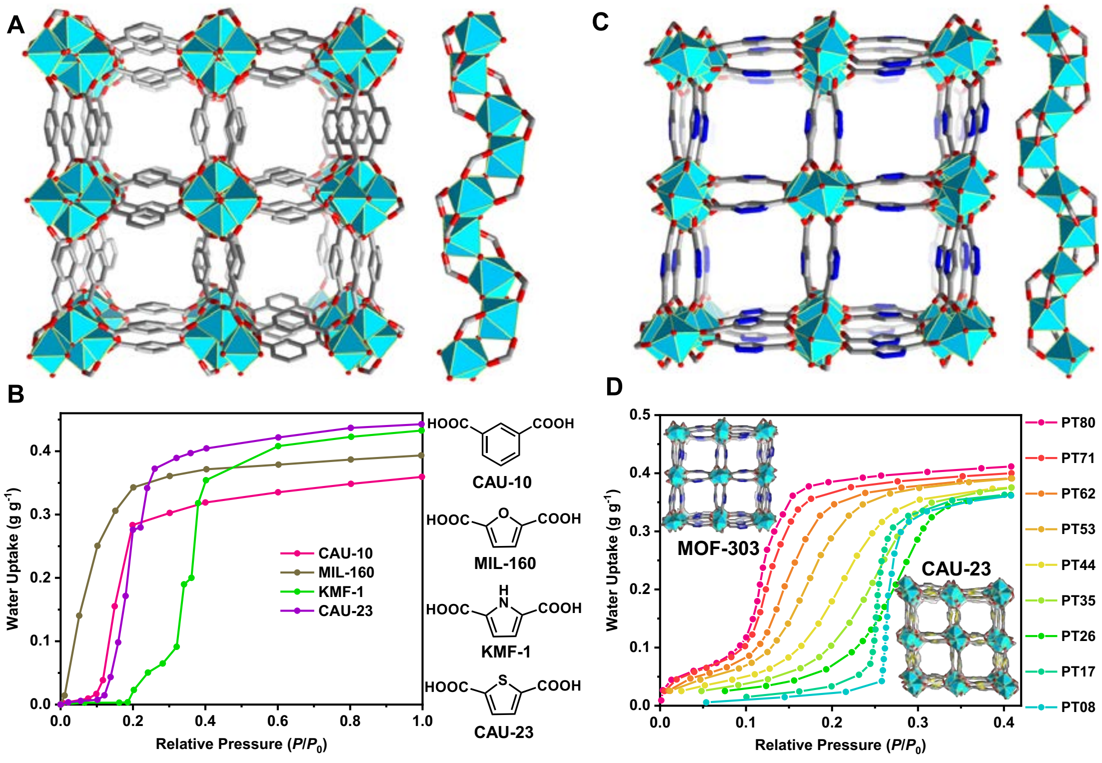

Figure 5. Aluminum chain-based MOFs.

(A) Crystal structure of CAU-10 contains (cis)$_4$-(trans)$_4$ alternating corned-shared AlO_6 octahedra.

(B) Water adsorption isotherms of aluminum-based MOFs isostructural to CAU-10. Data from ref [56-59]

(C) Crystal structure of MOF-303 contains cis-trans alternating corned-shared AlO_6 octahedra.

(D) Water adsorption isotherms of multivariate PT-MOF series. Data from ref [60]

To increase the water uptake capacity without reducing the pore volume, incorprating an aromatic linker that contains a polar heteroatom offers a viable strategy (**Figure 5**). For example, MIL-160, assembled from the polar 2,5-furandicarboxylic acid and rod-like Al units, revealed that a better water uptake capacity at low relative humidity and a slightly enhanced saturation capacity compared to isostructural CAU-10.[57] (**Figure 5B**). Qian and coworkers recently immobilized the Lewis basic nitrogen sites into MIP-200, and the generated Zr-adip exhibited an extremely high water uptake of 0.43 g g^{-1} at 25% RH, higher than pristine MOFs of MIP-200 (0.39 g g^{-1}).[61] *In-situ* X-ray diffraction and theoretical calculations revealed that the incorporated polar heteroatoms can serve as strong binding sites for water molecules and lead to the formation of water clusters, which then form chains of clusters, and finally a water network.[28,62] More interestingly, multicomponent approaches (e.g., multivariate and mixed-linkers approaches) offer a straightforward and inexpensive way to tailor pore properties like stability, hydrophilicity or hydrophobicity, and affinity of water molecules.[63] For example, Zhang and coworkers demonstrated that MAF-4 can be tuned to become more hydrophilic by partial or full replacement of the linker with 3-methyl-1,2,4-triazolate in MAF-7.[64] Similarly, Christoph and coworkers also showed that the hydrophilicity can be easily tuned through varying the ratio of linkers between the limits of MIL-160 and CAU-10-H.[65] Recently, Yaghi and coworkers reported a series of multivariate PT-MOFs based on the MOF-303 and CAU-23 platforms, which leads to a broader range of tunability in the low relative humidity range, the regeneration temperature, and the enthalpy of adsorption (**Figure 5C-D**).[60] The Farha group recently developed a *de novo* linker installation strategy to improve the stability of the Zr-MOF based on NU-600.[66] The resulting multicomponent MOFs show enhanced hydrolytic stability and water sorption performance compared to the prototype NU-600, highlighting that increasing the connectivity of the Zr_6 nodes can protect them from water attack.

In addition to the extended or functionalized linkers, modification of the metal nodes has also been employed to tune the water adsorption properties of the MOF. In general, exchanging the metal cations in the nodes can increase the hydrolytic stability of MOFs and move the pore-filling step to lower relative humidities.[40,47,67] Zhou, Eddaoudi, and our group successfully constructed a series of chromium-based MOFs via post-synthetic metal metathesis of the iron-based MOFs.[39,40,68] These MOFs exhibit superior stability and advanced water adsorption properties for many water vapor adsorption and desorption cycles, which is attributed to the strong chromium-carboxylate coordination bonds (**Figure 6A**). Recently, Han, Rosi, and coworkers reported a zinc-terephthalate-allopurinol MOF, ALP-MOF-1, which contains interconnected $Zn_4(\mu_2\text{-}H_2O)_2(ALP)_2(BDC)_2$ clusters.[69] SCXRD and DFT computations revealed that the open metal sites in ALP-MOF-1 play an important role in anchoring water molecules, which offers the tuning of the composition of metal ions as a viable strategy to adjust water uptake. Therefore, a series of isostructural framework analogues with different metal ratios (Co/Zn) can be obtained via metal ion metathesis, ultimately affording a MOF that exhibits tunable water isotherms below 20% RH (**Figure 6B**).

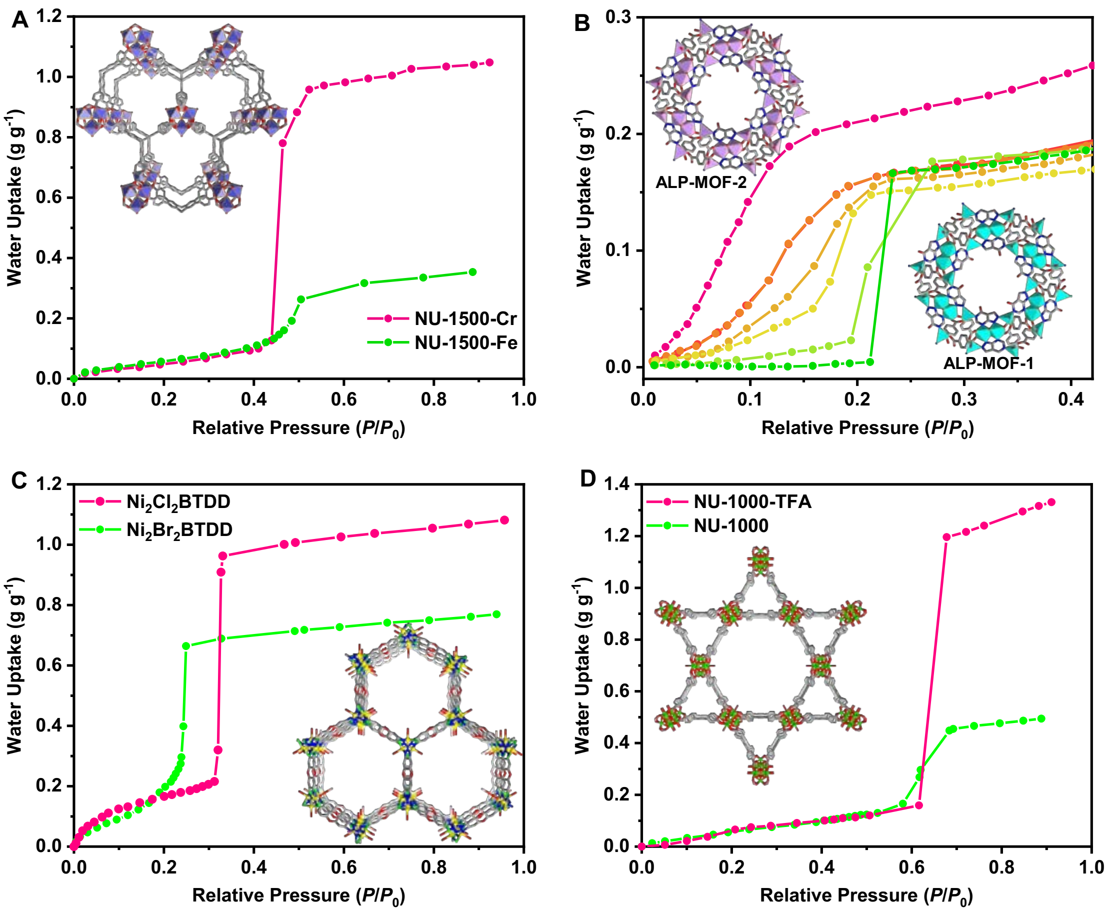

Figure 6. Influence of SBUs modification on the water adsorption properties

(A). Modification of water sorptionad properties conversion of NU-1500-Fe to NU-1500- Cr by metal ion exchange at the SBU. Data from ref[40]

(B) Variable metal ions composition to adjust water adsorption properties of ALP-MOF. Data form ref[69]

(C) Modification of water adsorption properties through conversion of Ni_2Cl_2BTDD to Ni_2Br_2BTDD by anion exchange at the SBU. Data from ref[48]

(D) Modification of water adsorption properties through node functionalization of NU- 1000. Data from ref[70]

In addition to the exchange of metal cations, node functionalization through post-synthetic modification methods offers a route to retain the stability of framework by reducing the strength of the interaction between water molecules and the nodes . For example, Farha and coworkers demonstrated that replacing the polar hydroxyl and aqua ligands on Zr_6 nodes with longer and flexible carboxylate-based ligands can effectively limit the accessibility by water molecules to the Zr_6 nodes.[71] Similarity, they recently exhibited that using a hydrophobic capping agent, trifluoroacetic acid (TFA), can significantly improve the water stability of the MOF. As a result, NU-1000-TFA with the **csq** net and NU-913-TFA with the **scu** net achieved remarkable water uptakes of around 1.32 g g^{-1} at 70 % RH and 0.85 g g^{-1} at 53% RH, respectively, and remain stable following consecutive water adsorption-desorption cycles (**Figure 6D**).[36,70] Likewise, Dincă and colleagues reported that post-synthetic modification of the nodes of the Ni-based MOF Ni_2Cl_2BTDD affords an enhancement of water uptake capacity at low pressures (**Figure 6C**). For example, Ni_2Br_2BTDD, obtained from the replacement of the Cl^- by Br^- anion in Ni_2Cl_2BTDD, displays a slight contraction of the pore diameters but the greatest water uptake capacity of 0.64 g g^{-1} below 25 % RH.[48]

APPLICATIONS OF WATER ADSORPTION

The development of MOFs for water sorption-related applications strongly depends on the shape of the water adsorption isotherm and the uptake capacity of the MOF. In particular, MOFs that exhibit S-shaped water sorption isotherms are more desirable as they can offer both high working capacities and low regeneration energies, which is a rare combination of features amongst traditional water sorbents. In addition, the relative humidity (RH) at which the inflection point (α) occurs is a critical indicator for which specific water adsorption application the MOF is best suited for. For instance, water adsorption isotherms that exhibit inflections at extremely low RH values ($\alpha < 0.05$) would work well for the gas desiccation. In comparison, α values in the range of 0.1 to 0.3 indicate that the material suited to the applications of adsorptive heat transformation and water harvesting. Reversible adsorption-desorption branches from $0.45 < \alpha < 0.65$ match well with the ideal humidity range of healthy indoor environments, meaning these MOFs would be well-suited to maintain indoor humidity.

Atmospheric water harvesting

Shortages of freshwater resources comprise an increasing risk to the global population. In this regard, atmospheric water harvesting (AWH) technologies show great potential as a solution to this water crisis since, in principle, water harvesting is accessible everywhere.[2,72] Three primary categories of AWH technologies include fog harvesting, dewing, and adsorption-based approaches.[73] The first two require high humidity environments and relatively large energy consumption, which precludes the application of these AWH technologies in most regions of the world. Conversely, adsorption-based water harvesting systems can easily work worldwide, even in arid regions.[73,74] In adsorption-based AWH systems, water vapor from the ambient environment concentrates in the adsorbent, and then water vapor releases from the adsorbent upon application of a temperature or pressure swing. Notably, powering these swings by low-grade energy sources, such as solar thermal energy or waste heat, would further reduce the environmental impact of this approach. Finally, the water vapor released from the sorbent is then introduced to a condenser, which enables the collection of fresh water from the apparatus.

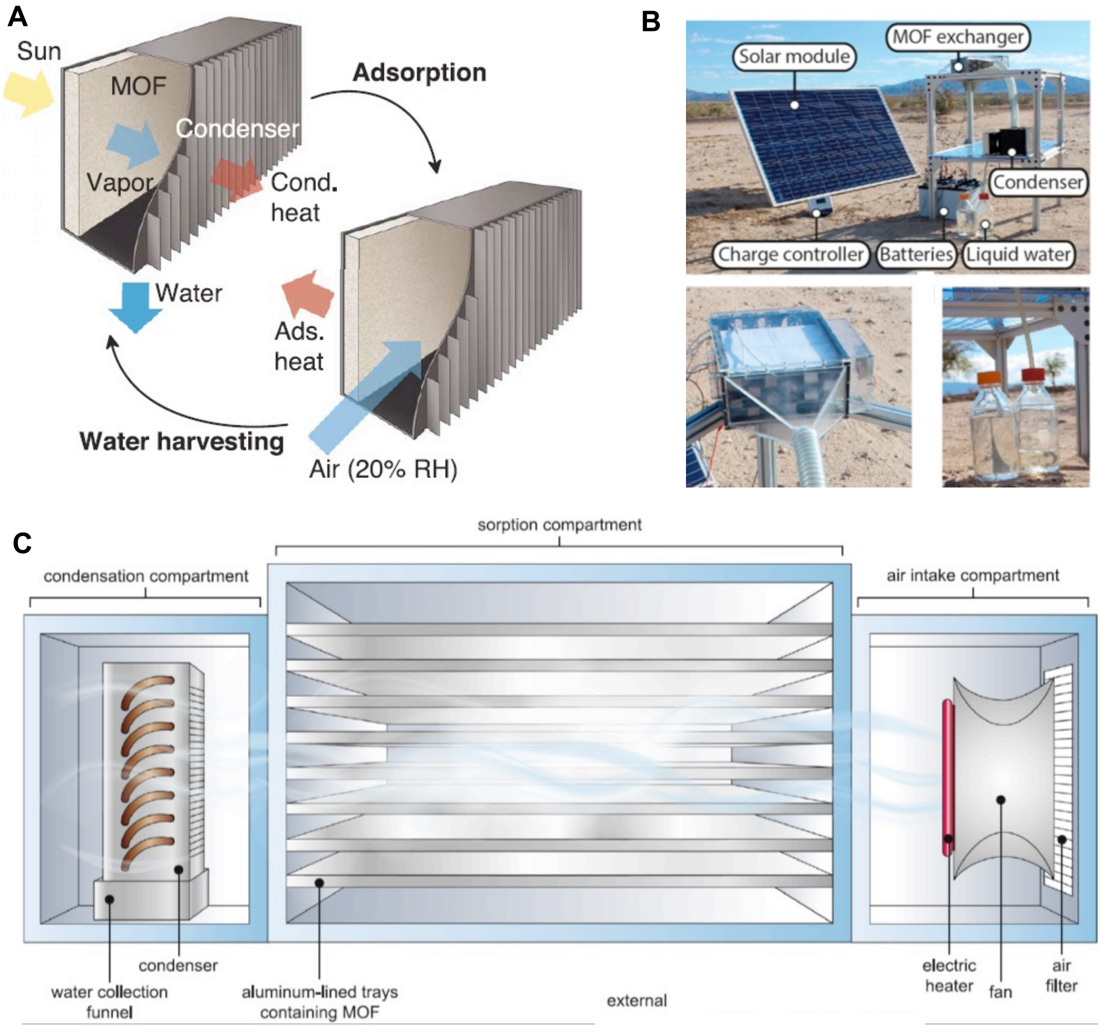

Figure 7. Three classes of practical MOF water harvesters.

(A) A passive, monocyclic water harvester. Reprinted with permission from Yaghi et al.[21] Copyright 2017, American Association for the Advancement of Science.

(B) An active, multicyclic water harvester. Reprinted with permission from ref. [44] Copyright 2019 American Chemical Society.

(C) An adaptive, multicyclic water harvester. Reprinted with permission from Cordova et al.[75] Copyright 2022 Springer Nature.

Two key components are required for the development of MOF water harvesters:[3] MOF-based adsorbents and water-harvesting devices. Generally, hydrophilic MOFs work best for this application as they can capture water vapor in extremely dry air and simultaneously exploit the abundant solar energy in arid areas to minimize the energy cost for potable water production. In the past several years, researcher explored a series of hydrophilic MOFs that are suitable for the ideal sorbents, such as MOF-801,[21] MOF-841,[33] Co_2Cl_2BTDD,[46] CAU-10,[76] and MOF-303.[77] These MOFs all exhibit the cabaility to capture water up to 0.25-0.84 g g^{-1} at relatively low RH values (10% < RH < 40%) and low regenerated temperature temperature (~65 °C) that can be attained by solar thermal energy or waste heat.

In addition to the development of MOFs with high water uptake capacites, fast adsorption kinetics, and low desorption temperatures, the other equally important aspect in the development of AWH devices for use in practical applications. Yaghi and coworkers first reported a proof-of-concept MOF water harvester based on passive adsorption-desorption in a monocyclic mode.[3,21] The device consists of a small sorbent container, large vapor condenser and surrounding walls (**Figure 7A**). At night when RH values peak, moist air diffuses into the MOF bed. During the daytime when RH is at its lowest, heat generated by sunlight is used to release the water vapor from the MOF and subsequently condenses on the surrounding walls of the device. MOF-801 was tested in this device and exhibited a productivity of 0.1 L $kg_{MOF\text{-}801}^{-1}$ per day in the desert of Arizona, USA.[77] However, the fundamental drawback of passive water harvesters is that their productivity is limited by the sorbent capacity.

To overcome this drawback, active harvester devices based on multicyclic adsorption-desorption cycles have been developed.[44] The device is comprised of adsorbent beds, electrically powered components, and exchangers (**Figure 7B**). Since the adsorption and desorption processes are electrically powered, the uptake and release of water vapor can occur in any time of day and night. This results in a substantial increase in productivity for these active harvester devices compared to that of passive water harvesters. In the first example of an active water harvester device, MOF-303 was used due to its rapid adsorption-desorption kinetics. As a result, this active device could generate 1.3 L kg_{MOF}^{-1} per day at 32% RH, which corresponds to a greater than four-fold increase compared to that of the passive device under the same conditions. In contrast to previous devices that mainly focused on the saturated sorption capacity of materials, the success of this device demonstrated that controlling and exploiting the dynamic water capacity of the MOF is an equally important aspect of high-efficiency water production under atmospheric water harvesting conditions.

Recently, Cordova and coworkes developed a new water harvester based on multicyclic adsorption-desorption cycles, termed adaptive water harvesting.[75] The device is similar to the active device, consisting of an air intake compartment, sorption compartment, and condensation compartment (**Figure 7C**). However, the adaptive mode of this device can optimize the timing and efficiency of each sorption cycle through sensors that correlate the real-time temperature and RH of the ambient environment to the dew points from a database. MOF-801 was used to evaluated to the actual water production ability for this device, which demonstrated a greater than 169% increase in water production compared to the active harvesting device. Furthermore, the adaptive device is capable of continuously producing water with no loss in performance after operation more than 12 months. The development of this adaptive device has laid the foundation for a commercially available MOF water harvester.

Adsorptive Heat Transformation

The adsorption of water vapor on porous solid surfaces is well suited for low temperature heat transformation applications, such as adsorption heat pumps (AHPs) or adsorption driven chillers (ADCs).[78] Notably, these adsorbent-based heat transformations can significantly help minimize primary energy consumption and greenhouse gas emissions, providing a promising approach towards reducing the carbon footprint. In these systems, water is the working fluid and is evaporated, and then it is adsorbed by the sorbents, which causes heat to be released at an intermediate temperature level. The details of how these devices operate can be found in other reviews,[8] so we refer the reader there for more information.

A promising adsorbent should have a high affinity toward water to meet the requirement of refrigeration but a low regeneration temperature to minimize the energy required to release and collect water. Moreover, facile water adsorption/desorption kinetics for energy efficiency and excellent stability in multicycle adsorption-desorption cycles are both equally important to achieve high coefficients of performance for heating ($COP_H < 2.0$) and cooling ($COP_C < 1.0$), respectively. Commercially available water sorbents (e.g., silica gel and zeolites) exhibit weak hydrophilicity at low relative pressure or require high regeneration temperature, which are not suitable for the application of ADCs and AHPs. In this regard, MOFs that exhibit S-shaped water sorption isotherms, high uptake capacities at low relative pressures, and facile regeneration at low temperatures should be favorable for these applications. Toward this end, many MOF materials with excellent water stability have been tested for their applicability in adsorptive heat transformation. Among them, aluminum chain-based MOFs have shown a high potential for application in AHPs or ADCs due to their high working capacities, low regeneration temperatures, and stability in multicycle adsorption-desorption experiments. For example, MIL-160 has demonstrated a high loading capacity (2.35 kg kg^{-1}) in the first water loading lift within a typical AHP cycle,[57] which is slightly higher than that of commercial SAPO-34. Regarding ADC applications, MIL-160 shows a COP_C of 0.74 but requires a somewhat high regeneration temperature (> 90), which makes it inefficient in ADC devices. Another Al-chain-based MOFs, CAU-23, shows a high water loading at relatively low RH values (RH < 30%) and is stable beyond 5000 adsorption-desorption cycles.[59] In addition, CAU-23 has a notably high COP_C of 0.8 for refrigeration at a low driving temperature below 60 , which render it as an ideal material to realize ultra-low temperature-driven ADC devices. Recently, Chang, Maurin, and coworkers leveraged a computational predction approach to discover a unique Al-based MOF, KMF-1, which features S-shaped water sorption isotherms, as well as record volumetric working and specific energy capacities under cooling working conditions.[58] In particular, KMF-1 shows very high COP for both cooling (0.75) and heating (1.74), in addition to low driving temperatures below 70℃, which enables its use for both AHPs and ADCs applications. Aside from Al-based MOFs, the Co-based Co-CUK-1[79] and Zr-based MIP-200[35] comprise two striking examples of MOFs that demonstrate remarkable water sorption properties, including their high efficiencies for both chiller and heat pump applications with low driving temperatures. Additionally, Zr-adip, which is isostructural to MIP-200, exhibits both a higher COP_C (0.79) and COP_H (1.75), positioning Zr-adip as a promising candidate for both ADC and AHP applications.[61]

For the realization of an efficient adsorption heat pump or chiller, coating MOFs onto the heat exchanger can effectively increase mass transport of the adsorbent and thermal transfer during the adsorption-desorption processes, and thus enhance the efficiency that can be achieved in different conditions. For example, Stock, Henninger, and coworkers fabricated a full-scale heat exchanger coated with CAU-10-H for use in ADCs.[80] The MOF-coated heat exchanger yielded a good volumetric specific cooling power and a fast adsorption speed under the working conditions of an adsorption driven chiller, thus allowing for high cycling frequencies. Similarly, Serre and coworkers directly coated MIL-100 (Fe) onto heat exchangers to achieve a high COP of 0.79, offering the potential for use in industrial application.[81]

Autonomous Indoor humidity control

Indoor relative humidity is an important factor that determines indoor air quality, the thermal comfort of occupants, and the overall building energy consumption. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) suggests a relative humidity range between 40% to 65% RH to create the most habitable indoor environment.[6] Ideal materials for the autonomous regulation of indoor RH should meet the following criteria: S-shaped water adsorption isotherms; adsorption and desorption branches within the ASHRAE recommendations (i.e., 40% to 65%); high water vapor uptake within the operating vapor pressure window; low regeneration temperatures; highly reproducible cycling performance; high hygrothermal stability; non-toxicity; and resistance to corrosion. Eddaoudi and coworkers reported a rare earth cluster-based MOF, Y-**shp**-MOF-5,[6] which exhibits S-shaped water sorption isotherms with hysteresis loops between the adsorption (63% RH) and the desorption (37 %) branches, almost perfectly matching the suggested relative humidity range of 40% to 65% RH for optimal autonomous indoor humidity level control.

Although increasing the MOF pore size will lead to greater water uptake, larger pores will also enable capillary condensation of water to occur (typically at pore sizes greater than 20 Å),[46] which can lead to framework collapse under multicycle water adsorption-desorption.[22] In this regard, mesoporous MOFs containing highly inert coordination bonds between high valent metal ions and carboxylate linkers are promising candidate for such applications. For instance, Wang and coworkers reported a mesoporous and stable V-MOF, BIT-66, which shows reversible water sorption behavior in the humidity range of 45-60% RH and excellent stability after many water adsorption-desorption cycles.[7] Recently, this group presented a series of Al-carboxylate MOFs through ligand functionalization.[82] The resulting CAU-1-OH shows isotherm tunability in the range of 40-60% RH and maintained a working capacity of 0.41 g g^{-1} after 500 adsorption-desorption cycles. Similarly, Su and coworkers also prepared UiO-67-type single and mixed-linker MOFs by functionalized BPDC linkers carrying hydrophobic ($-CH_3$) and hydrophilic ($-NH_2$, -OH, or -COOH) groups.[52] Among these materials, the mixed-linker UiO-67-4Me-NH_2-38% shows adsorption and desorption inflection points occur in the range suggested by ASHRAE. In addition to these MOFs, high-valent chromium-based MOFs like Cr-**soc**-MOF-1 and NU-1500-Cr also exhibit outstanding working capacities under various indoor humidity levels and retain their work capacities after multiple adsorption desorption cycles.

Desiccation of natural gas

Natural gases (e.g., methane) produced from hydrocarbon extraction processes are stored in large sub-surface units, which are usually saturated with water vapor. This moist gas can cause many problems, including pipeline corrosion and blockage during transportation. The most common technique for removing water from natural gas is through dehydration with triethylene glycol (TEG). However, this strategy faces many disadvantages, such as the requirement for high energy inputs to regenerate the adsorbent, as well as contamination and degradation of the adsorbent. MOFs with a strong affinity for water, especially those showing high water uptake capacities at low relative humidity values, would be an attractive option for the desiccation of clean gas. In this context, Eddaoudi and coworkers reported a fluorinated MOF, KAUST-8, capable of acting as a desiccant material for natural gas dehydration.[5] KAUST-8 is built from Ni-pyrazine square-grid layers and trigonal bipyramid $(AlF_5)^{2-}$ inorganic building blocks, featuring a periodic array of open metal coordination sites and fluorine moieties within the contracted square-shaped one-dimensional channels. This MOF can selectively remove water vapor from different gas streams, including from higher hydrocarbons like natural gas. Notably, unlike conventional materials that need to be regenerated at temperatures of up to 250 ℃, KAUST-8 can be regenerated at the relatively moderate temperature of 105 ℃.

CONCLUSIONS AND OUTLOOK

MOFs have emerged as a very promising sorbent class for water adsorption-related applications, and researchers have made significant progress in understanding the relationship between MOFs and water. In this work, we highlighted how lerveraging reticular chemistry would greatly accelerate the exploration and discovery new high-performance materials. Moreover, isoreticular synthesis approaches are used to precisely tune water adsorption properties to render them suitable for desired applications, ranging from MOF water harvesters and MOF-based heat pumps to cooling devices and humidity pumps. To date, several MOF-based devices have been designed and are successfully operating in actual production. Despite this exciting progress, significant opportunities in terms of chemistry and material science, process engineering, and commercialization aspects remain as this emerging field continues to rapidly expand.

New MOFs with high water capture performance can be design and synthesized based on reticular chemistry. In this regard, high-throughput (HT) screening, including high-throughput synthesis and characterization, high throughput adsorption screening, and computation screening, provide an enabling tool to accelerate the discovery of new MOF materials and optimize synthetic procedures.[17,83,84] Moreover, HT methods are closely connected with the concepts of automation, parallelization, and miniaturization, which can further improve the efficiency of MOF discovery and development. Further enhancing water adsorption performance might require highly charged, high-valent metals (e.g., Al(III), Cr(III), Ti(IV), Zr(IV), Hf(IV)) and the incorporation of moieties with higher affinities to water. In addition, it is very important to choose suitable MOFs for targeted applications. For example, for potable water production, researchers would likely select low toxicity Al-based units as their primary choice when selecting building blocks. For moisture control applications, the high porosity and excellent stability of Cr-based MOFs makes them great choices in these settings. In addition, compared to the most reported rigid MOFs that exhibit S-shaped isotherms due to their pore-filling mechanism, structurally flexible MOFs can also exhibit S-shaped isotherms when stimuli from adsorption of water vapor trigger a switch from the closed phase to the open phase.[85] Moreover, in some studies, flexible MOFs exhibited stability over many water adsorption and desorption cycles and fast sorption kinetics that are comparable to those of rigid adsorbents such as MOF-303, Al-fumarate, and CAU-10-H.[86] Thus, researchers can further design and tune flexible MOFs with optimal kinetics and thermodynamics and explore them as smart materials for water adsorption.

Fast kinetics of water adsorption-desorption in MOFs becomes of primary importance to enable their industrial utility and efficient processing. However, powdered MOFs obtained from conventional syntheses cannot be directly used in practical applications because the accumulative effect of large amounts of powder will increase the size of the adsorption layer, meaning the entire device must be in larger size to accommodate these adsorption materials. Moreover, thermal conduction in powders is very low, which is detrimental to the heat-driven desorption process.[87] To overcome these drawbacks, densification or shaping of MOFs into thin layers, pellets, or various monoliths can increase the contact between adsorbent particles, which is beneficial to heat transfer in the water desorption process.[88] However, when a certain amount of adsorbent powder is pressed into a regular shaped block, MOF particles stack up to afford a thick and compact adsorption layer, hindering both the vapor diffusion rate and mass transfer rate. Therefore, to balance heat transfer and mass transfer, shaping technique need to be improved. In one alternative strategy, directly coating MOFs onto the heat exchangers can maximize the amount of adsorption for fast and efficient heat and mass transfer, providing a route to achieve fast adsorption-desorption cycling in large-scale process engineering.[81,89] Freeze-drying methods that form porous foams and sponge-like structures, as well as and emerging 3D printing technologies, are also a scalable way to convert MOFs into condensable feedstocks.

For the successful commercialization of MOFs, researchers must consider factors beyond MOF performance, such as economic and environmental considerations. In terms of economic feasibility, MOFs must be able to be synthesized at low costs and high yields. The development of scaled up synthetic routes will greatly reduce costs and make MOFs competitive with other benchmark materials.[90] Specifically, continuous-flow production techniques, including electrochemical synthesis, microwave synthesis, and mechanochemical methods, can be implemented in industrial-scale batch synthesis routes.[91] Some startup companies, such as BASF, Framergy, novoMOF, and NuMat, have already begun commercializing MOFs by employing large-scale syntheses with cost-saving solvent recycling systems. Additionally, Water Harvesting Inc. (WaHa), founded in 2018, is devoted to exploiting promising MOF-based adsorbent materials to efficiently collect pure water from atmospheric vapor. In addition, researchers must also ensure that these scaled up synthetic routes are as “green,” or environmentally benign, as possible. The commercial production of MOFs must be safer and less polluting than conventional synthesis methods. Therefore, slurry synthesis water-based synthetic approaches have become particularly important to effectively avoid the use of highly toxic and flammable solvents.[92] Finally, techno-economic analyses should be conducted to evaluate the entire route of production, including the selection of ligands and metal salts. These analyses should then be fed back to the researchers for further improvements to their synthetic approaches from both an economic and environmental perspective.

ACKNOWLEDGEMENTS

Z. C. gratefully acknowledges support by the National Natural Science Foundation of China (Grant No. 22201247) and the startup funding from Zhejiang University. O. K. F gratefully acknowledges support from the Army Research Office (W911NF2020136); the Defense Threat Reduction Agency (HDTRA12210041); the Department of Energy (DE-SC0022332 and DE-FG02-08ER15967) and the National Science Foundation (CBET 2119433). K. O. K. gratefully acknowledges support from the IIN Postdoctoral Fellowship and the Northwestern University International Institute for Nanotechnology. We thank the staffs from BL17B beamline of National Facility for Protein Science in Shanghai (NFPS) at Shanghai Synchrotron Radiation Facility, for assistance during data collection.

AUTHOR CONTRIBUTIONS

L.S., Z. C. and O. K. F. proposed the topic of the manuscript. All authors were involved in the writing of the manuscript and approved the final version of the manuscript.

DECLARATION OF INTERESTS

O. K. F. has a financial interest in NuMat Technologies, a startup company that is seeking to commercialize MOFs. All other authors declare no competing interests.

REFERENCES

1. Liu, X., Wang, X., and Kapteijn, F. (2020). Water and Metal–Organic Frameworks: From Interaction toward Utilization. Chem. Rev. *120*, 8303-8377. 10.1021/acs.chemrev.9b00746.

2. Wang, J., Hua, L., Li, C., and Wang, R. (2022). Atmospheric water harvesting: critical metrics and challenges. Energy. Environ. Sci. *15*, 4867-4871. 10.1039/d2ee03079a.

3. Hanikel, N., Prevot, M.S., and Yaghi, O.M. (2020). MOF water harvesters. Nat. Nanotechnol. *15*, 348-355. 10.1038/s41565-020-0673-x.

4. Kalmutzki, M.J., Diercks, C.S., and Yaghi, O.M. (2018). Metal-Organic Frameworks for Water Harvesting from Air. Adv. Mater. *30*, e1704304. 10.1002/adma.201704304.

5. Amandine, C., Youssef, B., Karim, A., M., B.P., S., P.R., Aleksander, S., Charlotte, M.-C., Guillaume, M., and Mohamed, E. (2017). Hydrolytically stable fluorinated metal-organic frameworks for energy-efficient dehydration. Science *356*, 731-735.

6. AbdulHalim, R.G., Bhatt, P.M., Belmabkhout, Y., Shkurenko, A., Adil, K., Barbour, L.J., and Eddaoudi, M. (2017). A Fine-Tuned Metal-Organic Framework for Autonomous Indoor Moisture Control. J. Am. Chem. Soc. *139*, 10715-10722. 10.1021/jacs.7b04132.

7. Ma, D., Li, P., Duan, X., Li, J., Shao, P., Lang, Z., Bao, L., Zhang, Y., Lin, Z., and Wang, B. (2020). A Hydrolytically Stable Vanadium(IV) Metal-Organic Framework with Photocatalytic Bacteriostatic Activity for Autonomous Indoor Humidity Control. Angew. Chem. Int. Ed. *59*, 3905-3909. 10.1002/anie.201914762.

8. de Lange, M.F., Verouden, K.J., Vlugt, T.J., Gascon, J., and Kapteijn, F. (2015). Adsorption-Driven Heat Pumps: The Potential of Metal-Organic Frameworks. Chem. Rev. *115*, 12205-12250. 10.1021/acs.chemrev.5b00059.

9. Canivet, J., Fateeva, A., Guo, Y., Coasne, B., and Farrusseng, D. (2014). Water adsorption in MOFs: fundamentals and applications. Chem. Soc. Rev. *43*, 5594-5617. 10.1039/c4cs00078a.

10. Ng, E.-P., and Mintova, S. (2008). Nanoporous materials with enhanced hydrophilicity and high water sorption capacity. Microporous and Mesoporous Mater. *114*, 1-26.

10.1016/j.micromeso.2007.12.022.

11. Furukawa, H., Cordova, K.E., O'Keeffe, M., and Yaghi, O.M. (2013). The chemistry and applications of metal-organic frameworks. Science *341*, 1230444. 10.1126/science.1230444.

12. Horike, S., and Kitagawa, S. (2022). The development of molecule-based porous material families and their future prospects. Nat. Mater. *21*, 983-985. 10.1038/s41563-022-01346-7.

13. Li, B., Wen, H.-M., Zhou, W., Xu, Jeff Q., and Chen, B. (2016). Porous Metal-Organic Frameworks: Promising Materials for Methane Storage. Chem *1*, 557-580. 10.1016/j.chempr.2016.09.009.

14. Chen, Z., Kirlikovali, K.O., Idrees, K.B., Wasson, M.C., and Farha, O.K. (2022). Porous materials for hydrogen storage. Chem *8*, 693-716. 10.1016/j.chempr.2022.01.012.

15. Mondloch, J.E., Katz, M.J., Isley Iii, W.C., Ghosh, P., Liao, P., Bury, W., Wagner, G.W., Hall, M.G., DeCoste, J.B., Peterson, G.W., et al. (2015). Destruction of chemical warfare agents using metal–organic frameworks. Nat. Mater. *14*, 512-516. 10.1038/nmat4238.

16. Chen, Z., Jiang, H., Li, M., O'Keeffe, M., and Eddaoudi, M. (2020). Reticular Chemistry 3.2: Typical Minimal Edge-Transitive Derived and Related Nets for the Design and Synthesis of Metal-Organic Frameworks. Chem. Rev. *120*, 8039-8065. 10.1021/acs.chemrev.9b00648.

17. Chen, Z., Li, P., Anderson, R., Wang, X., Zhang, X., Robison, L., Redfern, L.R., Moribe, S., Islamoglu, T., Gomez-Gualdron, D.A., et al. (2020). Balancing volumetric and gravimetric uptake in highly porous materials for clean energy. Science *368*, 297-303.

18. Küsgens, P., Rose, M., Senkovska, I., Fröde, H., Henschel, A., Siegle, S., and Kaskel, S. (2009). Characterization of metal-organic frameworks by water adsorption. Microporous and Mesoporous Mater. *120*, 325-330. 10.1016/j.micromeso.2008.11.020.

19. Platero-Prats, A.E., Mavrandonakis, A., Gallington, L.C., Liu, Y., Hupp, J.T., Farha, O.K., Cramer, C.J., and Chapman, K.W. (2016). Structural Transitions of the Metal-Oxide Nodes within Metal-Organic Frameworks: On the Local Structures of NU-1000 and UiO-66. J. Am. Chem. Soc. *138*, 4178-4185. 10.1021/jacs.6b00069.

20. Dietzel, P.D., Johnsen, R.E., Blom, R., and Fjellvag, H. (2008). Structural changes and coordinatively unsaturated metal atoms on dehydration of honeycomb analogous microporous metal-organic frameworks. Chem. Eur. J. *14*, 2389-2397. 10.1002/chem.200701370.

21. Kim, H., Yang, S., Rao, S.R., Narayanan, S., Kapustin, E.A., Furukawa, H., Umans, A.S., Yaghi, O.M., and Wang, E.N. (2017). Water harvesting from air with metal-organic frameworks powered by natural sunlight. Science *356*, 430-434.

22. Burtch, N.C., Jasuja, H., and Walton, K.S. (2014). Water Stability and Adsorption in Metal–Organic Frameworks. Chem. Rev. *114*, 10575-10612. 10.1021/cr5002589.

23. DeCoste, J.B., Peterson, G.W., Jasuja, H., Glover, T.G., Huang, Y.-g., and Walton, K.S. (2013). Stability and degradation mechanisms of metal–organic frameworks containing the

Zr6O4(OH)4 secondary building unit. J. Mater. Chem. A. *1*, 5642-5650. 10.1039/c3ta10662d.

24. Wang, K., Li, Y., Xie, L.H., Li, X., and Li, J.R. (2022). Construction and application of base-stable MOFs: a critical review. Chem. Soc. Rev. *51*, 6417-6441. 10.1039/d1cs00891a.

25. Yuan, S., Feng, L., Wang, K., Pang, J., Bosch, M., Lollar, C., Sun, Y., Qin, J., Yang, X., Zhang, P., et al. (2018). Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. Adv. Mater. *30*, e1704303. 10.1002/adma.201704303.

26. Chen, Z., Kirlikovali, K.O., Shi, L., and Farha, O.K. (2023). Rational design of stable functional metal-organic frameworks. Mater. Horiz., 1039/d1033mh00541k. 10.1039/D3MH00541K.

27. Ferey, G., Serre, C., Mellot-Draznieks, C., Millange, F., Surble, S., Dutour, J., and Margiolaki, I. (2004). A hybrid solid with giant pores prepared by a combination of targeted chemistry, simulation, and powder diffraction. Angew. Chem. Int. Ed. Engl. *43*, 6296-6301. 10.1002/anie.200460592.

28. Hanikel, N., Pei, X., Chandra, S., Lyu, H., Jeong, W., Sauer, J., Gagliardi, L., and Yaghi, O.M. (2021). Evolution of water structures in metal-organic frameworks for improved atmospheric water harvesting. Science *374*, 454-459.

29. Cavka, J.H., Jakobsen, S., Olsbye, U., Guillou, N., Lamberti, C., Bordiga, S., and Lillerud, K.P. (2008). A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. J. Am. Chem. Soc. *130*, 13850-13851.

30. Yaghi, O.M., O'Keeffe, M., Ockwig, N.W., K., C.H., Eddaoudi, M., and Kim, J. (2003). Reticular synthesis and the design of new materials. Nature *423*, 705-714.

31. Chen, Z., Kirlikovali, K.O., Li, P., and Farha, O.K. (2022). Reticular Chemistry for Highly Porous Metal-Organic Frameworks: The Chemistry and Applications. Acc. Chem. Res. *55*, 579-591. 10.1021/acs.accounts.1c00707.

32. Chen, Z., Hanna, S.L., Redfern, L.R., Alezi, D., Islamoglu, T., and Farha, O.K. (2019). Reticular chemistry in the rational synthesis of functional zirconium cluster-based MOFs. Coor. Chem. Rev. *386*, 32-49. 10.1016/j.ccr.2019.01.017.

33. Furukawa, H., Gandara, F., Zhang, Y.B., Jiang, J., Queen, W.L., Hudson, M.R., and Yaghi, O.M. (2014). Water adsorption in porous metal-organic frameworks and related materials. J. Am. Chem. Soc. *136*, 4369-4381. 10.1021/ja500330a.

34. Li, J., Huang, J.-Y., Meng, Y.-X., Li, L., Zhang, L.-L., and Jiang, H.-L. (2023). Zr- and Ti-based metal–organic frameworks: synthesis, structures and catalytic applications. Chem. Commun. *59*, 2541. 10.1039/D2CC06948B.

35. Wang, S., Lee, J.S., Wahiduzzaman, M., Park, J., Muschi, M., Martineau-Corcos, C., Tissot, A., Cho, K.H., Marrot, J., Shepard, W., et al. (2018). A robust large-pore zirconium carboxylate metal–organic framework for energy-efficient water-sorption-driven refrigeration. Nat. Energy *3*, 985-993. 10.1038/s41560-018-0261-6.

36. Gong, W., Xie, H., Idrees, K.B., Son, F.A., Chen, Z., Sha, F., Liu, Y., Cui, Y., and Farha, O.K. (2022). Water Sorption Evolution Enabled by Reticular Construction of Zirconium Metal-Organic Frameworks Based on a Unique [2.2]Paracyclophane Scaffold. J. Am. Chem. Soc. *144*, 1826-1834. 10.1021/jacs.1c11836.

37. Ferey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surble, S., and Margiolaki, I. (2005). A Chromium Terephthalate–Based Solid with Unusually Large Pore Volumes and Surface Area. Science *309*, 2040-2042.

38. Seo, Y.-K., Yoon, J.W., Lee, J.S., Hwang, Y.K., Jun, C.-H., Chang, J.-S., Wuttke, S., Bazin, P., Vimont, A., Daturi, M., et al. (2012). Energy-Efficient Dehumidification over Hierachically Porous Metal-Organic Frameworks as Advanced Water Adsorbents. Adv. Mater. *24*, 806-810. 10.1002/adma.201104084.

39. Towsif Abtab, S.M., Alezi, D., Bhatt, P.M., Shkurenko, A., Belmabkhout, Y., Aggarwal, H., Weseliński, Ł.J., Alsadun, N., Samin, U., Hedhili, M.N., and Eddaoudi, M. (2018). Reticular Chemistry in Action: A Hydrolytically Stable MOF Capturing Twice Its Weight in Adsorbed Water. Chem *4*, 94-105. 10.1016/j.chempr.2017.11.005.

40. Chen, Z., Li, P., Zhang, X., Li, P., Wasson, M.C., Islamoglu, T., Stoddart, J.F., and Farha, O.K. (2019). Reticular Access to Highly Porous acs-MOFs with Rigid Trigonal Prismatic Linkers for Water Sorption. J. Am. Chem. Soc. *141*, 2900-2905. 10.1021/jacs.8b13710.

41. Ho, C.H., Valentine, M.L., Chen, Z., Xie, H., Farha, O., Xiong, W., and Paesani, F. (2023). Structure and thermodynamics of water adsorption in NU-1500-Cr. Commun Chem. *6*, 70. 10.1038/s42004-023-00870-0.

42. Schoedel, A., Li, M., Li, D., O'Keeffe, M., and Yaghi, O.M. (2016). Structures of Metal-Organic Frameworks with Rod Secondary Building Units. Chem. Rev. *116*, 12466-12535. 10.1021/acs.chemrev.6b00346.

43. Fröhlich, D., Pantatosaki, E., Kolokathis, P.D., Markey, K., Reinsch, H., Baumgartner, M., van der Veen, M.A., De Vos, D.E., Stock, N., Papadopoulos, G.K., et al. (2016). Water adsorption behaviour of CAU-10-H: a thorough investigation of its structure–property relationships. J. Mater. Chem. A. *4*, 11859-11869. 10.1039/c6ta01757f.

44. Hanikel, N., Prevot, M.S., Fathieh, F., Kapustin, E.A., Lyu, H., Wang, H., Diercks, N.J., Glover, T.G., and Yaghi, O.M. (2019). Rapid Cycling and Exceptional Yield in a Metal-Organic Framework Water Harvester. ACS Cent. Sci. *5*, 1699-1706. 10.1021/acscentsci.9b00745.

45. Zhang, J.-P., Zhang, Y.-B., Lin, J.-B., and Chen, X.-M. (2011). Metal Azolate Frameworks: From Crystal Engineering to Functional Materials. Chem. Rev. *112*, 1001-1033. 10.1021/cr200139g.

46. Rieth, A.J., Yang, S., Wang, E.N., and Dinca, M. (2017). Record Atmospheric Fresh Water Capture and Heat Transfer with a Material Operating at the Water Uptake Reversibility Limit. ACS Cent. Sci. *3*, 668-672. 10.1021/acscentsci.7b00186.

47. Rieth, A.J., Wright, A.M., Rao, S., Kim, H., LaPotin, A.D., Wang, E.N., and Dincă, M. (2018).

Tunable Metal–Organic Frameworks Enable High-Efficiency Cascaded Adsorption Heat Pumps. J. Am. Chem. Soc. *140*, 17591-17596. 10.1021/jacs.8b09655.

48. Rieth, A.J., Wright, A.M., Skorupskii, G., Mancuso, J.L., Hendon, C.H., and Dinca, M. (2019). Record-Setting Sorbents for Reversible Water Uptake by Systematic Anion Exchanges in Metal-Organic Frameworks. J. Am. Chem. Soc. *141*, 13858-13866. 10.1021/jacs.9b06246.

49. Rieth, A.J., Tulchinsky, Y., and Dincă, M. (2016). High and Reversible Ammonia Uptake in Mesoporous Azolate Metal–Organic Frameworks with Open Mn, Co, and Ni Sites. J. Am. Chem. Soc. *138*, 9401-9404. 10.1021/jacs.6b05723.

50. Valentine, M.L., Yin, G., Oppenheim, J.J., Dinca, M., and Xiong, W. (2023). Ultrafast Water H-Bond Rearrangement in a Metal-Organic Framework Probed by Femtosecond Time-Resolved Infrared Spectroscopy. J. Am. Chem. Soc. *145*, 11482-11487. 10.1021/jacs.3c01728.

51. Lu, F.-F., Gu, X.-W., Wu, E., Li, B., and Qian, G. (2023). Systematic evaluation of water adsorption in isoreticular UiO-type metal–organic frameworks. J. Mater. Chem. A *11*, 1246-1255. 10.1039/d2ta07392g.

52. Zhu, N.X., Wei, Z.W., Chen, C.X., Xiong, X.H., Xiong, Y.Y., Zeng, Z., Wang, W., Jiang, J.J., Fan, Y.N., and Su, C.Y. (2022). High Water Adsorption MOFs with Optimized Pore-Nanospaces for Autonomous Indoor Humidity Control and Pollutants Removal. Angew. Chem. Int. Ed. Engl. *61*, e202112097. 10.1002/anie.202112097.

53. Zheng, J., Vemuri, R.S., Estevez, L., Koech, P.K., Varga, T., Camaioni, D.M., Blake, T.A., McGrail, B.P., and Motkuri, R.K. (2017). Pore-Engineered Metal-Organic Frameworks with Excellent Adsorption of Water and Fluorocarbon Refrigerant for Cooling Applications. J. Am. Chem. Soc. *139*, 10601-10604. 10.1021/jacs.7b04872.

54. Mondloch, J.E., Katz, M.J., Planas, N., Semrouni, D., Gagliardi, L., Hupp, J.T., and Farha, O.K. (2014). Are Zr6-based MOFs water stable? Linker hydrolysis vs. capillary-force-driven channel collapse. Chem. Commun. *50*, 8944-8946. 10.1039/c4cc02401j.

55. Hanikel, N., Kurandina, D., Chheda, S., Zheng, Z., Rong, Z., Neumann, S.E., Sauer, J., Siepmann, J.I., Gagliardi, L., and Yaghi, O.M. (2023). MOF Linker Extension Strategy for Enhanced Atmospheric Water Harvesting. ACS Cent. Sci. *9*, 551-557. 10.1021/acscentsci.3c00018.

56. Reinsch, H., van der Veen, M.A., Gil, B., Marszalek, B., Verbiest, T., de Vos, D., and Stock, N. (2012). Structures, Sorption Characteristics, and Nonlinear Optical Properties of a New Series of Highly Stable Aluminum MOFs. Chem. Mater. *25*, 17-26. 10.1021/cm3025445.

57. Cadiau, A., Lee, J.S., Damasceno Borges, D., Fabry, P., Devic, T., Wharmby, M.T., Martineau, C., Foucher, D., Taulelle, F., Jun, C.H., et al. (2015). Design of hydrophilic metal organic framework water adsorbents for heat reallocation. Adv. Mater. *27*, 4775-4780. 10.1002/adma.201502418.

58. Cho, K.H., Borges, D.D., Lee, U.H., Lee, J.S., Yoon, J.W., Cho, S.J., Park, J., Lombardo, W., Moon, D., Sapienza, A., et al. (2020). Rational design of a robust aluminum metal-

organic framework for multi-purpose water-sorption-driven heat allocations. Nat. Commun. *11*, 5112. 10.1038/s41467-020-18968-7.

59. Lenzen, D., Zhao, J., Ernst, S.J., Wahiduzzaman, M., Ken Inge, A., Frohlich, D., Xu, H., Bart, H.J., Janiak, C., Henninger, S., et al. (2019). A metal-organic framework for efficient water-based ultra-low-temperature-driven cooling. Nat. Commun. *10*, 3025. 10.1038/s41467-019-10960-0.

60. Zheng, Z., Hanikel, N., Lyu, H., and Yaghi, O.M. (2022). Broadly Tunable Atmospheric Water Harvesting in Multivariate Metal-Organic Frameworks. J. Am. Chem. Soc. *144*, 22669-22675. 10.1021/jacs.2c09756.

61. Li, B., Lu, F.F., Gu, X.W., Shao, K., Wu, E., and Qian, G. (2022). Immobilization of Lewis Basic Nitrogen Sites into a Chemically Stable Metal-Organic Framework for Benchmark Water-Sorption-Driven Heat Allocations. Adv. Sci. *9*, e2105556. 10.1002/advs.202105556.

62. van der Veen, M.A., Canossa, S., Wahiduzzaman, M., Nenert, G., Frohlich, D., Rega, D., Reinsch, H., Shupletsov, L., Markey, K., De Vos, D.E., et al. (2023). Confined Water Cluster Formation in Water Harvesting by Metal–Organic Frameworks: CAU‐10‐H versus CAU‐10‐CH3. Adv. Mater., 2210050. 10.1002/adma.202210050.

63. Dong, Z., Sun, Y., Chu, J., Zhang, X., and Deng, H. (2017). Multivariate Metal–Organic Frameworks for Dialing-in the Binding and Programming the Release of Drug Molecules. J. Am. Chem. Soc. *139*, 14209-14216. 10.1021/jacs.7b07392.

64. Zhang, J.P., Zhu, A.X., Lin, R.B., Qi, X.L., and Chen, X.M. (2011). Pore surface tailored SOD-type metal-organic zeolites. Adv. Mater. *23*, 1268-1271. 10.1002/adma.201004028.

65. Schlüsener, C., Xhinovci, M., Ernst, S.-J., Schmitz, A., Tannert, N., and Janiak, C. (2019). Solid-Solution Mixed-Linker Synthesis of Isoreticular Al-Based MOFs for an Easy Hydrophilicity Tuning in Water-Sorption Heat Transformations. Chem. Mater. *31*, 4051-4062. 10.1021/acs.chemmater.9b00617.

66. Chen, Y., Idrees, K.B., Mian, M.R., Son, F.A., Zhang, C., Wang, X., and Farha, O.K. (2023). Reticular Design of Precise Linker Installation into a Zirconium Metal–Organic Framework to Reinforce Hydrolytic Stability. J. Am. Chem. Soc. *145*, 3055-3063. 10.1021/jacs.2c11830.

67. Wright, A.M., Rieth, A.J., Yang, S., Wang, E.N., and Dinca, M. (2018). Precise control of pore hydrophilicity enabled by post-synthetic cation exchange in metal-organic frameworks. Chem. Sci. *9*, 3856-3859. 10.1039/c8sc00112j.

68. Park, J., Feng, D., and Zhou, H.-C. (2015). Dual Exchange in PCN-333: A Facile Strategy to Chemically Robust Mesoporous Chromium Metal–Organic Framework with Functional Groups. J. Am. Chem. Soc. *137*, 11801-11809. 10.1021/jacs.5b07373.

69. Han, Y., Das, P., He, Y., Sorescu, D.C., Jordan, K.D., and Rosi, N.L. (2022). Crystallographic Mapping and Tuning of Water Adsorption in Metal-Organic Frameworks Featuring Distinct Open Metal Sites. J. Am. Chem. Soc. *144*, 19567-19575. 10.1021/jacs.2c08717.

70. Yang, L., Idrees, K.B., Chen, Z., Knapp, J., Chen, Y., Wang, X., Cao, R., Zhang, X., Xing,

H., Islamoglu, T., and Farha, O.K. (2021). Nanoporous Water-Stable Zr-Based Metal–Organic Frameworks for Water Adsorption. ACS Appl. Nano Mater. *4*, 4346-4350. 10.1021/acsanm.1c00638.

71. Deria, P., Chung, Y.G., Snurr, R.Q., Hupp, J.T., and Farha, O.K. (2015). Water stabilization of Zr6-based metal–organic frameworks via solvent-assisted ligand incorporation. Chem. Sci. *6*, 5172-5176. 10.1039/c5sc01784j.

72. Tu, Y., Wang, R., Zhang, Y., and Wang, J. (2018). Progress and Expectation of Atmospheric Water Harvesting. Joule *2*, 1452-1475. 10.1016/j.joule.2018.07.015.

73. LaPotin, A., Kim, H., Rao, S.R., and Wang, E.N. (2019). Adsorption-Based Atmospheric Water Harvesting: Impact of Material and Component Properties on System-Level Performance. Acc. Chem. Res. *52*, 1588-1597. 10.1021/acs.accounts.9b00062.

74. Ejeian, M., and Wang, R.Z. (2021). Adsorption-based atmospheric water harvesting. Joule *5*, 1678-1703. 10.1016/j.joule.2021.04.005.

75. Almassad, H.A., Abaza, R.I., Siwwan, L., Al-Maythalony, B., and Cordova, K.E. (2022). Environmentally adaptive MOF-based device enables continuous self-optimizing atmospheric water harvesting. Nat. Commun. *13*, 4873. 10.1038/s41467-022-32642-0.

76. van der Veen, M.A., Canossa, S., Wahiduzzaman, M., Nenert, G., Frohlich, D., Rega, D., Reinsch, H., Shupletsov, L., Markey, K., De Vos, D.E., et al. (2023). Confined Water Cluster Formation in Water Harvesting by Metal-Organic Frameworks: CAU-10-H versus CAU-10-CH(3). Adv Mater, e2210050. 10.1002/adma.202210050.

77. Fathieh, F., Kalmutzki, M.J., Kapustin, E.A., Waller, P.J., Yang, J., and Yaghi, O.M. (2018). Practical water production from desert air. Sci. Adv. *4*, eaat3198.

78. Henninger, S.K., Jeremias, F., Kummer, H., and Janiak, C. (2011). MOFs for Use in Adsorption Heat Pump Processes. Eur. J. Inorg. Chem. *2012*, 2625-2634. 10.1002/ejic.201101056.

79. Lee, J.S., Yoon, J.W., Mileo, P.G.M., Cho, K.H., Park, J., Kim, K., Kim, H., de Lange, M.F., Kapteijn, F., Maurin, G., et al. (2019). Porous Metal-Organic Framework CUK-1 for Adsorption Heat Allocation toward Green Applications of Natural Refrigerant Water. ACS Appl. Mater. Interfaces *11*, 25778-25789. 10.1021/acsami.9b02605.

80. Lenzen, D., Bendix, P., Reinsch, H., Frohlich, D., Kummer, H., Mollers, M., Hugenell, P.P.C., Glaser, R., Henninger, S., and Stock, N. (2018). Scalable Green Synthesis and Full-Scale Test of the Metal-Organic Framework CAU-10-H for Use in Adsorption-Driven Chillers. Adv. Mater. *30*. 10.1002/adma.201705869.

81. Cui, S., Qin, M., Marandi, A., Steggles, V., Wang, S., Feng, X., Nouar, F., and Serre, C. (2018). Metal-Organic Frameworks as advanced moisture sorbents for energy-efficient high temperature cooling. Sci. Rep. *8*, 15284. 10.1038/s41598-018-33704-4.

82. Zhang, J., Li, P., Zhang, X., Ma, X., and Wang, B. (2020). Aluminum Metal-Organic Frameworks with Photocatalytic Antibacterial Activity for Autonomous Indoor Humidity

Control. ACS Appl. Mater. Interfaces *12*, 46057-46064. 10.1021/acsami.0c12693.

83. Wollmann, P., Leistner, M., Grählert, W., Throl, O., Dreisbach, F., and Kaskel, S. (2012). Infrasorb: Optical detection of the heat of adsorption for high throughput adsorption screening of porous solids. Microporous and Mesoporous Mater. *149*, 86-94. 10.1016/j.micromeso.2011.08.028.

84. Clayson, I.G., Hewitt, D., Hutereau, M., Pope, T., and Slater, B. (2020). High Throughput Methods in the Synthesis, Characterization, and Optimization of Porous Materials. Adv. Mater. *32*, e2002780. 10.1002/adma.202002780.

85. Krause, S., Bon, V., Stoeck, U., Senkovska, I., Tobbens, D.M., Wallacher, D., and Kaskel, S. (2017). A Stimuli-Responsive Zirconium Metal-Organic Framework Based on Supermolecular Design. Angew. Chem. Int. Ed. Engl. *56*, 10676-10680. 10.1002/anie.201702357.

86. Shivanna, M., Bezrukov, A.A., Gascon-Perez, V., Otake, K.I., Sanda, S., O'Hearn, D.J., Yang, Q.Y., Kitagawa, S., and Zaworotko, M.J. (2022). Flexible Coordination Network Exhibiting Water Vapor-Induced Reversible Switching between Closed and Open Phases. ACS Appl. Mater. Interfaces. *14*, 39560-39566. 10.1021/acsami.2c10002.

87. Chen, Z., Shao, Z., Tang, Y., Deng, F., Du, S., and Wang, R. (2022). Study of the Scale-Up Effect on the Water Sorption Performance of MOF Materials. ACS Mater. Au *3*, 43-54. 10.1021/acsmaterialsau.2c00052.

88. Camur, C., Babu, R., Suarez Del Pino, J.A., Rampal, N., Perez-Carvajal, J., Hugenell, P., Ernst, S.J., Silvestre-Albero, J., Imaz, I., Madden, D.G., et al. (2023). Monolithic Zirconium-Based Metal-Organic Frameworks for Energy-Efficient Water Adsorption Applications. Adv. Mater., e2209104. 10.1002/adma.202209104.

89. Kummer, H., Jeremias, F., Warlo, A., Füldner, G., Fröhlich, D., Janiak, C., Gläser, R., and Henninger, S.K. (2017). A Functional Full-Scale Heat Exchanger Coated with Aluminum Fumarate Metal–Organic Framework for Adsorption Heat Transformation. Ind. Eng. Chem. Res. *56*, 8393-8398. 10.1021/acs.iecr.7b00106.

90. Chen, Z., Wasson, M.C., Drout, R.J., Robison, L., Idrees, K.B., Knapp, J.G., Son, F.A., Zhang, X., Hierse, W., Kühn, C., et al. (2021). The state of the field: from inception to commercialization of metal–organic frameworks. Faraday Discuss. *225*, 9-69. 10.1039/d0fd00103a.

91. Rubio-Martinez, M., Hadley, T.D., Batten, M.P., Constanti-Carey, K., Barton, T., Marley, D., Monch, A., Lim, K.S., and Hill, M.R. (2016). Scalability of Continuous Flow Production of Metal-Organic Frameworks. ChemSusChem *9*, 938-941. 10.1002/cssc.201501684.

92. Zheng, Z., Nguyen, H.L., Hanikel, N., Li, K.K., Zhou, Z., Ma, T., and Yaghi, O.M. (2023). High-yield, green and scalable methods for producing MOF-303 for water harvesting from desert air. Nat. Protoc. *18*, 136-156. 10.1038/s41596-022-00756-w.