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MOF water harvesters

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The advancement of additional methods for freshwater generation is imperative to effectively address the global water shortage crisis. In this regard, extraction of the ubiquitous atmospheric moisture is a powerful strategy allowing for decentralized access to potable water. The energy requirements as well as the temporal and spatial restrictions of this approach can be substantially reduced if an appropriate sorbent is integrated in the atmospheric water generator. Recently, metal–organic frameworks (MOFs) have been successfully employed as sorbents to harvest water from air, making atmospheric water generation viable even in desert environments. Herein, the latest progress in the development of MOFs capable of extracting water from air and the design of atmospheric water harvesters deploying such MOFs are reviewed. Furthermore, future directions for this emerging field, encompassing both material and device improvements, are outlined.

Over fifty percent of the global population experiences water stress[1]. This number is projected to increase because of climate change, growth of the global population and ongoing water pollution[2]. In this context, the uneven spatial and temporal distribution of freshwater resources is particularly problematic, as lack of access to safe water leads to decline of health and quality of life, and can trigger severe conflicts[3,4]. While improved water management systems could alleviate the situation in some countries, overall, supplemental generation of freshwater will be necessary—especially in arid regions. In this regard, desalination is a powerful technology, yet only viable for coastal regions[5]. As such, land-locked nations and rural areas in developing countries are unlikely to benefit from desalination because of limitations in water transport capabilities associated with financial and infrastructural factors. A decentralized strategy for freshwater generation, which makes water transport requirements obsolete, is the direct generation of water from the ubiquitous atmospheric moisture. Importantly, this method has the potential to provide mobile, distributed, community-managed, off-grid access to safe potable water without environmental costs[6].

Atmospheric water generation can be achieved through three different processes: (1) fog collection by means of large nets, (2) cooling air below its dew point (the temperature at which the air is saturated with water) and (3) sorbent-assisted water capture. The first method—albeit relatively inexpensive and low-maintenance—depends heavily on frequent occurrence of fog and is thus usually restricted to mountainous, coastal areas[7]. In contrast, dewing has a much broader range of geographic applicability, however, its energy efficiency and water productivity are heavily dependent on the local climate (Fig. 1), with the dew point and ambient temperature being the key limiting factors[8]. To initiate condensation, moist air needs to be cooled below the dew point through removal of the associated sensible heat (energy transfer required to cool down the air). Furthermore, the phase change of water is accompanied by latent heat (energy dissipation during condensation). For a given amount of collected water, the latent heat is approximately constant under typical ambient conditions and corresponds to the unavoidable, minimal energetic investment for the dewing process. In contrast, the sensible heat per amount of captured water can vary substantially, to a point where dewing under hot and dry conditions

becomes very energy intensive and sometimes infeasible, in that the sensible heat can reach several times the amount of the latent heat.
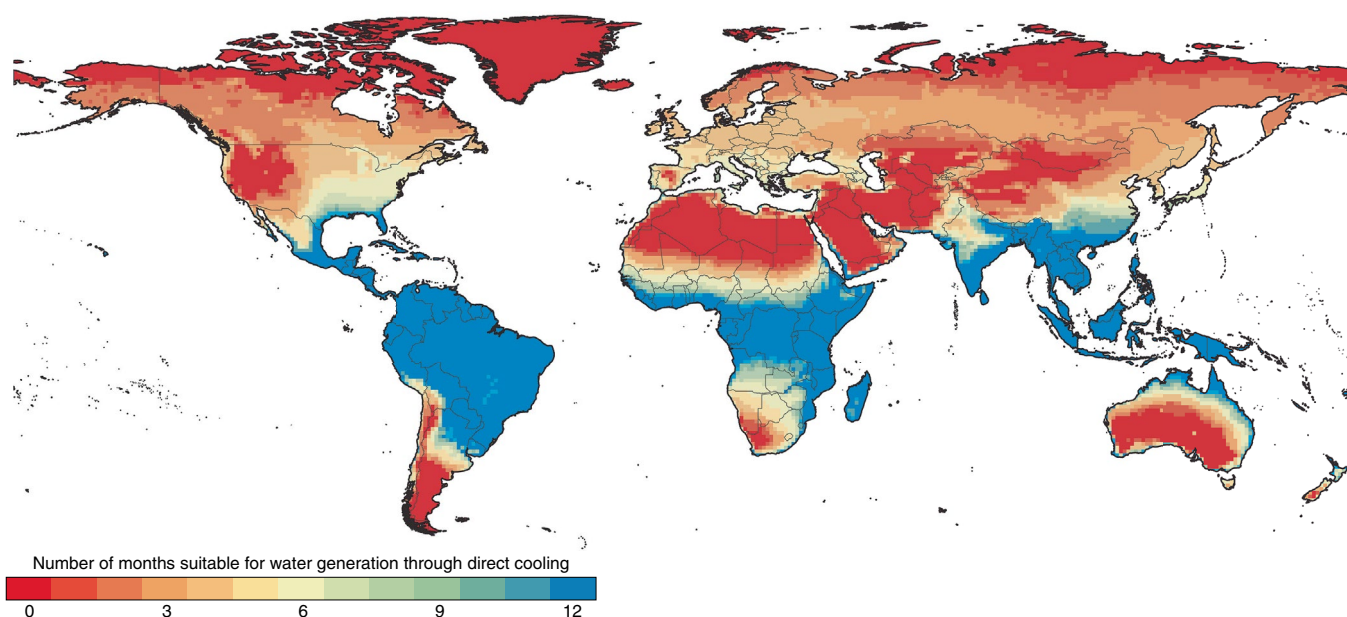
To evaluate the feasibility of atmospheric water harvesting through direct cooling, a moisture harvesting index (MHI) was defined as the ratio of latent heat to total heat (latent and sensible heat, Fig. 1)[9]. Naturally, low MHI values are associated with unfavourable conditions for direct cooling. To avoid chilling down large amounts of air to extract only small amounts of water under such disadvantageous conditions, sorbent-assisted water harvesting has been conceived[10,11]. This technology relies on ad- or absorption of atmospheric water by a desiccant. This water vapour is then released from the sorbent by applying a temperature or pressure swing, preferentially powered by low-grade energy sources, such as solar thermal or waste heat. Finally, the generated concentrated water vapour is introduced to a condenser. This process substantially reduces the sensible heat and consequently the specific energy consumption for water condensation under arid conditions, thus making water harvesting a viable strategy for generating freshwater. Notably, the sorbent-assisted approach is neither spatially nor temporally restricted and can, in principle, be employed at any location and at any time of the year.

Sorbents for water harvesting

An ideal sorbent for water harvesting needs to (1) maintain its water capacity after a multitude of water uptake and release cycles, (2) exhibit a high water sorption working capacity under operational conditions (step-shaped isotherms with negligible hysteresis are generally preferred), (3) have a low regeneration (removal of water molecules) temperature and (4) possess desirable dynamic water sorption properties.

In principle, absorbents—substances which take up water into their bulk phase—can be used for water harvesting. An inexpensive class of absorbents are hygroscopic salts, such as LiCl or $CaCl_2$, which can take up water at low relative humidity. However, they tend to deliquesce (become liquid through absorbing moisture from air) leading to desiccant leakage and subsequent corrosion of the water harvesting unit. To overcome this problem, impregnating salts onto a porous matrix has been proposed, but only with limited success in preventing desiccant spillover and salt particle agglomeration[12]. Another proposed alternative is the use of concentrated salt

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Fig. 1 | World map displaying the spatial and temporal feasibility of atmospheric water generation through direct cooling. The data is plotted onto a gridded map with a resolution of 1° × 1°. For each grid point and month, the moisture harvesting index is calculated as the ratio of latent heat to total heat (latent and sensible heat) that needs to be dissipated during the condensation process. A condensation temperature of 4 °C is assumed and a moisture harvesting index value lower than 0.3 is considered unfavourable for water generation from air through dewing[9]. Accordingly, the number of months favourable for water production through direct cooling are indicated for each grid point through colour coding, as specified in the legend. The gridded temperature and dew point data are obtained from the NASA Goddard Earth Sciences Data and Information Services Center (GES DISC)[60]. While the map implicates that in polar regions direct cooling is infeasible because of the low dew point, these areas are usually not water stressed. The other areas marked in yellow to red are often water-stressed, however, water harvesting becomes feasible with the appropriate sorbent.

solutions acting as liquid sorbents, but they usually require a complex apparatus, high capital costs and diligent management[6].

Much more attractive, because of their easier processability and lower cost of implementation, are adsorbents—porous solids with an accessible internal surface where water molecules can bind to—followed by subsequent pore filling. The most common water adsorbents are silica gels and zeolites. While silica gels exhibit a low working capacity due to the linear isotherm profile, zeolites are highly hydrophilic and energy intensive to regenerate, a severe limitation if low-grade heating is to be used for water desorption. Noteworthy, zeotype materials—inorganic, crystalline sorbents with network topologies similar to zeolites (for example, aluminophosphates)—could be interesting for water harvesting applications because they tend to be less hydrophilic than zeolites and can exhibit step-shaped water isotherm profiles. However, most of them are not hydrothermally stable with few promising exceptions[13,14].

A unique class of adsorbents are MOFs, constructed from inorganic clusters (or secondary building units, SBUs) linked by organic molecules ('linkers') to form robust, crystalline and permanently porous framework structures[15]. A large variety of SBUs, linker molecules and network topologies can be implemented in MOFs, allowing for a high degree of chemical and structural tunability, and the ability to tailor their properties for a plethora of applications[16,17]. Moreover, the ultra-high porosity exhibited by some of these materials can be used for large gas and vapour uptakes[18–20]. Consequently, MOFs have been proposed and utilized as sorbents for atmospheric water harvesting[11,21–24]. In this Review Article, we would like to highlight the enormous potential of this class of materials for moisture capture from air by addressing both MOF development and its practical integration in water harvesters.

Reticular design of MOFs for water harvesting

Several comprehensive summaries addressing water stability and structure–function relationships of MOFs for water sorption have recently been published[25–27]. Herein, we would like to focus on the main achievements of reticular design of MOFs for atmospheric water harvesting (Fig. 2).

Stability under operational conditions. A fundamental prerequisite for a water harvesting material is hydrolytic stability. Many MOFs—usually constructed through metal–carboxylate coordination bonds—may not have long-term water stability, which is attributable to hydrolysis of the coordination bond between SBU and the linker. In this regard, using azolate-based linker molecules (for example, pyrazolates), stronger Brønsted bases which thus form stronger metal–linker coordination bonds, has been shown to be a viable strategy to design hydrolysis-resistant MOFs[28]. Another successful method is the generation of kinetically water-stable MOFs by employment of highly connected SBUs, such as $Zr_6O_4(OH)_4(\text{-COO})_{12}$ or $(Al(OH)(\text{-COO})_2)_\infty$, where hydrolysis is prevented by steric screening of the SBU by the linkers (Fig. 2)[11,23]. Notably, this can also be achieved by using bulky linkers[29]. Furthermore, inert cations (for example, Cr^{3+} in octahedral coordination geometry) can be utilized in MOFs, such that any potential hydrolysis would be negligibly slow, making the corresponding framework hydrolytically metastable, and capable of long-term use in water harvesters[30].

In addition to hydrolytic resilience, the MOF has to exhibit high architectural stability to withstand the capillary forces acting on the pore walls during water release[31]. While hydrolysis can easily be predicted based on basic chemical principles and steric effects, architectural stability is rather difficult to predict and needs to be experimentally determined. The best way to gauge the stability of
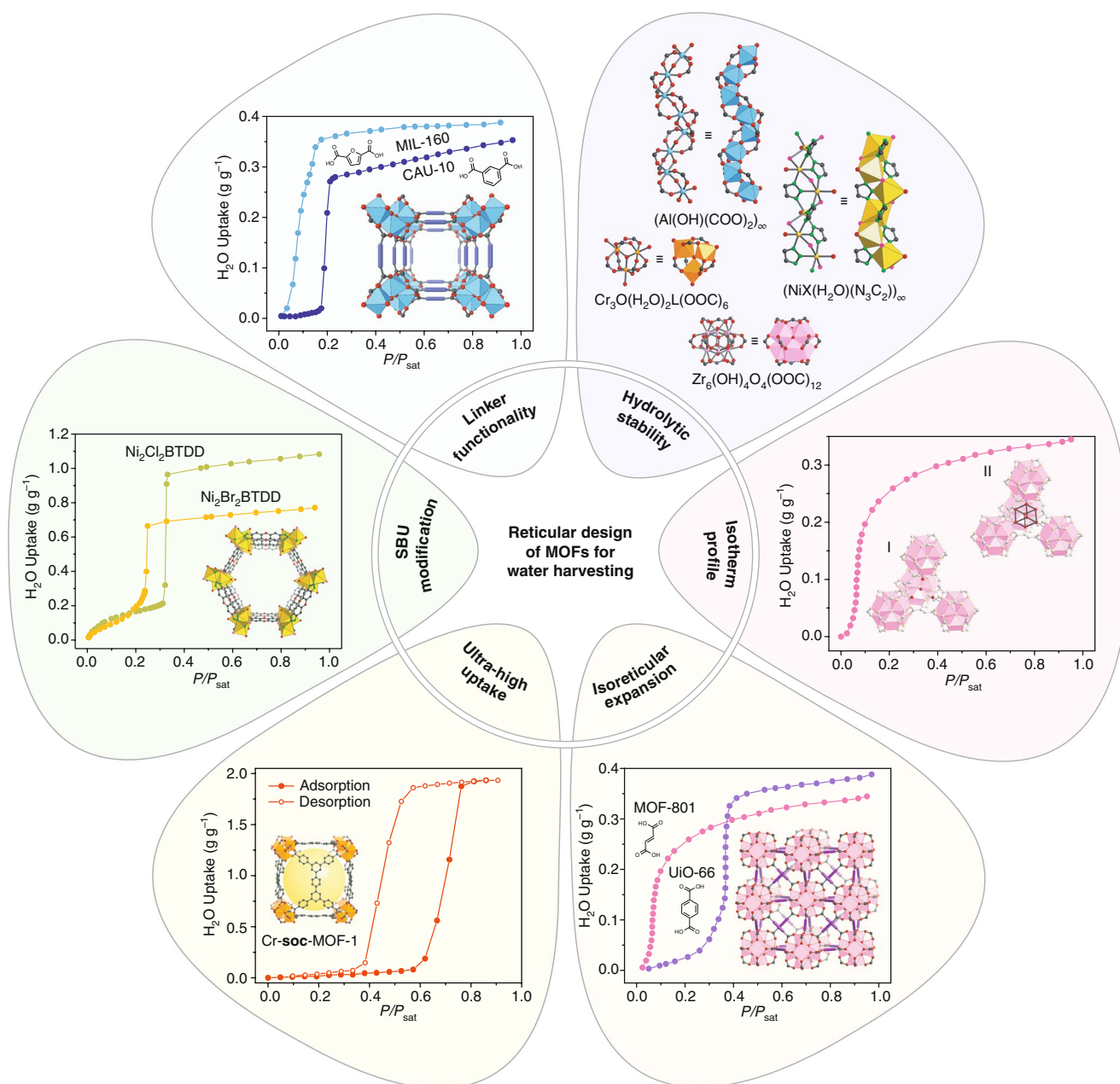
Fig. 2 | Reticular design of MOFs for atmospheric water harvesting. Important features of reticular chemistry rendering MOFs a unique class of sorbents for atmospheric water harvesting are represented by selected examples with respective water sorption isotherms, if applicable. Clockwise, starting from the upper-right corner: examples of secondary building units (SBUs) which can render a MOF hydrolytically stable; step-shaped isotherm profile of MOF-801 associated with water cluster formation upon pore filling[11]; effect of pore volume on water sorption characteristics in the isoreticular frameworks MOF-801 and UiO-66[11]; Cr-**soc**-MOF-1, a water-stable MOF with the highest reported water uptake[35]; modification of water sorption properties through conversion of Ni₂Cl₂BTDD to Ni₂Br₂BTDD by anion exchange at the SBU[41]; influence of linker functionality on the water sorption properties in the isoreticular frameworks CAU-10 and MIL-160[38]. The SBUs are shown in their hydrated forms where applicable. All hydrogen atoms are omitted for clarity. Pink, Zr; orange, Cr; yellow, Ni; blue, Al; grey, C; red, O; green, N; P, water vapour pressure; P_{sat}, saturation water vapour pressure.

a MOF under operational conditions is to conduct a water adsorption–desorption cycling experiment, which probes both the hydrolytic and architectural stabilities.

Step-shaped isotherm profile. Step-shaped water sorption isotherms are preferred for water harvesting, because large water uptakes and releases can be achieved through relatively small temperature or pressure gradients—a necessary prerequisite for energy efficient water release from the sorbent. Simultaneously, the position of the step fundamentally determines the operation regime

of a sorbent, as the uptake at partial vapour pressures below this step is usually small or negligible. Unlike amorphous sorbents and hygroscopic salts, MOFs tend to exhibit step-shaped isotherm profiles. The occurrence of step-shaped water sorption isotherms can be explained by the formation of ordered, hydrogen-bonded water molecule networks within the crystalline MOF during the pore-filling process. A study on MOF-801 ($Zr_6O_4(OH)_4($fumarate$)_6$), using both X-ray and neutron diffraction techniques, showed that at low partial pressures water molecules first adsorb at the so-called primary adsorption sites located close to the μ_3-OH

groups of the Zr-SBU. With increasing vapour pressure, additional water molecules bind cooperatively to the water molecules at the primary adsorption sites to form water cubane clusters within the MOF pores (Fig. 2)[11]. Analogously, formation of ordered water molecule clusters was shown in the one-dimensional channels of the aluminium-based MOF MIL-160 (Al(OH)(FDC), where FDC^{2-} is 2,5-furandicarboxylate), constructed from infinite chains of *cis*-shared AlO$_6$-octahedra connected by FDC^{2-} linkers[32]. Further studies of water molecules in the confined micropore environments of MOFs could lead to advanced framework designs for manipulation of water behaviour on the molecular level and thus further improvement of the framework's water harvesting properties.

Isoreticular expansion. One of the unique features of reticular chemistry of MOFs is isoreticular synthesis: once the synthetic conditions for the formation of a MOF with a particular SBU have been found, they can be reused, sometimes with slight modifications, for linkers of the same modality but different size, length and/or bearing different side chains to obtain frameworks of the same underlying net but with different pore size and/or environment[33]. Naturally, this can be of great use for water harvesting, as the water uptake capacity of an adsorbent is dependent on its pore volume, which can be enhanced through an isoreticular expansion of the MOF with a longer linker. An example for two isoreticular MOFs is MOF-801 and UiO-66 (Zr$_6$O$_4$(OH)$_4$(BDC)$_6$, where BDC^{2-} is 1,4-benzenedicarboxylate) (Fig. 2). The former is constructed from fumarate and the latter is made from the slightly longer BDC^{2-} linker[11,34]. As a result, UiO-66 exhibits a larger pore volume and thus a larger water capacity. However, with the increase in volume, the pore becomes less hydrophilic and consequently, the pore-filling step occurs at higher partial pressures. We note that an isoreticular expansion of a MOF may become unstable under cycling conditions, thus, this approach cannot always be used to generate a MOF with higher water uptake capacity[31].

Ultra-high uptake. It has been shown that MOFs with ultra-high porosity, exhibiting pore volumes of up to 5 cm^3 g^{-1}, can be synthesized and that these large pores can be made accessible to gas molecules by desolvation without pore collapse[20]. Nevertheless, the most porous reported MOFs are either made from the octahedral Zn$_4$O(-COO)$_6$ or the Cu$_2$(-COO)$_4$ paddle wheel SBU, both of which render the respective frameworks hydrolytically unstable[18–20,25]. The highest water uptake of a water-stable MOF was achieved by Cr-**soc**-MOF-1 (Cr$_3$O(TCPT)$_{1.5}$(H$_2$O)$_2$Cl, where TCPT^{4-} is 3,3',5,5''-tetrakis(4-carboxylatephenyl)-*p*-terphenyl), taking up to 1.95 g g^{-1} while exhibiting a pore volume of 2.1 cm^3 g^{-1} (Fig. 2)[35]. This suggests that water-stable MOFs with even higher water uptakes should, in principle, be feasible, as the water uptake of a material is correlated with its pore volume. However, an important consideration is the architectural stability of the framework, which becomes crucial during regeneration due to the enormous capillary forces of water acting upon the framework walls. Moreover, the hydrophobicity of the framework increases with increasing pore volume, making it less viable for water harvesting under arid conditions. An additional challenge is the occurrence of capillary condensation for materials with a pore diameter larger than 20.76 Å (at 25 °C). This translates into hysteresis in the water sorption isotherm and consequently an additional energy barrier during the regeneration process.

Linker functionality. Following the aforementioned principle of isoreticular synthesis, there have been considerable efforts to tune the shape of the water sorption isotherm by introducing functional side chains to the MOF backbone. In particular, for water harvesting applications in arid environments, it is interesting to use hydrophilic groups (for example, -COOH, -OH, -NH$_2$) to effectively shift the steep uptake region to lower relative humidities. Hydrophobic groups (for example, -OCH$_3$, -CH$_3$), on the contrary, shift the pore-filling step to higher partial pressures, while hydroneutral groups (-NO$_2$, -COOR, -COR) do not (significantly) change the step's position[26]. Adding hydrophilic side groups to a framework might make it more suitable for water adsorption in dry environments, however, a clear limitation of this approach is the reduction of the free pore volume and thus of the total water uptake capacity[36,37]. An elegant way to increase the hydrophilicity and retain the pore volume is the use of heterocycles in the MOF backbone. This strategy was pursued for the synthesis of the isoreticular framework MIL-160 with higher water affinity compared to the parent MOF CAU-10 (Al(OH)(isophthalate)) (Fig. 2)[38].

SBU modification. Different methods for SBU modifications have been developed[17] and employed to tune the water sorption properties of the framework. For instance, it is possible to exchange the metal cations in the SBU by submerging the MOF in a solution containing a different cation of the same valency and comparable size[39]. This method was used to increase the hydrolytic stability of frameworks constructed from Fe^{3+} to generate the more stable Cr^{3+} equivalents[30,35]. Cation exchange has also been employed to move the pore-filling step to lower relative humidities by successfully replacing coordinatively saturated cations with coordinatively unsaturated cations, thus introducing strongly binding metal sites into the framework, rendering it overall more polar[40]. Similar to the aforementioned introduction of heterocycles into the framework backbone, this method allows tuning of the MOF hydrophilicity without compromising the pore volume.

Likewise, anions in the SBU can be exchanged, as exemplified by the replacement of the Cl$^-$ by Br$^-$ anions in Ni$_2$Cl$_2$BTDD (BTDD^{2-}, bis (1*H*-1,2,3-triazolato[4,5-*b*],[4',5'-*i*])dibenzo[1,4]dioxin) to obtain Ni$_2$Br$_2$BTDD. This modification led to a slight contraction of the pore diameter by 0.1 nm, thus shifting the pore-filling step from a partial pressure of 0.32 to 0.24 (Fig. 2). As anticipated, the exchange to the heavier anion led to a significant decrease in gravimetric water uptake, but the volumetric uptake was shown to be only 15% lower compared to the parent MOF, making it a strong candidate for water harvesting under arid conditions[41].

Development of MOF water harvesters

All sorbent-assisted water harvesters have the same underlying principle: First, the water vapour is concentrated in the sorbent. Then, it is released from the sorbent by decreasing the relative vapour pressure of water in the environment around the MOF—initiated by either a temperature or a pressure swing. The generated, concentrated water vapour is then condensed to produce liquid water. This sorbent-assisted water harvesting process can be conducted once a day (monocyclic) or several times a day (multicyclic). Additionally, water release and condensation can be driven by an external energy source, such as through electric heating of the MOF, and vapour-compression or thermoelectric refrigeration, respectively, in an active water harvester. The passive device operates under ambient sunlight and natural cooling (Fig. 3).

Monocyclic water harvesters. A monocyclic water harvester relies on water uptake during the night, when the relative humidity is comparatively high due to the nocturnal temperature drop, and subsequent release of water during the day, when the sorbent is exposed to direct thermal radiation by the sun. The released vapour is concentrated in a confined space and can then be easily condensed due to its relatively high dew point. In the first reported proof-of-concept MOF water harvester, a condenser was interfaced with a thermoelectric cooler. However, only mild cooling was applied, suggesting that a passive device was, in principle, possible[21]. This was subsequently shown by the follow-up water harvester, where a heat sink
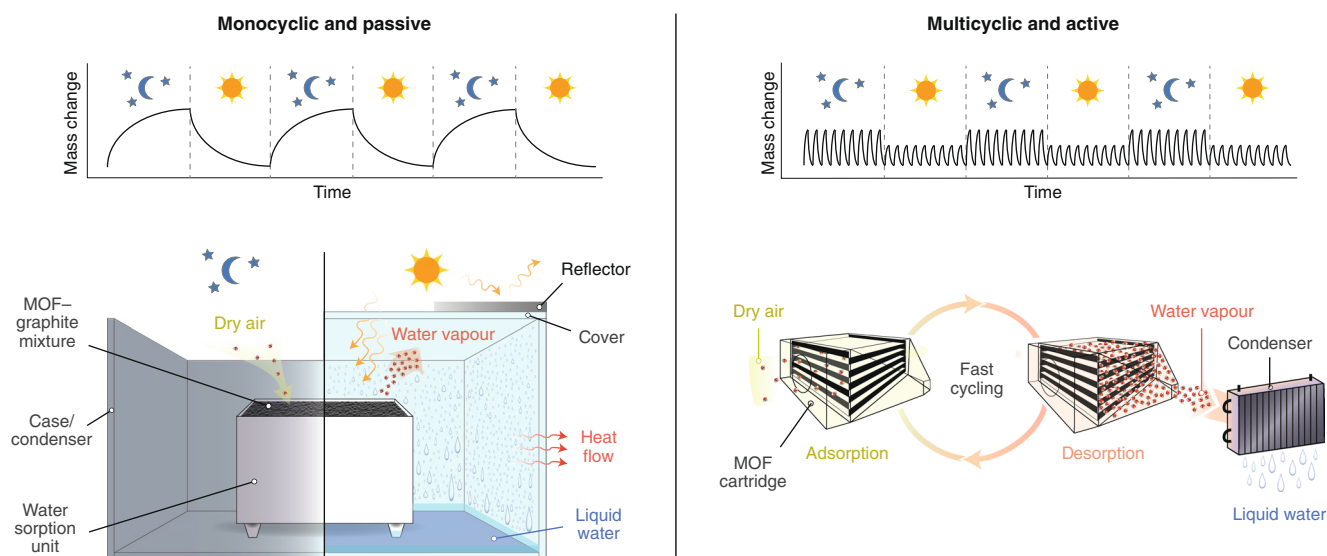
Fig. 3 | Juxtaposition of two classes of practical MOF water harvesters. A passive, monocyclic (left column)[23] and an active, multicyclic (right column)[24] water harvester. In the top row, the mass change associated with water uptake and release is sketched against time for both operation regimes. In the bottom row, the reported practical MOF water harvesters are depicted with important features and components labelled. Bottom-right image adapted with permission from ref. [24], American Chemical Society (ACS). Further permissions related to this material should be directed to the ACS.

was used to dissipate the condensation heat to the atmosphere[22]. Indeed, if the ambient temperature is below the dew point, condensation can be initiated passively by natural cooling. Notably, at high ambient temperatures—typical in desert environments—and to boost condensation efficiency, active cooling can be employed with the disadvantage of having higher energetic and maintenance requirements associated with the condenser apparatus.

Following the aforementioned principles of monocyclic, passive devices, the first scaled-up MOF water harvester delivering tangible amounts of water was constructed[23]. It was engineered from two sturdy, inexpensive parts: (1) a water harvesting unit holding ~1 kg of a MOF/graphite mixture and (2) a sealable enclosure built around the water harvesting unit that functioned as a condenser based on natural cooling. The use of graphite additive improved the solar absorptivity and heat conductivity of the mostly reflective and thermally isolating MOF powder. Additionally, a solar reflector was placed on top of the device to screen the enclosure walls from sunlight, such that they remained cool to allow for efficient condensation (Fig. 3). On average, this device exhibited a productivity of ~0.1 L kg_{MOF}^{-1} day^{-1} and was shown to be operable in the Sonoran Desert, Arizona (USA). In essence, this simple construct, made from inexpensive components, is capable of generating drinking water without external energy sources when outfitted with a MOF.

Multicyclic water harvesters. A fundamental drawback of monocyclic water harvesters is that their productivity is limited by the sorbent capacity. To overcome this restriction a multicyclic, scaled-up MOF water harvester has been developed[24]. It performed multiple adsorption–desorption cycles per day, resulting in a substantial increase in productivity compared to the previous device generations (~1 L kg_{MOF}^{-1} day^{-1}). The water harvester was active, solar-powered by a photovoltaic module to allow uptake and release cycling during day and night. The active design allowed for mild heating of the MOF with heating elements, leading to a compact device architecture since direct sun exposure of the MOF bed was not required. To enable fast heat and mass transfer, the MOF was placed in thin trays. These were assembled into a cartridge with two orthogonal sets of channels; one of which was used to supply large amounts of air to the MOF bed during the adsorption phase and
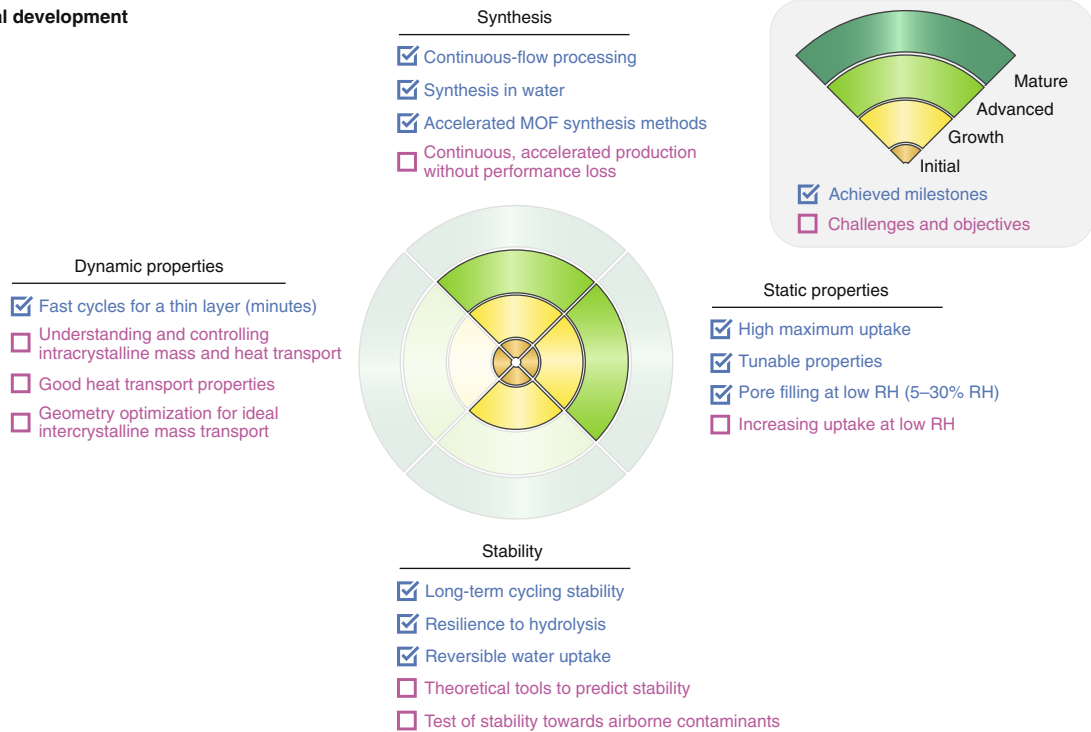
the other set of channels was used to slowly propel the water vapour liberated during the desorption phase to the condenser (Fig. 3). Notably, this harvester reliably delivered water during its three-day continuous operation in the Mojave Desert, California (USA).

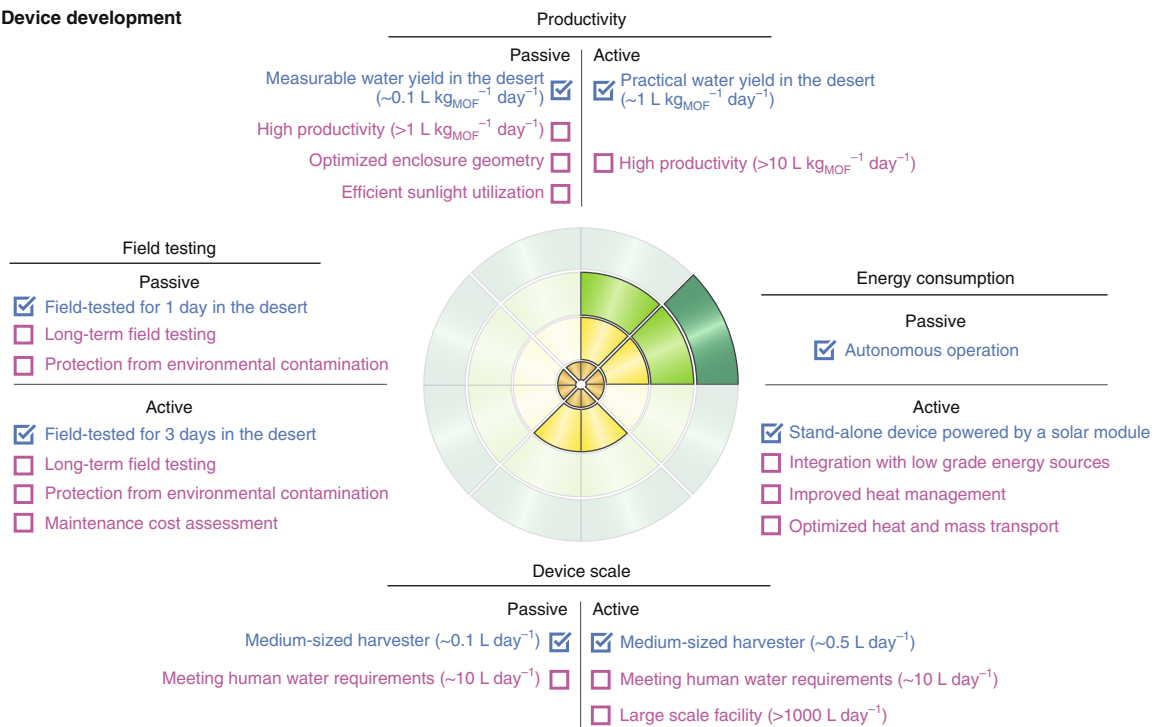## Current state of the art and future directions
MOFs have emerged as a very promising sorbent class for atmospheric water harvesting, especially in arid environments. Significant progress has been made in understanding the relationship between the reticular chemistry of MOFs and the respective static water sorption properties. Moreover, several MOF-assisted atmospheric water harvesters were engineered and successfully operated in desert environments. Nevertheless, there remain many research opportunities to expand this emerging and exciting field on both the material and device development level. A summary of the different aspects of this technology, the corresponding state of the art, and proposed opportunities for future directions of investigation is provided in Fig. 4.

Material development. An important pre-requisite for commercialization of MOF-based atmospheric water harvesters is the cost-effective production and processing of MOFs on a large scale, preferentially through environmentally sustainable means. In this regard, a great variety of methods have been developed to reduce the reaction time from days—typical for the conventional solvothermal synthesis—to hours and even minutes (for example, electrochemical, microwave, mechanochemical and spray-drying synthesis)[42]. Additionally, successful syntheses of the relevant MOFs have recently been shown in water as a solvent and some of them even under a continuous-flow regime[23,38,43,44]. It is worth noting that the latest progress in MOF powder processing made large-scale MOF applications and production viable and profitable[42,45]. Hence, several companies aiming to facilitate the industrial production of MOFs have been founded and it is safe to assume that production costs will drop significantly in the future. One current challenge is the retention of the water sorption performance upon accelerated, large-scale synthesis, which can promote the existence of structural defects[44] and in turn can significantly affect the water sorption properties[46].

Material development

Synthesis

☑ Continuous-flow processing
☑ Synthesis in water
☑ Accelerated MOF synthesis methods
☐ Continuous, accelerated production without performance loss

Mature
Advanced
Growth
Initial

☑ Achieved milestones
☐ Challenges and objectives

Dynamic properties

☑ Fast cycles for a thin layer (minutes)
☐ Understanding and controlling intracrystalline mass and heat transport
☐ Good heat transport properties
☐ Geometry optimization for ideal intercrystalline mass transport

Static properties

☑ High maximum uptake
☑ Tunable properties
☑ Pore filling at low RH (5–30% RH)
☐ Increasing uptake at low RH

Stability

☑ Long-term cycling stability
☑ Resilience to hydrolysis
☑ Reversible water uptake
☐ Theoretical tools to predict stability
☐ Test of stability towards airborne contaminants

Device development

Productivity

Passive | Active

Measurable water yield in the desert ($\sim$0.1 L kg_{MOF}^{-1} day^{-1}) ☑ | ☑ Practical water yield in the desert ($\sim$1 L kg_{MOF}^{-1} day^{-1})

High productivity (>1 L kg_{MOF}^{-1} day^{-1}) ☐

Optimized enclosure geometry ☐ | ☐ High productivity (>10 L kg_{MOF}^{-1} day^{-1})

Efficient sunlight utilization ☐

Field testing

Passive

☑ Field-tested for 1 day in the desert
☐ Long-term field testing
☐ Protection from environmental contamination

Active

☑ Field-tested for 3 days in the desert
☐ Long-term field testing
☐ Protection from environmental contamination
☐ Maintenance cost assessment

Energy consumption

Passive

☑ Autonomous operation

Active

☑ Stand-alone device powered by a solar module
☐ Integration with low grade energy sources
☐ Improved heat management
☐ Optimized heat and mass transport

Device scale

Passive | Active

Medium-sized harvester ($\sim$0.1 L day^{-1}) ☑ | ☑ Medium-sized harvester ($\sim$0.5 L day^{-1})

Meeting human water requirements ($\sim$10 L day^{-1}) ☐ | ☐ Meeting human water requirements ($\sim$10 L day^{-1})

| ☐ Large scale facility (>1000 L day^{-1})

Fig. 4 | Assessment of the current state of the art and future directions of atmospheric water harvesting with MOFs. The different evaluated aspects are subdivided in material and device development. The current development stage, achieved milestones and future directions are indicated through progress bars and colour coding, as specified in the legend. RH, relative humidity.

Considerable efforts have been invested in understanding water stability and sorption properties of MOFs[25–27], leading to impressive achievements (Fig. 2). Importantly, developing theoretical tools to predict stability and water sorption properties would greatly accelerate the exploration and discovery of new high-performance materials. Moreover, studying water stability in the presence of air-borne contaminants, such as SO_x and NO_x, would resemble authentic field conditions, which would help in narrowing down suitable MOF candidates before employment in a water harvester. Another scarcely explored realm is the study of dynamic water

sorption properties. They are likely to vary significantly not only between different MOF structures—a result of different geometry and chemistry of the respective pore system—but also within the same material, under conditions corresponding to different points on the water sorption isotherm[47]. Furthermore, while intracrystalline mass transport in micrometre-sized MOF crystals can be fairly fast[24], heat transfer in these highly porous structures is, on the contrary, commonly very limited because of the low atomic density and the short phonon mean path[48,49]. Finding ways to circumvent this intrinsic constraint is of paramount importance to improve the efficiency of the temperature-actuated water harvesting cycle. For instance, optimizing MOF processing (for example, thin films or shaped bodies) or creating composites sharing the excellent sorption properties of MOFs and good heat transfer capabilities of another material are intriguing avenues of research. Some progress has been made on this front, but further improvement is needed to achieve better thermal properties[50–52].

Device development. When it comes to device development, atmospheric water harvesting with MOFs has been validated and demonstrated in medium-sized passive and active devices (Fig. 3). Henceforth, several aspects could be advanced beyond the current state of the art. First, the next stage in device development should be the design of a prototype operating a larger quantity of MOF, and capable of harvesting as much as several litres of water per day, matching human daily needs. This can be achieved by: (1) increasing the productivity of the MOF in a monocyclic device by optimizing enclosure geometry and sunlight utilization, or (2) reaching a productivity of several tens of litres of water per kilogram of MOF in a multicyclic harvester operating a large number of cycles per day, an aspect requiring study and optimization of heat and mass transport in the engineered MOF. Concomitantly, while passive harvesters are already fully autonomous, it is important to implement ways to manage energy efficiently in the upcoming generations of active harvesters. First, device geometry and materials need to be optimized[53]. For instance, a well-insulated cross-flow exchanger with thin MOF layers coated on a thermally conductive surface could be a promising architecture. Moreover, using a heat recuperation exchanger to redistribute the adsorption heat and the heat radiated by the condenser to the MOF, thus facilitating water desorption, should help mitigating energetic losses. Indeed, waste heat recovery has been shown to markedly improve the economic and environmental benefits of seawater desalination, another energy-intensive technology[54,55]. Additionally, it would be interesting to limit the energy cost of condensation, for instance by using nanostructures on the surface of the condenser in order to promote dropwise condensation, a bio-inspired approach reported to greatly improve heat transfer—although long-term stability remains a challenge[56,57]. Furthermore, combining pressure management with temperature swings to trigger water desorption could help in optimizing the energy requirement to perform a water harvesting cycle by lowering the desorption temperature and allowing the integration of the harvester with low-grade sources of heat. This would also alleviate the need for expensive thermal insulation in the device. A more advanced design which uses a pressure gradient in a multi-stage setup could aid in approaching ideal latent heat recovery by limiting entropy losses (although this approach is more suitable for large-scale installations and entails higher capital costs)[55,58,59].

Ultimately, the productivity and stability of upcoming generations of MOF water harvesters should be monitored and maintained over several months in the field. In this context, an installed protection mechanism against environmental contamination might increase the harvester's longevity and will also help to comply with health regulations. Finally, a detailed assessment of the associated maintenance costs will be necessary in order to demonstrate the readiness of the technology for long-term field operation and its potential to effectively address the global water shortage crisis.

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Acknowledgements

Competing interests

O.M.Y. is co-founder of Water Harvesting Inc., aiming at commercializing related technologies.

Additional information

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