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## Covalent organic frameworks enable efficient atmospheric water harvesting in arid climates

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Atmospheric water harvesting (AWH) may present a sustainable solution to global water scarcity, particularly in arid regions where conventional water resources are limited. Sorption-based AWH (SAWH) using covalent organic frameworks (COFs) has emerged as a promising technology for low-humidity conditions (<40% RH), yet challenges in adsorption capacity, energy efficiency, and material stability persist. This review comprehensively analyzes the unique advantages of COFs for low-humidity SAWH, emphasizing their tunable pore structures, hydrophilic engineering, and exceptional cycling stability. We systematically compare COFs with conventional sorbents (e.g., hydrogels, salt composites) and demonstrate their superior performance, such as COF-ok (*ortho*-ketoenamine)'s working capacity of 0.4 g g<sup>-1</sup> at 30% RH and solar-driven regeneration at 45 °C. By elucidating water adsorption mechanisms (surface adsorption, micropore filling, capillary condensation) through isotherm analysis and molecular simulations, we establish design principles for optimizing COFs. Furthermore, we discuss innovative strategies, including topological design, composite systems, and post-synthetic modifications, to enhance low-humidity performance. Finally, we outline future directions, such as computational screening and device engineering, to bridge laboratory-scale achievements with practical applications. This work provides a foundational guide for advancing next-generation SAWH materials to address water scarcity in the most challenging climates.

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### Water impact

Global water scarcity disproportionately affects arid regions, where conventional solutions fail due to low humidity (<40% RH). While atmospheric water harvesting offers promise, most sorbents perform poorly under these conditions. Covalent organic frameworks (COFs) represent a breakthrough in materials, combining high water uptake, tunable hydrophilicity, and solar-regenerable properties to address this critical gap. This review establishes design principles for COF-based harvesters, connecting molecular-scale engineering to real-world deployment in water-stressed communities. By overcoming the low-humidity challenge, COFs could transform atmospheric water harvesting from a niche technology to a scalable solution for drought resilience.

## 1. Introduction

Water scarcity has emerged as one of the most pressing challenges of the 21st century.<sup>1–4</sup> With conventional freshwater resources under unprecedented stress from overexploitation, pollution, and climate change, nearly half of the global population is projected to face water shortages

by 2050.<sup>5</sup> The increasing frequency and severity of droughts, combined with the growing demand for water from agriculture, industry, and domestic use, have exacerbated the problem. This crisis has spurred intense research into alternative water sources, among which atmospheric water—a vast reservoir estimated at 12 900 trillion liters—represents perhaps the most globally accessible solution.<sup>6</sup>

Atmospheric water is continuously replenished through natural hydrological cycles, making it a sustainable and renewable resource. The potential of atmospheric water harvesting (AWH) to alleviate water scarcity has been recognized globally, and various technologies have been developed to harness this resource.<sup>7</sup> AWH technologies have evolved along three primary pathways: (1) fog harvesting, effective in high-humidity (>80% relative humidity, RH) coastal or mountainous regions but geographically

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limited;<sup>8–11</sup> (2) dew collection, which is energy-intensive at low humidity due to thermodynamic constraints on condensation;<sup>12–15</sup> and (3) sorption-based AWH (SAWH), the most versatile approach, capable of operating across wide humidity ranges using adsorbent materials.<sup>16–21</sup> Among these, SAWH stands out for its adaptability and potential for low-energy operation, making it a promising solution for regions with varying humidity levels.<sup>22</sup>

Over 60% of water-scarce arid and semi-arid regions experience ambient humidity below 40% RH. This creates a crucial technological gap, as most sorbent materials show optimal performance either at high humidity (hydrogels: 4.2 g g<sup>-1</sup> at >80% RH) or mid-range humidity (salt composites: 0.7–2.2 g g<sup>-1</sup> at 20–80% RH), but fail to meet practical water production targets in arid conditions (<40% RH).<sup>18,19</sup> The scientific challenges for low-humidity SAWH are multifaceted. First, lower water vapor pressure in low-humidity environments reduces the driving force for adsorption, making it difficult for sorbents to capture water molecules efficiently. Second, slower diffusion and nucleation at low vapor concentrations mean that water molecules take longer to interact with the sorbent surface, thereby reducing the overall adsorption rate. Third, stronger water–sorbent interactions, while beneficial for adsorption, increase the energy required for regeneration, making the process less sustainable. Finally, repeated cycling under harsh conditions, such as high temperatures and varying humidity levels, accelerates sorbent degradation, reducing the lifespan and effectiveness of the sorbent materials. Addressing these challenges is essential for developing SAWH technologies that can effectively operate in low-humidity environments, where the need for alternative water sources is most critical.<sup>17</sup>

Covalent organic frameworks (COFs) have emerged as particularly promising materials for addressing the challenges of low-humidity SAWH. First applied to SAWH in 2015, COFs offer a unique combination of attributes that make them well-suited for this application.<sup>23</sup> They provide atomic-level control over pore size and functionality, allowing for the design of materials with optimal pore dimensions and surface properties for water adsorption.<sup>24,25</sup> The ability to systematically vary the hydrophilicity and hydrophobicity of COFs enables the fine-tuning of their interaction with water molecules, optimizing both adsorption and desorption processes.<sup>26–29</sup> Robust covalent linkages within COFs resist hydrolysis and degradation, ensuring long-term stability and durability under repeated cycling conditions. Furthermore, the conjugated frameworks of COFs enable solar-driven regeneration, reducing the energy input required for desorption and making the process more sustainable.<sup>30</sup> These unique properties position COFs as a leading material platform for developing next-generation SAWH technologies capable of addressing water scarcity in low-humidity regions. Recent reviews on COFs for SAWH applications have provided valuable insights. Sakai *et al.* investigated CO<sub>2</sub> adsorption by COFs and transferred its adsorption capacity to water

adsorption, indicating the possibility of COFs for AWH;<sup>31</sup> Huang *et al.* summarized the progress of COFs for AWH applications with respect to the density and distribution of action sites;<sup>32</sup> Feng *et al.* summarized kinetic and thermodynamic strategies for optimizing COF;<sup>33</sup> Nguyen *et al.* also commented.<sup>34</sup> But they have not focused on the specific advantages of COFs in low-humidity water harvesting and the underlying principles and designs that enable their superior performance under such conditions.

In this review, we provide a comprehensive analysis of covalent organic frameworks (COFs) for low-humidity sorption-based atmospheric water harvesting (SAWH) applications. By comparing the performance of COFs with other sorbent materials, we highlight the unique advantages of COFs in low-humidity environments. We explore the molecular-level interactions between water molecules and COF surfaces, elucidating the role of COFs' unique structural features in enhancing efficient water adsorption and desorption processes. We also discuss recent advancements in the design and synthesis of COFs that have led to improved water harvesting performance. This review aims to establish clear design principles for next-generation SAWH materials capable of addressing water scarcity in the world's most arid regions. By connecting molecular-level insights with macroscopic performance metrics, we provide a comprehensive overview of the current state of COF-based SAWH technologies and offer guidance for future research directions in this field.

## 2. Comparative advantages of COFs for low-humidity SAWH

Currently, adsorbents employed for SAWH primarily comprise hydrogels, composite materials, metal–organic frameworks (MOFs), and COFs. In this work, we provide a systematic evaluation of COFs alongside other major classes of adsorbent materials. As shown in Fig. 1, the systematic evaluation of water adsorption performance across different sorbent materials reveals the distinctive advantages of COFs for SAWH under low-humidity conditions. In the critical 20–40% RH range characteristic of arid regions, COFs demonstrate superior water uptake capacities compared to conventional alternatives (Fig. 1a and e). Hydrogels exhibit a significant decline in water uptake capacity at 30% relative humidity (RH) (Fig. 1b). Although composite sorbents—which require integration with a matrix material—show improved performance, such enhancements are primarily observed under high-humidity conditions (Fig. 1c). In contrast, COFs demonstrate superior water absorption within the critical 20–40% RH range characteristic of arid regions compared to conventional sorbent alternatives. For instance, specific COF materials such as DHTA-Pa achieve a water uptake of 0.48 g g<sup>-1</sup> at 30% RH, while COF-ok maintains 0.36 g g<sup>-1</sup> under the same conditions.<sup>30,35</sup> These values are significantly higher than those of hydrogels, which typically show uptake capacities below 0.05 g g<sup>-1</sup> at 30% RH, and are also better than salt





Fig. 1 Water extraction performance and characteristics of representative adsorbents used in the SAWH field. (a) Applicable RH and water absorption range for adsorption water intake of COFs, MOFs, hygroscopic polymers, and salt-based composites. Characteristics and representative materials of (b) hygroscopic polymers,<sup>39</sup> (c) salt-based composites,<sup>40</sup> (d) MOFs,<sup>41</sup> and (e) COFs.<sup>23</sup> Characteristics of COFs suitable for SAWH: (f) rich and controllable pore structure,<sup>42</sup> (g) flexible and adjustable hydrophilicity,<sup>35</sup> and (h) clear structure–function relationship.<sup>43</sup>

composites like TpPa-1@LiCl, which achieve  $0.37 \text{ g g}^{-1}$  in this humidity range.<sup>36</sup> This superior performance under low-humidity conditions is a key factor that sets COFs apart as promising materials for AWH in arid regions. Furthermore, COFs possess several distinctive properties that make them

particularly well-suited for SAWH, underscoring a strong structure–function relationship.

The exceptional structural stability of COFs arises from their robust covalent bonding, high degree of structural order, and rationally designed chemical and topological



frameworks (Fig. 1f). COFs such as COF-432, which feature a unique mtf topology, have been shown to maintain their adsorption capacity for over 300 continuous cycles without any noticeable degradation.<sup>25</sup> This level of stability is particularly noteworthy when compared to metal–organic frameworks (MOFs), which often suffer from instability due to their metal–coordination bonds.<sup>16,37,38</sup> The all-organic nature of COFs eliminates concerns about potential toxicity risks associated with leachable metal ions, thereby providing robust framework integrity (Fig. 1d). This durability is crucial for the long-term effectiveness of AWH systems under harsh environmental conditions, ensuring that COFs can maintain their performance over extended periods of use.

Functional tunability is another defining characteristic of COFs that enables precise optimization for low-humidity operation (Fig. 1g). Pore surface engineering through careful monomer selection allows systematic control over hydrophilicity. COF-ok, with its *ortho*-ketoenamine configuration, achieves a working capacity of 0.36 g g<sup>-1</sup> below 40% RH, while COF-pe, with its *para*-enolimine structure, only reaches 0.16 g g<sup>-1</sup> under identical conditions.<sup>30</sup> This tunability extends to pore architecture, as demonstrated by materials like 3D-CageCOF-1, which show how structural design can influence water transport properties.<sup>24</sup> The ability to fine-tune these properties makes COFs highly adaptable for AWH applications under various humidity conditions.

The tunable design and precise control over pore structures in COFs enable a comprehensive understanding of their adsorption dynamics, thereby highlighting their pronounced advantages in energy-efficient conservation and regeneration processes (Fig. 1h). COF-based systems can achieve complete desorption at 45 °C, compared to the 60–80 °C typically required for hydrogels and salt composites. This lower energy requirement for regeneration enhances the economic viability and practicality of COFs for large-scale AWH applications. Field performance data further

substantiate the practical advantages of COFs. Outdoor testing of COF-ok has demonstrated a water harvesting capacity of 161 g kg<sup>-1</sup> per day using solely solar energy, while DHTA-Pa exhibits remarkably fast adsorption kinetics of 0.72 L kg<sup>-1</sup> h<sup>-1</sup> at 298 K.<sup>30,35</sup> These operational metrics surpass those of alternative technologies and validate the potential of COFs for real-world applications in arid regions.

### 3. Development of COFs for low-humidity SAWH applications

The evolution of COFs for SAWH has followed a clear trajectory of innovation, with each developmental milestone addressing specific challenges in low-humidity operation. The foundational work by Lotsch *et al.* in 2015 established critical structure–property relationships through their comparative study of AB-COF and ATFG-COF.<sup>23</sup> While both materials shared similar topological structures and pore sizes, their divergent water adsorption behaviors revealed the profound impact of polarity engineering. The less polar AB-COF exhibited a sharp increase in water uptake from 2.6 wt% to 28 wt% between 0.22 and 0.26  $P/P_0^{-1}$ , reaching as high as 41 wt% at 0.90  $P/P_0^{-1}$ , characterized by a steep S-shaped V-type isotherm. In contrast, the more polar ATFG-COF began to adsorb water at significantly lower pressures ( $P/P_0^{-1} = 0.15$ ) and achieved a water uptake of 25 wt% at 0.90  $P/P_0^{-1}$ , displaying a type IV isotherm and demonstrating stronger hydrophilicity.<sup>23</sup> This initial study highlighted the influence of hydrophobic/hydrophilic surfaces on capillary condensation and micropore filling, and the superior performance of the more polar ATFG-COF in low-humidity regimes would later inform targeted designs for arid environment applications.

A parallel work by Banerjee *et al.* in the same year systematically explored the effects of functional group modifications on water adsorption behavior.<sup>45</sup> Their



Fig. 2 Synthetic schemes (a) and water isotherms at 298 K (b) of Tp-based COFs with different functionalities.<sup>45</sup>



investigation of 12 distinct COF variants, modified with different functional groups (Fig. 2a) (hydrophobic  $-\text{CH}_3$ ,  $-\text{NO}_2$ ,  $-\text{F}$ , hydrophilic  $-\text{OH}$ ,  $-\text{OMe}$ , *etc.*), identified TpPa-1 as particularly promising. This COF exhibited an ideal S-shaped type V adsorption isotherm with a capacity of  $368 \text{ cm}^3 \text{ g}^{-1}$  at  $P/P_0^{-1} = 0.9$  and  $549 \text{ cm}^3 \text{ g}^{-1}$  at  $P/P_0^{-1} < 0.9$  (Fig. 2b). More importantly, this study established that pore size, hydrophilic/hydrophobic group distribution, surface area, crystallinity, and hydrogen bonding capacity collectively determined a COF's water uptake characteristics—principles that would become central to subsequent low-humidity optimization.

A critical breakthrough in the evolution of COFs for SAWH was marked by the development of hydrolytically stable COF architectures. Yaghi *et al.* developed COF-432 (Fig. 3a), which demonstrated hydrolytic stability by maintaining its structural integrity through 300 adsorption–desorption cycles and exhibited an advantageous S-shaped isotherm with a low-RH breakpoint at 20% (Fig. 3b).<sup>25</sup> This characteristic is particularly valuable for applications in arid regions. Concurrently, the development of three-dimensional COF structures addressed mass transport limitations through interconnected pore channels while preserving the desirable steep adsorption profile needed for efficient low-humidity operation. Cooper *et al.* synthesized the first cage-based 3D-CageCOF-1 (Fig. 3d), which can switch between microporous

and macroporous configurations. This innovative structure exhibited ideal adsorption behavior with an S-shaped water vapor adsorption isotherm and minimal desorption hysteresis (Fig. 3c), demonstrating the potential of using organic cages as building units to expand the structural complexity of 3D COFs.<sup>24</sup>

Recent years have witnessed remarkable progress in overcoming two persistent challenges in SAWH materials: weak water adsorption capacity at low humidity and high desorption energy requirements. Pythz-COF, developed by Tian *et al.*, achieved a breakthrough maximum water uptake of  $0.83 \text{ g g}^{-1}$  at 90% RH, while the TpPa-1@LiCl composite, developed by Liu *et al.*, demonstrated how strategic salt incorporation could enhance capacity to  $0.80 \text{ g g}^{-1}$ .<sup>36,46</sup> Most significantly, COF-ok, developed by Gu *et al.*,<sup>30</sup> represents a paradigm shift in low-humidity performance through its precisely engineered distribution of hydrophilic and hydrophobic sites. This innovative design achieved a working capacity of  $0.4 \text{ g g}^{-1}$  below 40% RH, a remarkable feat for such arid conditions, while enabling complete desorption at the modest temperature of  $45 \text{ }^\circ\text{C}$ . The practical viability of these advances was confirmed through outdoor testing, where COF-ok demonstrated a water harvesting capacity of  $161 \text{ g kg}^{-1}$  using solely solar energy, establishing a new benchmark for sustainable atmospheric water production (Fig. 5d).

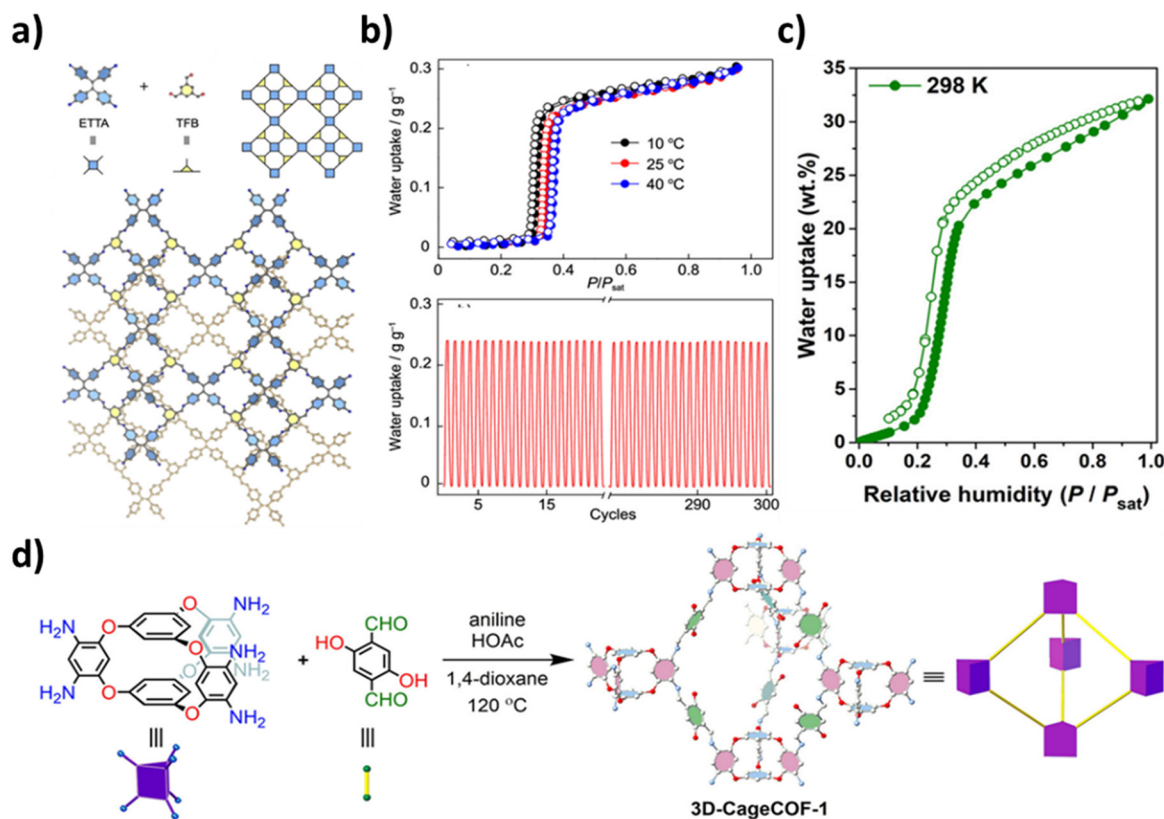


Fig. 3 (a) The synthesis and simulated structure of COF-432. (b) Water isotherms and water cycling stability tests of COF-432 at different temperatures.<sup>25</sup> (c) Water vapor sorption isotherms for 3D-CageCOF-1. (d) Scheme for the synthesis of 3D-CageCOF-1 from Cage-6-NH<sub>2</sub> and DHTPA (C: white, N: blue, O: red).<sup>24</sup>



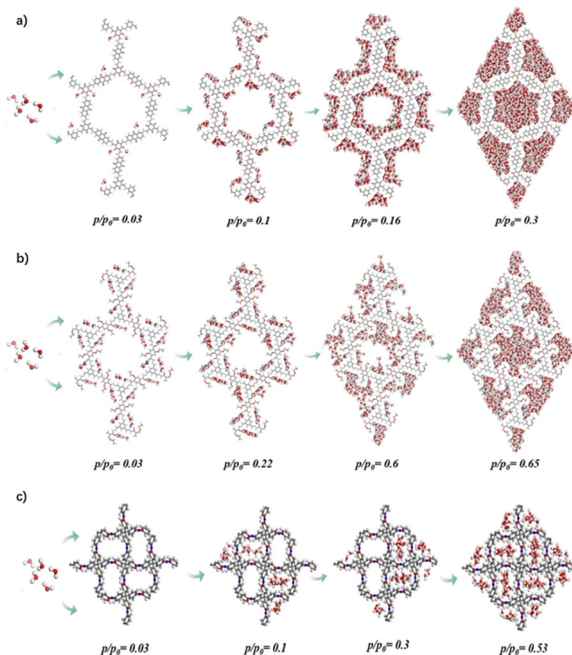


Fig. 4 Simulated snapshots of water molecules adsorbed in COF as a function of pressure at 298 K: (a) DAAQ-TFP, (b) COF-42 and (c) NPN-1.<sup>49</sup>

Beyond the significant strides made in cycling stability, low-RH capacity, and energy efficiency, COF materials have also seen notable advancements in other critical areas such as photothermal conversion efficiency, adsorption-desorption kinetics, and material processability, which are essential for practical solar-driven atmospheric water harvesting (SAWH) applications. Table 1 provides a comprehensive summary of the current state-of-the-art in COF-based SAWH materials, detailing their structural

characteristics, adsorption performance under various humidity conditions, and key operational parameters. Despite these significant advancements, which demonstrate the remarkable potential of COFs for low-humidity atmospheric water harvesting, it is important to recognize that COFs are still emerging as a novel class of porous materials for SAWH applications. Many critical issues such as the adsorption/desorption mechanisms and structural design need to be thoroughly investigated to further optimize their performance.

## 4. Water adsorption mechanisms in COFs

### 4.1 Evaluation methods and isotherm analysis

The water adsorption behavior in COFs is governed by three primary mechanisms: surface adsorption, micropore filling, and capillary condensation. These processes are critically influenced by pore structure and surface chemistry, which can be systematically characterized through adsorption isotherm analysis. Surface adsorption occurs on the walls of mesopores (2–50 nm) and macropores (>50 nm), where water molecules form ordered monolayers *via* hydrogen bonding with hydrophilic functional groups (*e.g.*,  $-\text{OH}$ ,  $-\text{C}=\text{O}$ ). This initial adsorption layer facilitates subsequent multilayer formation. Micropore filling (<2 nm) is driven by overlapping van der Waals potentials, leading to spontaneous water nucleation at the polar sites. Unlike surface adsorption, this process does not follow a layer-by-layer mechanism but rather a pore-filling progression. Capillary condensation occurs in mesopores at sub-saturation vapor pressures ( $P/P_0 = 0.4\text{--}0.8$ ), where adsorbed water transitions into a liquid phase.

The evaluation of sorbent performance for low-humidity SAWH applications encompasses several critical parameters,



Fig. 5 Effects of hydrophilic and hydrophobic site distribution on water adsorption behavior in COFs.<sup>30</sup> (a) *ortho*-Ketoenamine-linked COF and its hydrogen bonding interactions with water clusters. (b) *para*-Enolimine-linked COF and its hydrogen bonding interactions with isolated water molecules. (c) Densely packed water molecules in the COF-ok channel at the saturation stage with extensive hydrogen bonds. (d) Water adsorption/desorption isotherms at 25 °C. Single layer of COF-ok (e) and COF-pe (f). Ideal eclipsed (AA) structures of (g) COF-ok with hydrophobic and hydrophilic bands and (h) COF-pe with hydrophobic bands and hydrophilic chains.



**Table 1** The representative COF-based water harvesters

COFs	Inflection point	Working capacity (g g <sup>-1</sup> ) (RH = 0.10–0.40)	Total capacity (g g <sup>-1</sup> ) (RH = 0.90)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Cyclic test	Reference
ATFG-COF	0.20	0.08	0.25	520	4	23
DHTA-Pa	0.25	0.48	0.71	2099	80	35
DhaTab	0.80	0.32 (RH = 0.50–0.70)	0.57	N/A	5	45
Tp-azo	0.56	0.28 (RH = 0.60–0.85)	0.41	942	5	45
COF-432	0.34	0.23	0.29	895	300	25
Pythz-COF	0.6	0.38 (RH = 0.40–0.70)	0.83	1572	5	46
Pyurea-COF	0.62	0.35 (RH = 0.45–0.80)	0.65	1062	5	46
3D-CageCOF-1	0.3	0.22	0.33	1040	3	24
COF-ok	0.32	0.36	0.6	1194	20	30
COF-pe	0.41	0.16	0.45	795	N/A	30
COF-W2	0.48	0.36	0.40	1416	N/A	26
COF-W3	0.34	0.28	0.37	856	10	26
AB-COF	0.26	0.28	0.41	1125	4	23
COF-480-hydraide	0.20	0.32	0.45	989	230	28
PI-3-COF	0.40	0.20	0.45	1620	N/A	29
NO-PI-3-COF	0.25	0.15	0.25	664	10	29
TpPa-1	0.24	0.29	0.45	984	5	45
TpPa-1@LiCl	N/A	0.37	0.80	357	10	36
PCL-42	N/A	0.8	3.20	N/A	20	47

including operational conditions, water uptake capacity, adsorption–desorption kinetics, cycling stability, and regeneration energy consumption. Water adsorption tests are typically conducted to plot adsorption isotherms. Adsorption isotherms reflect the interactions between the sorbent and adsorbate, serving as a critical tool for characterizing sorbent properties. The inflection point reflects the applicable conditions of the adsorbent, the slope represents its adsorption rate, and the maximum value is the saturated adsorption capacity of the adsorbent. Isotherms are key tools to characterize adsorbent characteristics. The International Union of Pure and Applied Chemistry (IUPAC) classifies adsorption isotherms into six types, which are closely associated with pore structure characteristics.<sup>48</sup> COFs frequently exhibit type I, IV, and V adsorption isotherms, demonstrating superior water uptake performance under low RH conditions. Adsorption hysteresis, characterized by non-overlapping adsorption and desorption curves, is closely associated with specific pore structural features and the underlying adsorption mechanisms of the sorbent. This phenomenon serves as a critical parameter for estimating regeneration energy costs, and materials exhibiting minimal or no hysteresis loops are preferred for practical SAWH applications.

The Brunauer–Emmett–Teller (BET) equation is a fundamental tool for analyzing adsorption isotherms and provides insights into the surface area and pore distribution of sorbents. By comparing experimental adsorption results with theoretical calculations, researchers can evaluate the surface area and pore distribution of sorbents, offering critical insights into COFs' adsorption mechanisms and guiding the design of optimized COFs materials. Additionally, computational analysis of adsorption heat data reveals physicochemical changes during adsorption

processes, thereby furnishing energetic evidence to elucidate adsorption mechanisms.

Density functional theory (DFT), molecular simulation (MC), and grand canonical Monte Carlo (GCMC) simulations provide theoretical adsorption data. These methods help in understanding the adsorption mechanisms at the molecular level and in predicting the performance of COFs under different conditions. By combining experimental data with these theoretical approaches, researchers can gain a comprehensive understanding of the adsorption and desorption processes in COFs, which is essential for optimizing their performance in low-humidity SAWH applications.

#### 4.2 Structure-dependent adsorption behavior

The water adsorption behavior in COFs is co-determined by the pore size and pore wall environment. Li *et al.* observed the water adsorption behaviors of a series of COFs containing different functional groups, pore volumes, and pore sizes at the molecular level, identifying three distinct types: hydrophilic COFs (*e.g.*, DAAQ-TFP, TpPa-1) exhibit S-shaped type V isotherms.<sup>49</sup> At low RH, water molecules nucleate around hydrophilic sites. As RH increases, surface adsorption covers the internal pore surfaces of COFs, followed by gradual pore filling (Fig. 4a). Hydrophobic COFs (*e.g.*, COF-42, COF-43) display type IV multistage adsorption isotherms. Due to the presence of hydrophobic sites, water clusters formed during the initial adsorption remain isolated until RH increases and pore filling occurs, at which point an isotherm inflection appears (Fig. 4b). Small-pore COFs (*e.g.*, NPN-1, 3–5 Å) undergo spontaneous pore filling with limited water uptake, making them unsuitable for SAWH applications (Fig. 4c). In summary, macroporous hydrophilic COFs provide sufficient adsorption sites and filling space for water molecules, and can achieve



rapid water adsorption and high pore utilization, which is an ideal air adsorption structure.

The pore geometry and geometric characteristics of surface functional groups collectively influence the water adsorption performance of COFs by modulating water mass transfer within the pores. Jiang *et al.*<sup>43</sup> synthesized a series of trigonal microporous COFs with similar pore size distributions and pore volumes but subtle differences in pore wall chemistry by employing identical topological structures while substituting building units. Among these, HFPTP-PDA-COF and HFPTP-BPDA-COF exhibited similar characteristic S-shaped type V adsorption isotherms, displaying steep adsorption inflection points at  $P/P_0^{-1} = 0.4$  and  $P/P_0^{-1} = 0.5$ , respectively. In contrast, HFPTP-DMePDA-COF lacked a sharp adsorption inflection, instead showing gradual adsorption initiation at  $P/P_0^{-1} = 0.6$ . This behavior arises from severe steric hindrance caused by hydrophobic methyl units on the pore walls of HFPTP-DMePDA-COF, which obstruct water molecule ingress.

### 4.3 Design principles for optimal desorption

The presence of hydrophobic groups prevents excessive aggregation of water molecules within COFs, while a rational distribution of hydrophilic and hydrophobic sites significantly reduces the regeneration energy consumption of these materials. Gu *et al.*<sup>30</sup> compared the water adsorption behaviors of COF-ok (featuring dense hydrophilic *ortho*-ketoenamine belts) (Fig. 5a and e) and COF-pe (with dispersed hydrophilic chains) (Fig. 5b and f). They found that the “face-to-face” hydrophilic sites in COF-ok accelerate water capture and cluster nucleation at low RH (Fig. 5g), while the “back-to-back” hydrophobic naphthalene ring regions restrict excessive water aggregation *via* steric hindrance, thereby achieving an adsorption–desorption dynamic equilibrium (Fig. 5h). GCMC simulations in this work confirmed that gradient distributions of hydrophilic/hydrophobic sites reduce desorption activation energy, significantly lowering regeneration energy consumption. The desorption performance of COFs is governed by the interconnected pore channels formed through their structural architecture, which critically regulates the transport of water molecules within the framework following desorption (Fig. 5c).<sup>30</sup> Feng *et al.* synthesized DHTA-Pa, a COF demonstrating high water uptake ( $0.48 \text{ g g}^{-1}$  at 30% RH), rapid adsorption kinetics ( $0.72 \text{ L kg}^{-1} \text{ h}^{-1}$  at 298 K), and fast desorption rates ( $2.58 \text{ L kg}^{-1} \text{ h}^{-1}$  at 333 K). GCMC, DFT, and MD calculations confirmed that such a 2D-COF with a hydrophobic backbone, optimal hydrophilic site density, and 1D open channels effectively reduces barriers to water diffusion and desorption energy.<sup>35</sup>

## 5. Design strategies for LH-optimized COFs

### 5.1 Topological design for arid conditions

COFs are crystalline porous organic polymers that are formed through the ordered linkage of light elements such as

carbon, boron, nitrogen, and oxygen *via* strong covalent bonds.<sup>42</sup> The adsorption performance of COFs is primarily determined by their pore size, pore geometry, and surface chemical environment, which are modulated by the chemical composition and molecular length of the building blocks, as well as the framework topology. Similar to the covalent assembly of atoms in molecules, COFs achieve highly controllable structural design through the ordered spatial arrangement of organic building blocks along specific orientations.<sup>50–52</sup>

The selection of building blocks with distinct geometric configurations enables the construction of COFs with varied topological architectures. In recent years, numerous novel COF structures have been developed, some of which exhibit exceptional performance in SAWH. For instance, Yaghi *et al.*<sup>25</sup> synthesized a two-dimensional COF-432 with a novel mtf topology using tetratopic 1,1,2,2-tetrakis(4-aminophenyl) ethylene (ETTA,  $\text{C}_{26}\text{H}_{16}(\text{NH}_2)_4$ ) and tritopic 1,3,5-triformylbenzene (TFB,  $\text{C}_6\text{H}_3(\text{CHO})_3$ ) as building blocks. This COF-432 features square grids with high hydrolytic stability, maintaining functionality over 300 cycles (Fig. 3a). Similarly, Cooper *et al.*<sup>24</sup> developed the first cage-based three-dimensional COF (3D-CageCOF-1) by reacting pre-synthesized trigonal prismatic Cage-6- $\text{NH}_2$  with linear 2,5-dihydroxyterephthalaldehyde (DHTPA) under a twofold interpenetrated acs topology (Fig. 3d). This 3D-CageCOF-1 offers switchable cages ( $1.8 \leftrightarrow 3.2 \text{ nm}$ ) that adapt to varying adsorption needs.<sup>24</sup> These materials have demonstrated promising applicability in SAWH through adsorption experiments.

Building blocks are connected *via* chemical bonds to form ordered COF structures. To date, over a dozen distinct chemical linkages have been developed for constructing COFs, including boroxine, boronate-ester, imine, hydrazone, and azine.<sup>44,53–60</sup> These diverse linkages provide COFs with rich structural versatility, significantly enhancing their architectural diversity. However, the formation of these reversible covalent bonds typically requires mixed solvent systems, and reaction conditions (*e.g.*, solvent ratios, catalyst types, temperature) profoundly influence the crystallinity and porosity of the resulting COFs. For example, boronate-ester linkages are generally formed through dehydration–condensation reactions in polar/nonpolar mixed solvents, while imine linkages can be rapidly constructed *via* Schiff base reactions under mild conditions. Although extensive studies have been conducted to optimize these reaction parameters, the underlying reaction mechanisms and ideal synthetic conditions remain subjects requiring further in-depth investigation. Elucidating these mechanisms is essential for improving COFs' crystallinity and porosity, which in turn will establish a theoretical foundation for designing novel high-performance COFs, particularly those optimized for low-humidity applications.

The synthesis of COFs fundamentally constitutes a topology-guided reticular polymerization process of building blocks. By rationally selecting building units with specific



geometric symmetry and precisely controlling reaction conditions, COFs with high specific surface areas and regular pore channel structures can be prepared.<sup>61</sup> These design strategies are particularly crucial for optimizing COFs for low-humidity conditions, where the ability to capture and retain water molecules is paramount. The exceptional flexibility and tunability of COF design allow for the precise engineering of pore sizes and surface chemistries, which are essential for enhancing water adsorption at low RH. Further optimization of these design parameters provides an effective pathway for developing high-performance sorbents capable of efficient water harvesting in arid environments.

## 5.2 Hydrophilic engineering for low-RH capture

The exceptional adsorption capacity of COFs is attributed to their large surface areas and abundant pore structures, with hydrophilic sites being crucial for their application in SAWH. Hydrophilic modification of COFs is a highly efficient strategy for optimizing their SAWH functionality. Given that COFs are constructed *via* covalent bonding of building blocks, their structural and functional properties are determined by the constituent units and linkage types. Consequently, the primary approaches to COF functionalization involve introducing functional groups into building blocks and modifying linkage chemistries. Li *et al.*<sup>49</sup> demonstrated that the water adsorption capacity of COFs under low relative humidity correlates positively with the density of oxygen-containing surface functional groups. Feng *et al.* synthesized SHTA-Pa COF, DHTA-Pa COF, and THTA-Pa COF with progressively increased

ketone group content by condensing 2-hydroxybenzene-1,3,5-tricarbaldehyde (SHTA), 2,4-dihydroxybenzene-1,3,5-tricarbaldehyde (DHTA), and 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (THTA), respectively, with *p*-phenylenediamine (Pa) (Fig. 7c). Water adsorption tests at 298 K revealed leftward shifts in the adsorption isotherm inflection points (occurring at  $P/P_0^{-1} = 0.35, 0.20,$  and  $0.15$ ) as hydrophilic site density increased (Fig. 7d and e). Similarly, Huang *et al.* synthesized COF-W1, COF-W2, and COF-W3 by replacing benzene rings with pyridine units to incrementally enhance nitrogen content (Fig. 6a). Adsorption tests at 298 K showed analogous leftward shifts in isotherm inflection points with rising N content (Fig. 6b).<sup>26</sup>

Yaghi *et al.*<sup>28</sup> achieved post-synthetic oxidation of AB-COF by converting the hydrazine linkages into hydrazide linkages, yielding COF-480-hydrazide (Fig. 7a and b). This modification maintained the original crystallinity while attaining a 9.2% conversion rate, thereby incorporating additional polar oxygen atoms into the framework. Consequently, the water adsorption isotherm shifted toward lower RH with a slight enhancement in water uptake capacity (Fig. 7c). Similarly, Lotsch *et al.* implemented a two-step cascade conversion to transform imine-linked PI-3-COF into nitro-linked NO-PI-3-COF (Fig. 7d), resulting in a leftward shift of the adsorption isotherm inflection point from  $P/P_0^{-1} = 0.38$  to  $0.21$  (Fig. 7e).<sup>29</sup> The capture of water molecules by hydrophilic sites on COF pore surfaces initiates the water adsorption process in SAWH systems. A leftward shift in the water adsorption isotherm inflection point signifies enhanced hydrophilicity of the sorbent,



Fig. 6 (a) Schematic representation for the synthesis of COF-W1, COF-W2, and COF-W3.<sup>26</sup> (b) Water adsorption isotherms of COF-W1, COF-W2, and COF-W3.<sup>26</sup> (c) Schematic illustration of DHTA-Pa COF for fast water capture/release and low-temperature regeneration. (d) Water sorption isotherms of SHTA-Pa COF, DHTA-Pa COF, and THTA-Pa COF at 298 K. (e) Dynamic water vapor adsorption-desorption kinetics of SHTA-Pa COF, DHTA-Pa COF, and THTA-Pa COF.<sup>35</sup>





Fig. 7 (a) Overview of the synthesis of 2D hcb, 2D sql, and 3D dia hydrazide-linked COFs. (b) Synthetic scheme of transforming the hydrazine linkage into a hydrazide linkage. (c) Water isotherms of AB-COF and COF-480-hydrazide at 298 K.<sup>28</sup> (d) Synthetic scheme of transformation of the imine linkage into the nitron linkage. (e) Water isotherms of PI-3 COF and NO-PI-3 COF at 288 K.<sup>29</sup>

indicating its capability to achieve significant water uptake at lower RH. Functional group side chains in building blocks and chemical linkages formed during synthesis constitute the primary sources of COF structural sites. However, the reversibility constraints inherent to COF synthesis reactions render direct formation of certain chemical bonds challenging. Therefore, two effective strategies have emerged: (1) a bottom-up approach involving substitution of building blocks with hydrophilic functional groups and (2) a top-down strategy decoupling COFs synthesis into crystallization and bond formation stages, followed by post-synthetic hydrophilic modification of chemical linkages.<sup>62–66</sup> These methodologies enable the development of COFs with optimized SAWH functionality, critically advancing the design of sorbents adaptable to diverse environmental conditions.

### 5.3 Composite systems for arid applications

The tunable porous architectures and hydrophilicity of COFs make them ideal candidates for high-performance sorbents

in SAWH systems. These properties are further enhanced by their photoelectronic characteristics and thermal conductivity, which stem from their layered stacking structures. This allows COFs to be integrated as functional components in composite sorbents, optimizing pore structures and photothermal characteristics. For instance, Chen *et al.*<sup>47</sup> synthesized a PCL (PDMAPS-COF-LiCl) composite sorbent by incorporating TpPa-1 COF into a salt-loaded hydrogel. Within the hydrogel matrix, the COF acts as an intermolecular crosslinker, enhancing structural stability under saline conditions. The introduction of COF also induces a hierarchical porous architecture within the hydrogel, facilitating water molecule diffusion and improving overall water uptake. Additionally, the COF significantly enhances the hydrogel's photothermal performance, with the composite achieving a 12.5 °C increase in steady-state temperature under simulated solar irradiation (Fig. 8d).

COFs typically exist in powder form, which poses challenges for their industrial-scale deployment in SAWH systems. To address these challenges, composite strategies





Fig. 8 (a) The reaction mechanism for the synthesis of CVPAA. (b) Water vapor adsorption isotherms of COF-V, PAA and CVPAA. (c) Water uptake performance of COF-V, PAA and CVPAA at 25 °C and 38% RH.<sup>67</sup> (d) Schematic representation of the fabrication process of the PCL hydrogel.<sup>47</sup>

have emerged as critical pathways to enhance their practical application. Lei *et al.*<sup>67</sup> synthesized a CVPAA composite sorbent by copolymerizing COF-V with acrylic acid (AA) (Fig. 8a). At 25 °C and 38% RH, this composite enhanced water vapor adsorption capacities by 86.5% and 130.7% compared to pristine COF-V and polyacrylic acid (PAA), respectively, demonstrating synergistic enhancement (Fig. 8b and c). Currently, material compositing serves as an effective strategy to mitigate the intrinsic limitations of single-component materials while enhancing their overall performance. This approach has emerged as a novel research direction in the SAWH field. Through rational composite design, the physical properties of COFs can be optimized, and their application scope expanded to meet diverse environmental demands.<sup>20,68–72</sup> Future research should prioritize the development of innovative compositing methodologies and the establishment of structure-performance relationship models to accelerate the scalable deployment of COFs in SAWH technologies.

## 6. Summary and outlook

In conclusion, SAWH offers a promising approach to mitigating the global water crisis, particularly in arid regions where conventional water sources are scarce. Among various sorbents, COFs have emerged as the most promising materials for low-humidity environments, demonstrating exceptional water adsorption performance under relative humidity levels as low as 20–40%. Precise structural design and functional modifications provide a solid foundation for advancing this technology; however, COF-based SAWH remains largely confined to laboratory-scale research. To fully harness the potential of COFs in SAWH, it is essential to address key challenges in material selection, scalable synthesis, and device integration for long-term, large-scale outdoor applications.

Material selection involves considerations at two levels: performance and structure. First, it is essential to identify materials suited to the practical application environment. Subsequently, ideal COFs must be precisely designed and efficiently screened from a vast array of structural options according to specific performance requirements. This approach necessitates the establishment of a COF material database equipped with standardized evaluation criteria. On the one hand, under laboratory conditions, the water harvesting capacity of adsorbents is typically measured under optimal working conditions; however, their actual performance may vary significantly in real-world environments due to fluctuating climatic factors. Therefore, establishing a comprehensive material library of COFs optimized for low-humidity conditions (20–40% RH) and improving performance evaluation indicators, such as working capacity, kinetic characteristics, and stability under optimal working conditions, are crucial steps for promoting their large-scale application. On the other hand, although numerous COFs have been synthesized or proposed theoretically, only a limited number are suitable for SAWH applications. Li *et al.* quantified the influence of hydrogen-bond acceptors and pore size on the water adsorption behavior of COFs.<sup>49</sup> Furthermore, Balasubramanian *et al.* introduced an effective simulation approach to calculate the adsorption inflection points of COFs, which helps elucidate their pore-filling mechanisms and provides a pathway for large-scale screening of COFs for SAWH.<sup>73</sup> Integrating machine learning with computational chemistry represents a promising direction for future research.

Industrial applications demand the development of economically viable, environmentally friendly, and sustainable large-scale synthesis techniques for COFs, which represents a major focus of current research. The synthesis of COFs primarily utilizes solvothermal methods, which often involve the use of toxic organic solvents and result in



extremely low yields (at the  $\text{g mg}^{-1}$  level), making them unsuitable for industrial-scale production. The nucleation and growth mechanisms of COFs are still not fully understood, and the controllability of the synthesis process is relatively poor. Microwave-assisted synthesis,<sup>74</sup> intermediate conversion strategies,<sup>75</sup> and membrane fabrication techniques offer promising avenues to address these challenges.<sup>76,77</sup> Future work needs to develop synthesis methods that are cost-effective, environmentally friendly, scalable, and yield higher production rates to meet industrial needs.

The deployment of COFs in real-world SAWH applications depends critically on the integration with dedicated water harvesting devices.

The design of adsorption devices should be based on the mass transfer, heat transfer, and regeneration temperature properties of the adsorbent materials.<sup>19,78–80</sup> Current research on COFs for SAWH primarily focuses on elucidating water adsorption mechanisms and designing or improving new materials. However, to fully leverage the advantages of COFs and promote their practical applications, it is essential to design new devices tailored to the unique properties of COFs. These devices should be optimized for the specific conditions of arid regions, including the large diurnal temperature variations that can affect the desorption process. Developing devices that can efficiently capture and release water under these conditions will be critical for the successful deployment of COFs in real-world applications.

## Author contributions

Y. H. wrote the draft of the paper, J. Q. R. provided major revision to the manuscript, and all co-authors proofread and revised the paper; W. H. C. and C. P. provided valuable suggestions, including the framework design and writing. M. R. T. participated and discussed the paper.

## Conflicts of interest

The authors declare no competing interests.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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