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Three-dimensional covalent organic frameworks for advanced membrane separations

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ABSTRACT

Three-dimensional covalent organic frameworks (3D COFs) have emerged as a promising class of crystalline materials due to large surface areas, interconnected porosity, and accessible active sites. Their structural versatility, enabled by the judicious selection of organic building blocks, allows for precise tuning of pore size, architecture, and functionality. These unique attributes position 3D COFs as ideal candidates for the development of tailored membrane materials capable of high-performance separations. This review provides a comprehensive overview of the synthesis methodologies and applications of 3D COF-based membranes. The critical role of their pore size, topology, stability, hydrophilicity/hydrophobicity and surface charge on membrane structure and performance is examined. In addition, various fabrication methods for 3D COF-based membranes (e.g., blending, *in situ* growth, and interfacial polymerization) are presented. The usage of 3D COF-based membranes in diverse fields such as gas separation, water treatment, organic solvent nanofiltration, pervaporation, and proton exchange is also outlined. The review concludes by identifying key challenges and outlining future research directions for advancing the field of 3D COF-based membranes.

1. Introduction

Efficient separation processes are of paramount importance to the sustainable advancement of the chemical industry. Conventional separation technologies, primarily relying on energy-intensive thermal processes like distillation, lead to a high energy consumption. In response to global challenges such as energy scarcity, resource scarcity, and environmental degradation, membrane-based separations have emerged as a promising alternative due to their low energy consumption, modularity, and minimal environmental impact. However, conventional membrane materials like polyamide (PA), polyimide (PI), and polyvinylidene fluoride (PVDF) exhibit inherent limitations, including restricted porosity and inadequate pore connectivity. This frequently results in a trade-off between permeability and selectivity, hindering their wider separation-related applications [1]. To circumvent these limitations, many studies focus on developing porous membranes with customizable pore structures and selective channels. The incorporation of functional nanofillers with properly and orderly porous channels allows for fine tuning of pore size and functionality to achieve high selectivity and/or permeability. This approach synergistically combines the high throughput of polymeric matrices with the precise sieving capabilities of porous nanofillers, offering a promising pathway to overcome the challenges inherent in common membrane materials.

To date, covalent organic frameworks (COFs) have garnered significant attention as a novel class of crystalline porous materials. Distinguished by their exceptional porosity and precisely tunable pore apertures, COFs are constructed through the covalent assembly of organic building blocks, resulting in a topological structure with periodic organic frameworks and ordered nanochannels [2]. The seminal work by Yaghi and co-workers in 2005 unveiled the potential of functional COFs, sparking widespread research interest [3]. Subsequent studies have focused on developing functional COFs with desired attributes for a range

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of applications, including gas adsorption, catalysis, and energy storage [4]. Given their exceptional porosity, precise pore architecture, and customizable physicochemical properties, COFs emerge as promising candidates for the development of high-performance membranes for molecular and ionic separations. The structural versatility and tunable functionality of COFs offer an immense potential for fabricating novel, advanced separation membrane materials. Based on different dimensions of covalent connectivity, COFs are categorized into 2D layered structures or 3D extended networks. In contrast to the one-dimensional channels present in 2D COFs, 3D COFs feature more intricate structures, including open spatial frameworks and multidirectional interconnected networks. These structural attributes facilitate an enhanced accessibility to active sites and improved molecule/ion transport efficiency [5]. Additionally, while 2D COFs typically have relatively larger pore sizes (1–5 nm), 3D COFs feature narrower pore sizes (0.5–1.5 nm) due to the interpenetration of their 3D frameworks; this trait enhances the sieving efficiency [6–9]. In addition to their smaller pore apertures, 3D COFs offer larger surface areas and superior stability, further contributing to their exceptional potential for separation applications.

While research on advanced COF-based membranes has primarily centered on 2D COFs over the past decade, the unique attributes of 3D COFs offer a promising avenue for achieving membrane-based precise separations. The advantages of 3D COF materials lie in their tunable pore structures, high specific surface area, and low density, making their use in separation technologies an inevitable trend. Despite their exceptional properties, reports on large-scale applications of 3D COFs integrated into membranes remain limited, primarily due to the novelty of these materials. To fully unleash the potential of 3D COFs in this domain, a comprehensive understanding is essential. This review aims to provide a systematic overview of the application of 3D COFs in membrane separation. The crucial characteristics of 3D COFs relevant to membrane separation, including pore size, topology, stability, hydrophilicity/hydrophobicity and surface charge are comprehensively examined. The current state-of-the-art and development strategies for 3D COF-based membranes are also presented. Furthermore, the review identifies key challenges and outlines promising research directions to advance the application of 3D COFs in membrane-based separations.

2. Key attributes of 3D COF membranes for membrane separation

The performance of 3D COF-based membranes is intrinsically linked to their structural and compositional attributes. Ideally, such 3D-COF membranes selectively transport molecules or ions through their uniform, intrinsic pores, while effectively retaining large species exceeding the pore size. Achieving this requires precise control over the pore apertures and environments within 3D COF membranes. Additionally, robust component stability is essential for ensuring membrane durability under diverse operating conditions. To address the specific requirements of various separation applications, the hydrophilicity/hydrophobicity and topology of the 3D COF must also be carefully considered. By judiciously selecting 3D COFs based on their intrinsic properties, including pore size, topology, stability, hydrophilicity/hydrophobicity and surface charge, high-performance membranes capable of selective separations can be achieved. This section provides a summary of the essential characteristics of 3D COFs pertinent to various 3D COF-based membranes.

2.1. Pore size

Pore size adjustment is a pivotal strategy for optimizing membrane performance for task-specific applications. In 3D COFs, pore size is determined by the topological arrangement of the porous network, while pore dimensions are contingent upon the lengths of their constituent building blocks. As a result, the average pore size of 3D COFs can be predictably modulated by varying the lengths, geometries, and functional groups of organic building units. For instance, Wang et al. [8] prepared a 3D COF-based membrane that features interpenetrating nanochannels. The membrane was prepared with pore sizes ranging from 0.8 to 1.5 nm by tailoring and customizing the organic monomers (Fig. 1a). Self-supported, crystalline 3D-COF membranes with tunable thicknesses were attained following ripening pre-synthesized oligomers. The ordered interlocking of the 3D structural units endowed these membranes with narrow and interconnected microporous channels, ultimately facilitating effective sieving with selectivity exceeding 800 for monovalent and multivalent ions such as K^+ and Al^{3+}. In another study, Jiang et al. [7] presented a dual-acid-mediated interfacial polymerization strategy to fabricate a 3D sulfonic acid-functionalized COF membrane, characterized by extended and interconnected transport channels. In this method, sulfonic acid-functionalized aldehyde monomers reacted with tetra-(4-anilyl) methane monomers within a dual-acid organic-water biphasic system (Fig. 1b and c). The amine monomer-containing organic phase was gradually added to the aqueous phase with aldehyde monomers, forming a bilayer. The membrane remained flexible, and mechanically robust, exhibiting a Young modulus of 2.4 GPa (Fig. 1d and e). Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) analyses confirmed its uniform, homogeneous structure, with carbon, oxygen, nitrogen, and sulfur elements evenly distributed (Fig. 1f and i). The resulting 3D COF membrane exhibited ultramicroporous pore sizes of 0.97 nm and abundant sulfonic acid groups, which is conducive to rapid proton and cation transport as well as high selectivity for anions. Qin et al. [10] utilized a one-step solvothermal method to fabricate COF-300 membranes, which were characterized by a 3D framework structure, high specific surface area, and large porosity. The resultant COF-300 membrane exhibited pore sizes ranging from 0.89 to 1.68 nm, facilitating efficient water molecule transport while effectively rejecting dye molecules. Table 1 summarizes the pore sizes of various 3D-COFs applied for membrane separations, highlighting their utility across diverse applications. Therefore, a comprehensive screening of reported 3D COFs, coupled with the introduction of functional groups or side groups, presents promising avenues for identifying optimal candidates for membrane separations.

2.2. Topology

Topology is a critical determinant of pore structure, properties, and potential applications of the 3D framework, directly influencing the selective transport of molecules and ions. Variations in topology significantly affect the pore environment, thereby playing a crucial role in optimizing membrane performance for targeted separation applications. Topology is primarily governed by the valence of its constituent connectors. The tetrahedral configuration inherent to sp^3 hybridized carbon atoms has rendered them the most prevalent building blocks for constructing 3D frameworks. Methane derivatives, adamantane derivatives, and twisted tetrahedral derivatives represent the principal classes of tetrahedral monomers employed in the construction of 3D COFs. Yaghi and coworkers [19] introduced COF-300 in 2009, representing the first example of a 3D COF. This pioneering material was synthesized through the condensation reaction between four-connected tetrahedral monomer tetra-(4-anilyl) (TAPM) and two-connected linker terephthaldehyde. The synthesized COF-300 exhibited remarkable thermal stability, enduring temperatures up to 490 °C, and showcased remarkable permanent porosity with a high surface area of 1360 $m^2\ g^{-1}$.

Recent advancements have witnessed a surge in the development of high-valence and functionalized 3D COFs, significantly expanding the topological diversity of 3D COFs. This evolution has unlocked new possibilities for tailoring pore structure and functionality to specific applications. For instance, Zhu et al. [20] introduced a pioneering 3D COF constructed from triangular prism-shaped organic cages. This unique architecture resulted in a 2-fold interpenetrated acs topology capable of reversible structural transitions between small and large pore states under N,N-dimethylformamide (DMF) loading. Fang et al. [21] described the synthesis of a 3D COF with a large-pore structure and stp topology, assembled from a 6-connected triptycene-based monomer. The resulting

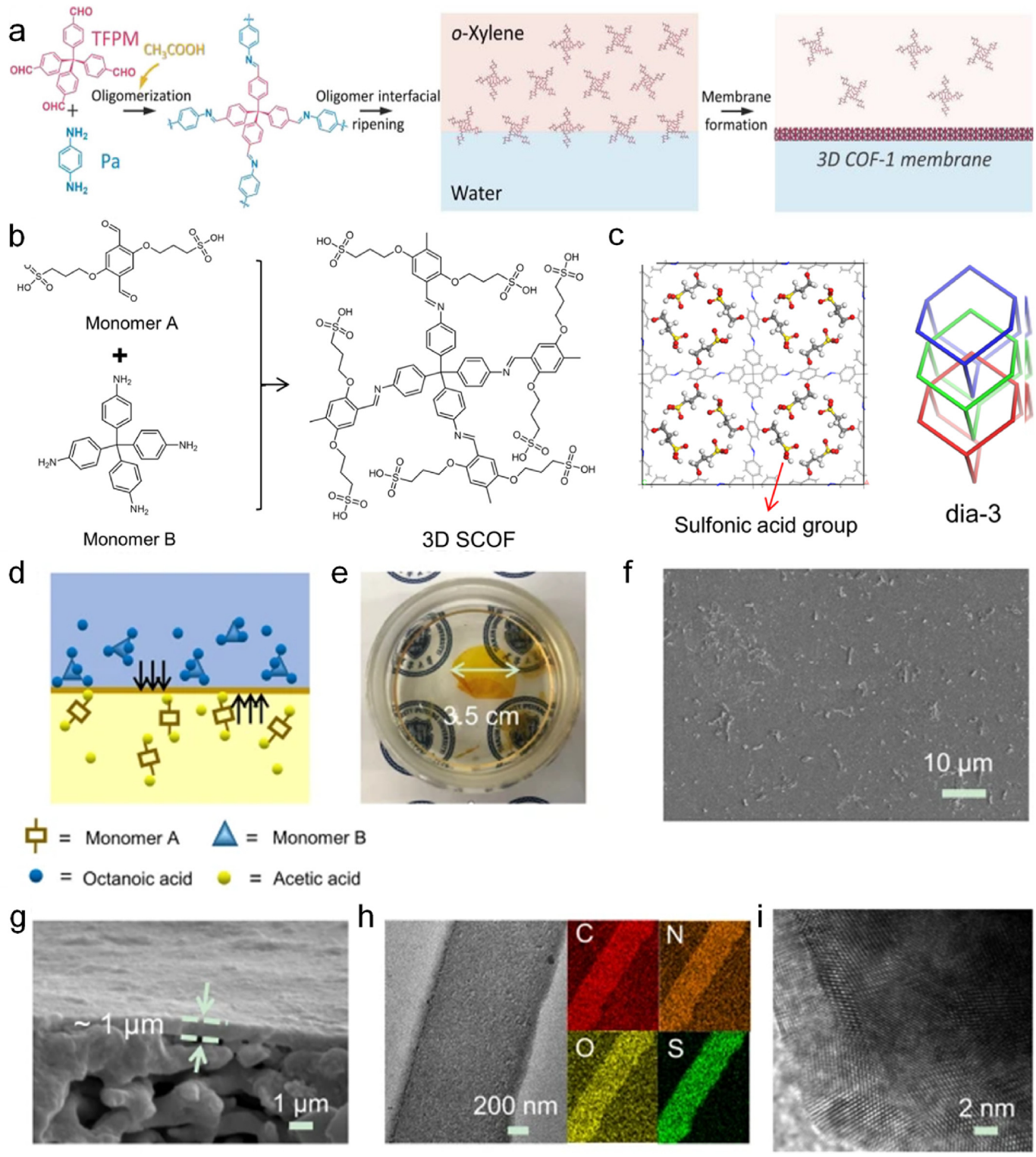


Fig. 1. (a) Depiction of the synthesis procedure [8]. (b) Schematic representation of the 3D SCOF synthesis through imine condensation. (c) Structural depiction of 3D SCOF. (d) Schematic overview to create the 3D SCOF membrane. (e) Digital photo of a 3D SCOF membrane. SEM image of the 3D SCOF membrane (top-view) (f) and (cross-section) (g). (h) TEM and EDS-mapping images of the sample. (i) TEM image of the 3D SCOF membrane in a high-resolution [7].

COFs showcased a significant pore size of 43 Å, and a remarkably low density of 0.108 g cm^{-3}, as revealed in Fig. 2.

The fabrication of crystalline 3D structures remains a significant challenge due to the limited topological diversity achievable with conventional building block. To expand the repertoire of accessible structures, researchers have explored the use of irregular or distorted polyhedral monomers. Additionally, the incorporation of porous organic cages as multi-connected building units offers a promising avenue for constructing complex 3D COFs. Furthermore, modulating reaction conditions provides a versatile approach to influence the resulting topology and product composition.

Table 1
Summary of frequently used 3D COFs in membranes for separation.

3D COFs	Linkages	Organic linkers	Pore size (Å)	Properties	Applications	Ref.
COF-300	Imine	Tetrakis(4-aminophenyl) methane; *p*-phthalaldehyde	3.3, 9.6	–	Proton conduction	[11]
	Imine	Tetraphenylmethaneamine; terephthalaldehyde	7.2	Hydrophobic	Osmotic energy conversion	[12]
	Imine	Tetra-(4-anilyl)methane; Terephthaldehyde	~4	–	Gas separation	[13]
Tam Dbta	Imine	Tetrakis(4-aminophenyl)methane; 2, 5-dibromoterephtahdehyde	11–13	Hydrophobic	Oil/water separation	[14]
TFPM-HZ	Imine	Tetrakis(4-formylphenyl)-methane; hydrazine hydrate	~7.5	Hydrophobic	OSN	[15]
TAPM-Tp	Imine	4-[tris(4-aminophenyl)methyl]aniline; 1,3,5-triformylphloroglucinol	21.5	Hydrophilic	Water treatment	[16]
3D-OH-COF	Imine	Tetrakis(4-formylphenyl)-methane; 3,3′-Dihydroxybenzidine	~8.8	Hydrophilic	Water treatment	[17]
3D COF-1	Imine	Tetrakis(4-formylphenyl)-methane; *p*-phenylenediamine	8–15	Neutral	Water treatment	[8]
3D SCOF	Imine	3,3'-((2,5-diformyl-1,4-phenylene) bis(oxy)) bis (propane-1-sulfonic acid); tetrahedral tetra-(4-anilyl) methane	9.7	–	Ion transport	[7]
Carbon−COF	C−C	Tetrakis(4-iodoophenyl)-methane; Diethynylbenzene	15.2	–	–	[18]
Boron− COF	B−C	Lithium tetrakis(4-iodophenyl)borate; Diethynylbenzene	15.2	–	–	[18]

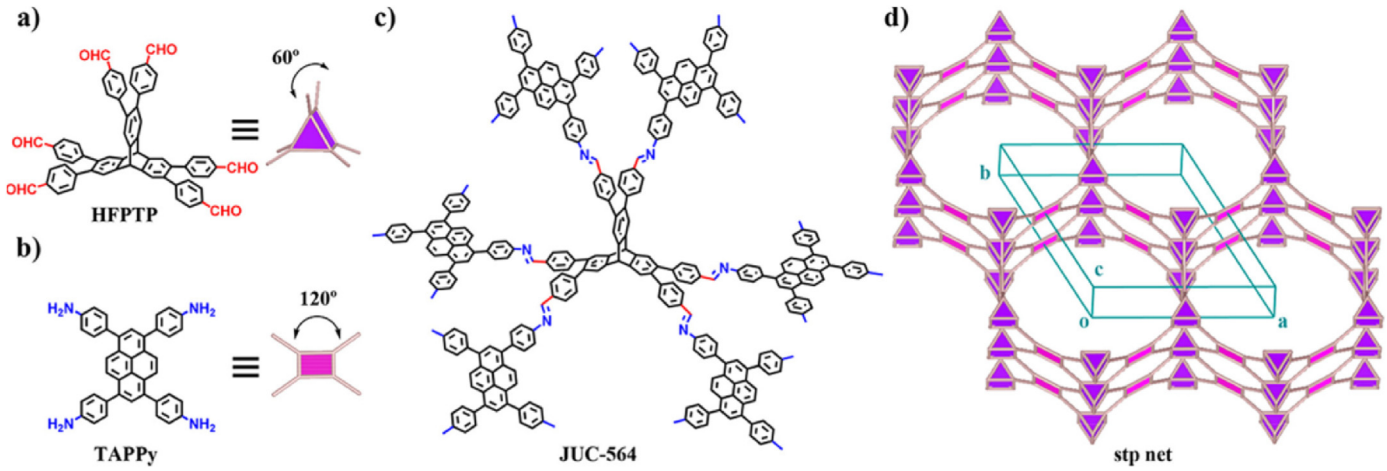


Fig. 2. Approach for building JUC-564 with stp topology [21].

2.3. Stability

The development of 3D COFs has been largely impeded by their insufficient stability, which adversely impacts their functionalization, performance, and practical applications. Enhancing the stability of these COF materials is crucial for their wider practical utilization. Consequently, research efforts have focused on enhancing both their chemical stability in aqueous and organic environments and their thermal stability during synthesis and application. Strategies to increase the robustness of 3D COFs have involved the introduction of additional forces to stabilize the frameworks, such as steric hindrance, Coulombic repulsion, and hydrophobic interactions, as well as the incorporation of sturdy linkages within the 3D structures, such as imide and amide bonds [22]. For example, Fang et al. [23] demonstrated the enhancement of COF stability through the incorporation of periodic isopropyl group within the framework. The resulting COFs exhibited high crystallinity, permanent porosity, and remarkable stability under harsh conditions such as strong acids, bases, and boiling water. Furthermore, these materials demonstrated an exceptional performance in oil/water separation across a wide pH range, achieving separation efficiencies exceeding 99 %. However, the synthesis of 3D COFs with high thermal stability remains a significant challenge. Wang et al. [24] presented the inaugural synthesis and characterization of a novel 3D azine-linked COF. This material displayed an exceptional stability under chemical and thermal conditions, along with a well-defined narrow pore size distribution. Notably, the COFs exhibited a 2-fold interpenetrated diamond topology. The material demonstrated an outstanding performance in selectively adsorbing CO_2 over N_2 and efficiently catalyzing the cycloaddition of propargylic alcohols with CO_2 to form carbonates under mild conditions.

A critical factor in the successful application of 3D COFs within membrane systems is the stability of the interface between the COF layer and the porous support. The integration of 3D-COFs with mechanically stable support requires robust bonding to prevent delamination and loss of functionality. Wang et al. [8] introduced an innovative approach to fabricate durable 3D COF membranes featuring interpenetrated nanochannels. This method involves maturing pre-synthesized oligomers at the organic-water interface, resulting in membranes with adjustable aperture sizes. These membranes demonstrated an exceptional precision in ion and molecule separation, highlighting the importance of strong interfacial adhesion for the long-term performance of 3D COF-based membranes.

2.4. Hydrophilicity/hydrophobicity

The hydrophilicity or hydrophobicity of 3D COFs is a critical factor influencing their performance in membrane applications. These attributes are primarily determined by the nature of the constituent building blocks and their functional groups. Rational design of their hydrophilicity or hydrophobicity is essential to achieve an optimal separation performance for specific target products. Hydrophobic 3D COFs, for

instance, have shown promise in selective adsorption applications. An illustrative example is TFAM-BDNP, a COF constructed from viologen units and tetrahedral neutral building blocks via irreversible tautomerization. This COF features open 3D hydrophobic channels, facilitating the selective diffusion of ions. With this superiority, Chen et al. [25] synthesized a novel 3D azine-linked COF, TFAM-BDNP, via a Zincke reaction. This COF demonstrated high adsorption capacity and rapid exchange kinetics for ReO^{4-}, reaching a maximum uptake of 998 mg g^{-1} with a rapid exchange rate of 60 s. This exceptional selectivity is attributed to the hydrophobic nature of its structure, which promotes the diffusion of ReO^{4-} ions while exhibiting selectivity toward this anion over a wide pH range (2–12) in the presence of competing anions. Beyond its adsorption capabilities, the hydrophobic nature of TFAM-BDNP also makes it appropriate for oil-water separation applications within the context of 3D COF-based membranes. Shetty et al. [14] introduced an innovative approach to modulate in the properties of 3D COF-based membranes via solvent-induced fragmentation. This ambient synthesis produces standalone membranes with diverse characteristics. The sample alteration of the solvent from chloroform to ethyl acetate transformed the membranes from hydrophilicity to hydrophobicity, facilitating selective oil permeation. Likewise, in organic solvent nanofiltration (OSN) applications, certain hydrophobic 3D COF-based membranes facilitate the passage of organic solvents while retaining water molecules on one side of the membrane. For example, Wang et al. [15] reported the development of exceptionally stable and selective OSN membranes based on hydrophobic 3D COFs with precisely defined pore apertures. These membranes exhibited an exceptional performance in separating water from organic solvents.

While hydrophobic 3D COFs have demonstrated promise in specific applications, their inherent hydrophobicity can pose challenges when employed in aqueous environments. The hydrophobic nature of these materials hinders water transport through the membrane, limiting their utility in certain separation processes. To address this limitation, strategies aimed at enhancing the hydrophilicity of 3D COFs have emerged as a critical area of research. Two primary approaches have been explored: (1) incorporation of hydrophilic functional groups into 3D COFs, and (2) selection of appropriate hydrophilic organic linkers during COF synthesis can facilitate the creation of inherently hydrophilic materials. For instance, Wang et al. [17] enhanced the surface hydrophilicity and charge characteristics of membranes by introducing carboxyl groups through reaction within the pores of 3D COFs. Similarly, Shetty et al. [26] developed a novel mixed matrix membrane combining a hydrophilic cellulose acetate (CA) polymer with a multifunctional porous 3D-COF (TamDbta). Both studies demonstrated the importance of hydrophilic functional groups in facilitating water transport within the membrane. The latter study specifically applied this for the removal of toxic phenol from industrial synthetic oil-water emulsions. The polar functional groups in CA enhanced the membrane's hydrophilicity, promoting the movement of water molecules through it. Du et al. successfully fabricated a self-standing 3D COF membrane through imine linkage formation. The presence of hydrophilic aldehyde functional group on TFPDA monomers facilitated the rapid water molecule passage. While hydrophilicity is crucial for many membrane applications, such as water treatment and desalination, hydrophobic 3D COFs have shown promise in specific processes like oil/water separation. Nonetheless, the development of hydrophobic 3D COF-based membranes for membrane distillation, where hydrophobicity is a desirable property, remains relatively unexplored.

2.5. Surface charge

In addition to the key factors previously discussed, surface charge plays a crucial role in dye separation and desalination through membrane-based methods. Both physical size sieving and electrostatic interactions work synergistically to repel solutes, thereby optimizing separation outcomes [27]. For example, industrial wastewater, including oil-produced water, varies in pH and salinity, significantly affecting the membrane removal efficiency in water treatment. In this context, Shetty et al. [26] investigated the phenol removal performance of the hybrid membrane (TamDbta-CA) under varying pH and salinity conditions. At pH = 2, the removal efficiency decreased to 75.5 %, while pH = 10, it increased to 91.6 %. Zeta potential analysis confirmed that higher pH levels resulted in an increase in surface negative charge, which enhanced the electrostatic repulsion between the membrane and phenolate. In contrast, lower pH levels reduced the surface negative charge due to protonation, leading to a slight decrease in phenol removal performance. Du et al. [28] investigated the significant impact of surface charge on the selective separation of dyes. In this study, the TFPDA-TFPOB-COF/PES membrane exhibited a significantly negative surface charge attributed to the COF layers, which was advantageous for the separation of positively charged dyes. Beyond size sieving, charge effects provide significant flexibility in adjusting the internal surface charge of COFs with closed pores. This flexibility can be utilized to enhance ion transport of dyes, including achieving selective separation based on the degree of donor binding bipolarity, which is essential for efficient dye separation.

3. Rational design strategy of 3D COF-based membranes

The ordered and densely packed pore structures inherent to 3D COFs distinguish them from other porous materials and offer unique advantages for membrane separations. The integration of 3D COFs into membrane architectures has emerged as a promising strategy to enhance separation performance. To fully harness the potential of 3D COFs, a growing number of studies start to develop effective fabrication strategies toward high-performance 3D-COF membranes. Currently, there are two main configurations of 3D-COF membranes used for membrane separation: 3D COF-based mixed matrix membranes and continuous 3D COF membranes. The former incorporates COFs as porous fillers that are mixed with polymer matrix membranes, providing additional pathways for the passage of gases, water, or solvents. While this approach offers a straightforward and facile route to membrane fabrication, the separation performance is often limited by the interfacial interactions between the COF particles and the polymer. In contrast, the development of continuous 3D COF membranes has garnered significant attention thanks to the potential for superior selectivity and permeability. Recent advancements in COF synthesis and processing have enabled the fabrication of continuous 3D-COF membranes with controlled pore structures. Continuous COF-based membranes are typically fabricated through methods such as blending, *in situ* growth, and interfacial polymerization (IP). This section introduces several applicable methods with the potential to manufacture high-performance 3D COF membranes, focusing particularly on recent breakthroughs in the synthesis of 3D COF membranes.

3.1. Blending

Non-solvent induced phase separation (NIPS) and IP are two commonly employed techniques for integrating 3D COF-based mixed matrix membranes. These methods offer relative simplicity and cost-effectiveness compared to other membrane preparation approaches. The organic nature of 3D COFs ensures an excellent compatibility with polymer matrices, thereby minimizing interfacial defects often observed with inorganic fillers. Additionally, the inherent porosity of 3D COFs provides additional pathways for the molecular transport, potentially enhancing the selectivity and permeability. In the typical NIPS, 3D COFs are dispersed into a polymer solution via blending, followed by casting the solution into a thin film onto glass plates or nonwoven fabrics. The formation of a porous mixed matrix membrane (MMM) structure occurs through phase separation induced by immersion in a non-solvent bath. This technique leverages the processability of polymers while incorporating the unique properties (e.g., interconnected pores) of 3D COFs. The resulting MMMs benefit from the combined advantages of both components, including enhanced porosity, selectivity, and mechanical stability.

Bae et al. [29] demonstrated the potential of 3D COFs as nanofiller in MMMs incorporating a 3D COF containing secondary amine functional groups into a 6FDA-DAM polymer matrix. The all-organic component ensured the excellent compatibility with the polymer matrix, while its porous structure and amine-rich moieties boosted both surface area and CO_2 affinity. The resulting MMMs exhibited improved the CO_2/CH_4 separation performance compared to the pristine polymer membrane. Zhao et al. [13] presented the usage of COF-300 as fillers within both 6FDA-DAM and Pebax for CO_2 capture and storage. The 6FDA-DAM polymer with bulky CF_3 groups exhibited a large free volume, enhancing gas permeability while the rubbery Pebax matrix facilitated efficient filler encapsulation and defect mitigation. The incorporation of COF-300 into both polymer matrices resulted in improved CO_2/CH_4 and CO_2/N_2 selectivity due to the combined effects of the porous structure of COF-300 and the polymer matrix properties.

In contrast to MMMs, thin-film nanocomposite (TFN) membranes are synthesized through interfacial polymerization (IP). This technique involves the formation of a thin polymer layer at the interface between aqueous and organic phases using two reactive monomers. The lower viscosity of the aqueous phase compared to polymer casting solutions facilitates rapid dispersion of 3D COFs within the formed polymeric film. The TFN membranes typically feature an ultrathin selective layer with

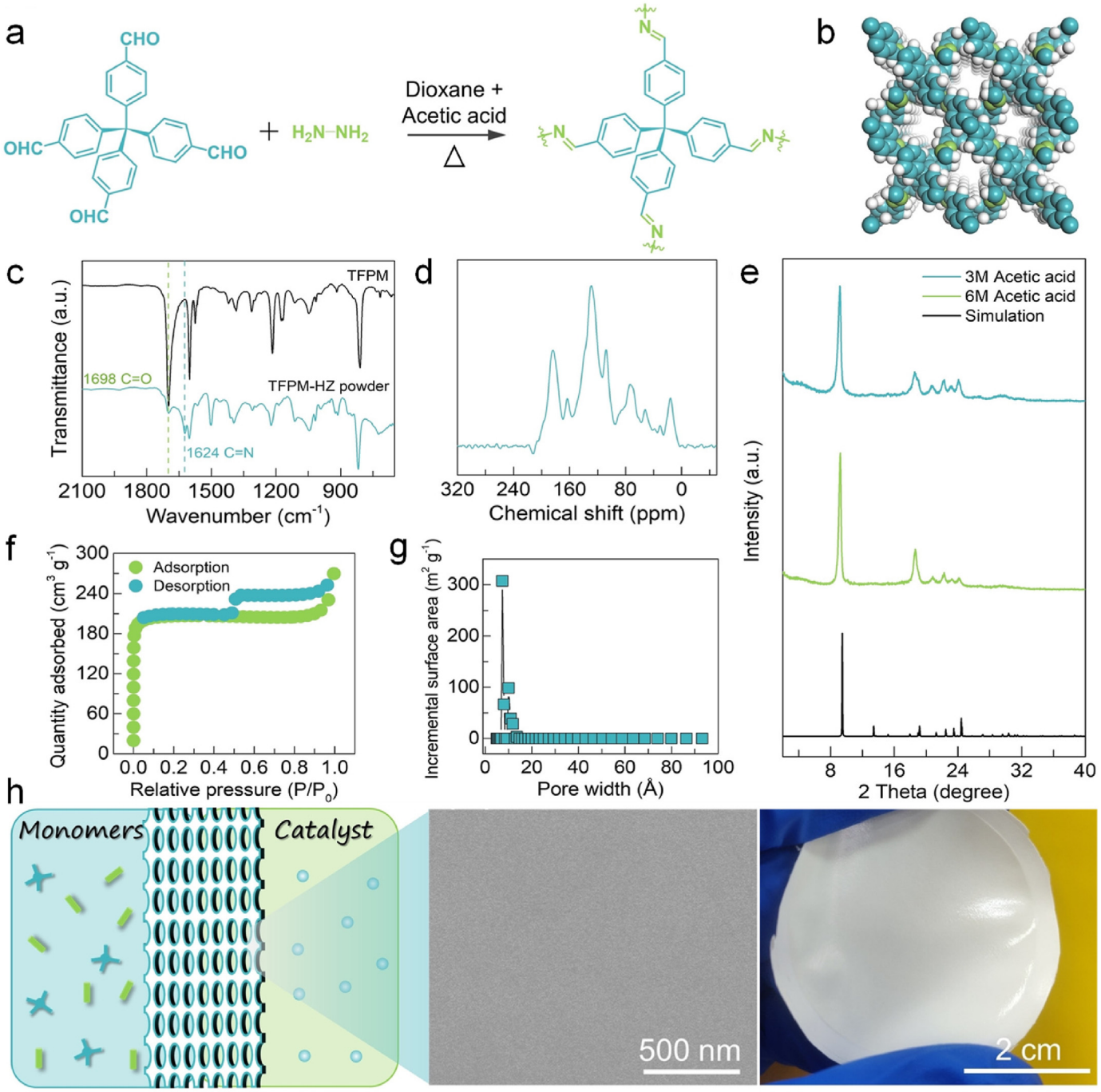


Fig. 3. (a) Schematic illustration of TFPM-HZ synthesis. (b) Molecular structure of TFPM-HZ. (c) FTIR spectra comparison between TFPM-HZ and TFPM. (d) ^{13}C solid-state NMR spectrum of TFPM-HZ. (e) PXRD patterns of TFPM-HZ. (f) Nitrogen adsorption-desorption isotherms of TFPM-HZ. (g) Pore size distribution of TFPM-HZ. (h) Preparation, SEM, and digital photo of TFPM-HZ/PAN membranes [15].

nanofillers, a porous substrate, and a support layer. The physicochemical characteristics of the 3D-COF fillers—such as size, shape, charge, porosity, and functionality—are crucial in determining the morphological structure and performance of the TFN membranes. In this context, the judicious selection and functionalization of 3D COFs as fillers is crucial for the optimization of the membrane performance. Furthermore, integrating 3D COFs into the thin active layer of TFN membranes leads to relatively low consumption of 3D COFs during membrane fabrication. Wang et al. [15] synthesized a molecular sieving 3D-COF layer by tetrakis(4-formylphenyl)-methane and hydrazine hydrate on porousPAN supports through moderated interfacial crystallization, as shown in Fig. 3a and b. FTIR analysis reveals a reduced intensity at approximately 1698 cm^{-1} for the C=O stretching vibration in TFPM, indicative of condensation, along with a new peak at around 1624 cm^{-1} attributed to imine bonds. ^{13}C solid-state NMR spectroscopy confirms the presence of C=N bonds at approximately 162 ppm. PXRD analysis demonstrates the crystallinity of TFPM-HZ, evidenced by peaks at 2θ values of 9.3°, 18.6°, 20.7°, 22.3°, and 24.1°. Nitrogen adsorption-desorption at 77 K reveals microporosity with a BET surface area of approximately 626 m^2/g. The pore width distribution, centered at 0.75 nm, indicates that TFPM-HZ is well-suited for high-performance OSN membranes (Fig. 3c–h). The 3D COF platform addresses critical challenges in OSN membranes by exploiting its distinctive characteristics, including rigid crystalline frameworks, hydrophobic pore chemistry and continuous channels. The uniform, non-deformable crystalline structure offers outstanding durability against solvent swelling and physical aging, enabling stable performance over extended periods. These attributes render the membrane particularly effective for the purification of diverse bioactive molecules, showcasing the broad applicability in the pharmaceutical industry.

3.2. *In situ growth*

To exploit the inherent advantages of 3D COFs for membrane separations, the development of continuous 3D COF membranes has emerged as a critical research area. *In situ* growth has gradually gained widespread attention due to its simplicity, ease of control, and versatility. This method enables the creation of both standalone 3D COF films and 3D COF-based composite membranes. In 2017, Banerjee et al. [30] devised an advanced fabrication technique for producing self-supporting, porous, and crystalline covalent organic materials (COMs) by thermally treating organic linkers with p-toluene sulfonic acid. The powdered aromatic diamine and PTSA·H_2O were co-mixed in water to synthesize an organic salt. This salt, along with Tp, was thoroughly vortexed to form a dough, which was subsequently knife-cast onto a glass substrate and baked at 60–120 °C for 12–72 h. The resulting COMs were sufficiently rinsed with distilled water and acetone. The thickness of the COMs could be precisely regulated by adjusting the gap between the knife and the glass substrate. These resultant COMs exhibited exceptional chemical and structural stability, even under harsh conditions (e.g., water, organic solvents, mineral acids). Additionally, these materials demonstrated a high porosity and promoted the rapid transport of solvents.

Although the construction of self-standing 3D-COF membranes remains challenging, the integration of 3D-COFs with porous supports provides a feasible route to strengthen the overall mechanical stability. *In situ* growth of 3D-COF films on pre-existing support membranes has gained increasing attention thanks to its potential for creating robust and high-performance composite membranes. This technique allows for precise control over the COF film thickness and the interaction with the underlying supports, enabling the optimization of membrane microstructures for task-specific separations. To address the issues of discontinuous crystal layers and weak particle adhesion to the substrate, Qin and co-workers [10] proposed a solvothermal *in situ* growth method to fabricate a high-quality COF-300 membrane on NH_2-modified porous ceramic supports (Fig. 4). In this work, a porous ceramic support was modified with 3-aminopropyltriethoxysilane (APTES) and terephthalaldehyde (TPA) to facilitate the covalent attachment of a COF-300 layer. This method generated a dense and uniform COF layer with excellent stability and water transport properties. Similarly, Li and co-workers [31] applied an *in situ* growth method to fabricate imine-linked COF-LZU1 and COF-300 membranes on ceramic substrates. These membranes demonstrated an exceptional performance in the separation of azeotropic mixtures, including acetone/n-hexane, acetone/cyclohexane, and methanol/benzene. The continuous and defect-free COF layers on a ceramic substrate demonstrated high solvent fluxes (20.0 kg m^{-2} h^{-1} for acetone and 4.9 kg m^{-2} h^{-1} for methanol) and high separation factors (30 for acetone/n-hexane, 13.4 for acetone/cyclohexane, 4.3 for methanol/benzene), which highlights the potential of these membranes for efficient solvent separation.

3.3. *Interface-assisted synthesis*

Analogous to IP employed in the fabrication of polyamide membranes, an interfacial-assisted approach can be utilized to fabricate thin and continuous 3D-COFs membranes. This technique involves the formation of a thin COF layer at the interface between two immiscible phases. The resulting TFC membranes exhibit a distinct structure, comprising a porous support and a thin selective COF layer. Furthermore, leveraging the ordered nanopores of 3D COFs, this technique offers a scalable route to produce continuous, defect-free COF layers, leading to membranes with enhanced permeability and selectivity. The TFC

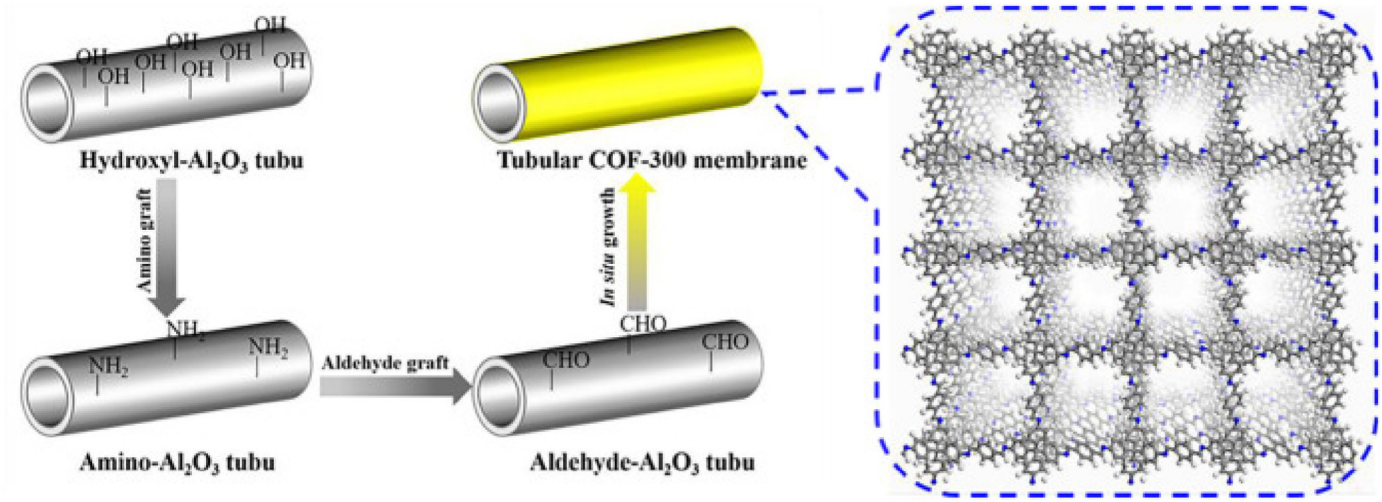


Fig. 4. Diagram depicting the *in situ* growth method for fabricating a COF-300 membrane [10].

configuration allows for the integration of 3D COFs into a scalable and industrially relevant membrane format. Unlike the *in situ* IP reaction conducted on the membrane substrate surface, the interfacial-assisted synthesis results in freestanding 3D COF-based membranes that necessitate an additional transfer process. A seminal study reported in 2017 demonstrated the preparation of continuous COF-based membranes using interfacial-assisted synthesis [32]. Beyond traditional 2D COFs, this approach has enabled the integration of 3D COFs into membrane structures, capitalizing on their unique properties including high porosity and crystallinity. For example, Bishnu and co-workers [33] employed a triple immiscible solvent system to fabricate 3D COF membranes, comprising ethyl acetate, water, and dichloromethane (corresponding to the top, middle and bottom layer). Tetrahedral amine linker (TAM) and a catalytic amount of *p*-toluenesulfonic acid (PTSA) were dissolved in the aqueous phase, while two distinct ditopic aldehyde linkers (DTP and DBD) were introduced into the respective organic phases. Acid-catalyzed Schiff-base polycondensation reactions at the ethyl acetate/water and water/dichloromethane interfaces resulted in the formation of free-standing, flexible 3D COF membranes, namely TAM-DTP and TAM-DBD. These membranes exhibited excellent transmittance and high intrinsic conductivities at THz frequencies, with promising scattering time and plasma frequency, demonstrating their potential for future optoelectronic applications (Fig. 5). In addition, Chen et al. [12] synthesized a series of continuous 3D COF-based membranes using an interface-assisted strategy for osmotic energy conversion. In this work, the free-standing COF-300 membrane served as an immobilization matrix, which was synthesized through interfacial condensation of tetraphenylmethaneamine (TAM) and terephthalaldehyde (TPA) at 35 °C over three days. On this basis, they developed a straightforward strategy to incorporate ionic dye molecules into the COF-300 matrix during membrane synthesis, creating Angström-sized ionic channels within the framework. This method produced stable and functional membranes capable of selectively transporting ions, mimicking biological processes. The resulting reverse electrodialysis (RED) stack exhibited impressive performance in osmotic energy conversion, approaching the power density of the best RED membrane-based systems.

4. 3D COF-based membrane applications

The customizable pore structures and sizes of 3D COFs render them highly suitable for diverse separation applications [28,34]. In particular, 3D COF-based mixed-matrix membranes, thin-film nanocomposite membranes, and continuous COF-based membranes have emerged as versatile materials for a range of separation processes, including gas separation, water treatment, OSN, pervaporation, and fuel cells. This section will delve into specific examples and advancements within these application areas.

4.1. Gas separation

Traditional membranes made from amorphous polymers often exhibit limitations in selectivity due to their disordered and inconsistent pore size distribution, making it difficult to achieve selectivity beyond the current Robeson upper limit. In contrast, 3D COFs feature a covalently bonded three-dimensional skeleton, and are eminent for well-defined pore structures, excellent chemical stability, and ease of functionalization. These unique properties of 3D COFs hold promise for achieving unprecedented levels of selectivity and permeability [35]. The first example of a COF studied for gas separation was reported by Zhu et al., in 2013 [36]. They synthesized a novel microporous crystalline material MCOF-1, featuring a narrow pore size of 0.64 nm. This COF could maintain structural stability and porosity after solvent evacuation and demonstrated high adsorption capacities for C_2H_4, C_2H_6, and C_3H_8. Notably, MCOF-1 exhibited an exceptional selectivity for C_3H_8 over CH_4, as well as for C_2H_6 and C_2H_4 over CH_4. Following this, Wang et al. [37] introduced the inaugural synthesis of a pyrene-based 3D COF (3D-Py-COF). This COF exhibits a unique two-fold interpenetrated pts topology, and additionally displayed a narrow pore size distribution,and selective CO_2 adsorption. Similarly, McGrier et al. [38] reported a mesoporous 3D COF with C3-symmetric π-electron conjugated dehydrobenzoannulene (DBA) and tetrahedral tetra-(4-dihydroxyborylphenyl)methane (TBPM) units. DBA forms robust metal complexes with Li, Ca, and transition metals in low oxidation states, similar to porphyrin and phthalocyanine ligands. They demonstrated that DBA and TBPM monomers form a crystalline 3D polymer network. Subsequent metalation with nickel yielded Ni-DBA-3D-COF, which retained good crystallinity and demonstrated a minimal surface area reduction to 4763 m^2/g. Both 3D DBA-COFs exhibited significant ethane and ethylene uptake capacities. In another case, Feng et al. [39] presented the fabrication of 3D anionic COFs using aliphatic and flexible macrocyclic γ-cyclodextrin units connected by spiroborate linkages with various counterions. These CD-COFs exhibited a high surface area of up to 934 m^2/g, diverse counterions, and dynamic functionalities. Notably, CD-COF-Li demonstrated significant Li ion conductivity and adjustable CO_2 adsorption capacity, highlighting the potential of this framework for energy-related applications. Additionally, Wang et al. [40] developed a 6-connected triangular prism node derived from triphenylbenzene to facilitate the synthesis of 3D-TMTAPB-COF through imine condensation. The resulting 3D COF, designated as 3D-TMTAPB-COF, demonstrated a superior gas separation performance, as evidenced by its high SF_6 adsorption capacity (60.9 cm^3/g) and superior SF_6/N_2 selectivity of 335 at 298 K and 1 bar, underscoring the potential for efficient gas separation. This work demonstrates the feasibility of synthesizing large single-crystal 3D COFs with strong covalent bonds using solvothermal methods without modulators, while also introducing a novel node for future COF designs.

The development of COF-based membranes for gas separation has

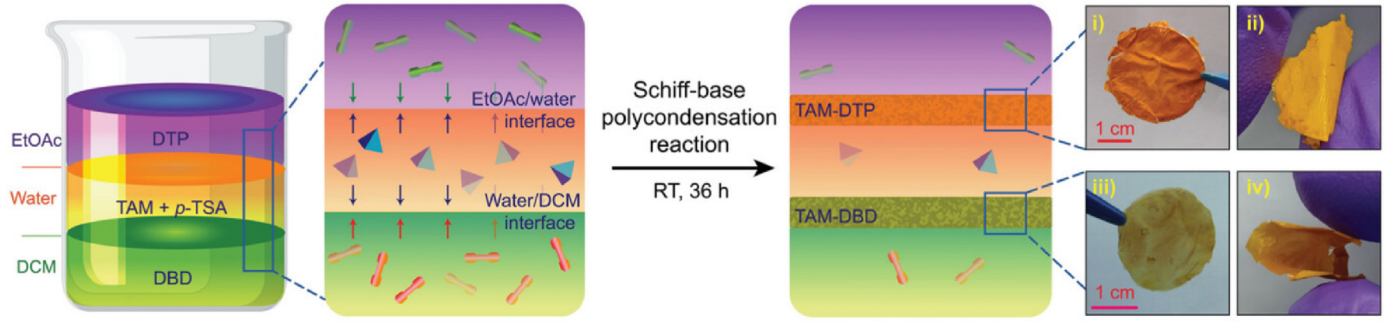


Fig. 5. Diagram illustrating the TLDI method for synthesizing TAM-DTP and TAM-DBD COF membranes, and digital images of TAM-DTP and TAM-DBD membranes [33].

garnered significant attention in recent years [41]. For example, Fang et al. [42] presented a novel strategy for constructing continuous, self-standing COF membranes (2D N-COF and 3D COF-300) for H_2/CO_2 separation (Fig. 6a–c). These membranes demonstrated a high selectivity (13.8 for N-COF, 11 for COF-300) and an exceptional H_2 permeance (4319 GPU for N-COF, 5160 GPU for COF-300), exceeding the Robeson upper bound, and demonstrated good long-term stability (Fig. 6d–i). This study represents the first example of self-standing COFMs for H_2/CO_2 separation, significantly advancing the development of efficient H_2 purification methods. Another strategy involves combining 3D COFs and MOFs to fabricate composite membranes for gas separations. This approach leverages the synergistic interaction between the porous materials to achieve an excellent separation performance. For example, Qiu et al. [43] pioneered the development of COF-MOF composite membranes in 2016, demonstrating the synergistic potential of combining these two porous materials. The composite membranes showed separation factors of 12.6 and 13.5, respectively, surpassing the Robeson upper bound. The enhanced selectivity was attributed to the chemical bonds formed between the COF and MOF components, highlighting the potential of such hybrid materials for gas separation applications. Ben et al. [44] further explored the potential of combining COFs and MOFs by fabricating a composite membrane with COF-300 and UiO-66. This composite membrane presented a superior H_2/CO_2 separation performance compared to its individual components. This exceptional performance was due to the synergistic interaction of the used porous materials.

Beyond hydrocarbon separations, the unique pore architecture of 3D COFs has attracted significant interest for the separation of inert gas mixtures. Tong et al. [45] evaluated the structure-property relationships of COFs for separating binary mixtures of noble gases at room temperature under the industrial vacuum (VSA) and pressure swing adsorption (PSA) conditions. A CoRE COF database comprising 187 computation-ready COFs was constructed. For Xe/Kr separation, COFs with small pores (largest cavity diameter around 4–10 Å) exhibited an excellent performance in VSA, whereas 3D-COFs with ctn or dia topology (largest cavity diameter around 9–13 Å) are optimal in PSA. These 3D-COFs demonstrated a superior performance due to their unique pore structures, making them comparable or even superior to MOFs for Xe/Kr separation. For Rn/Xe separation, VSA processes benefit from 3D-COFs with dia or ctn topology (largest cavity diameter around 9–13 Å), as well as 2D-COFs with specific pore shapes. In contrast, 3D-COFs with pore sizes of 10–20 Å excel under PSA conditions. This work provides a valuable database for future research. The unique advantages of 3D COFs, especially their well-defined and tunable pore sizes, significantly contribute to their high performance in these separation processes.

4.2. Water treatment

As the global population and urbanization accelerate, freshwater scarcity emerges as a critical challenge. To ensure sustainable water resources, advanced technologies and materials are imperative for efficient water purification. Among these, 3D COFs provides a promising platform for effectively removing contaminants from aquatic environments [46]. The pore size of 3D COFs is pivotal in water treatment applications, as it allows for the selective separation of pollutants based on size exclusion. This versatility, tailored to specific pore size requirements, makes 3D COFs highly effective for applications such as seawater desalination, dye separation, heavy metal removal, pollutant detection and other water purification processes.

The complex aquatic systems require a comprehensive consideration of 3D COF properties (e.g., surface properties, hydrophilicity, and charge) to optimize their efficacy in diverse water treatment scenarios. Additionally, enhancing the performance of 3D COF materials in water treatment necessitates their structural stability as a fundamental prerequisite. Wang et al. [47] presented a durable and imidazole-linked 3D COF (BUCT-COF-7) through a one-pot Debus-Radziszewski reaction (Fig. 7a–b). The synthesized membranes demonstrated an excellent oxygen reduction reaction (ORR) activity and high hydrogen peroxide (H_2O_2) selectivity (83.4 %). As a cathode catalyst, it achieved a significant H_2O_2 production rate of 326.9 mmol g^{-1} h^{-1}, effectively degrading methylene blue through the Fenton reaction (Fig. 7c–e). Besides, Ghahari et al. [27] examined the adsorption behavior of dyes on 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) in 3D COFs. Molecular dynamics and metadynamics simulations evaluated the adsorption capacity of COFs for seven dyes, with the MO/COFs system exhibiting an exceptional stability due to the total interaction energy of −448.54 kJ/mol. The unique design of TFPPy-COF offered ultrafast kinetics, high adsorption capacity, and excellent reusability, demonstrating significant potential for dye removal from aqueous environments.

Based on simulation studies, tailoring the linking groups of 3D COFs allows modulation of their structure and hydrophilicity, significantly impacting the desalination performance of 3D COF-based membranes. This strategy holds promise for enhancing the suitability of 3D-COFs for seawater desalination. Guan et al. [48] employed MD simulations to analyze the desalination properties of NPN-X membranes with different linking groups. Highlighting superior desalination efficiency for NPN-1 and NPN-2 exhibited a superior desalination efficiency, with water permeances two orders of magnitude higher than those of traditional reverse osmosis membranes. Despite the larger pore size of NPN-3, NPN-2 showed the highest water permeance attributed to enhanced hydrophilicity of its linking group. Additionally, the stronger ion interactions and narrower pore structures of NPN-1 and NPN-2 further optimized the performance, offering insights for the design of advanced desalination membranes. Yan et al. [49] introduced a 3D COFs (3D-OH-COF) with excellent crystallinity and large surface areas. MD simulations revealed that these COFs could achieve 100 % salt rejection and a water flux of 41.44 L cm^2 day^{-1} MPa^{-1}, outperforming commercial reverse osmosis membranes and other theoretical models, as revealed in Fig. 8a and b. Fig. 8c depicts the time-dependent increase in water molecules permeating through 3D-OH-COF membranes of varying thicknesses under a pressure of 100 MPa, indicating stable water flow. Fig. 8d shows that as membrane thickness increases, water flux decreases because of higher energy barriers. Fig. 8e highlights an almost linear correlation between water flux and pressure for a 3D-OH-COF membrane with a thickness of 44.1 Å. Salt rejection rates improve with membrane thickness, reaching 100 % for membranes thicker than 29.4 Å. Fig. 8f indicates that salt rejection for the 44.1 Å membrane is 100 % at 100 MPa but declines to 90 % at 250 MPa, suggesting enhanced ion rejection at lower pressures. The 3D-OH-COF membrane ($n = 6$) demonstrates exceptional desalination performance, achieving 100 % salt rejection at 100 MPa and a water permeability of 41.44 L cm^{-2} day^{-1} MPa^{-1}. This performance represents an improvement of over two orders of magnitude compared to commercial reverse osmosis membranes and is four times greater than that of monolayer MoS_2. Additionally, it surpasses bilayer 2D-CAP membranes by nearly 28 % in permeability. The 3D-OH-COF membrane with a thickness of 44.1 Å also maintains 100 % salt rejection. Ion transport studies indicate that Na^+ and Cl^- ions are predominantly retained in the feed chamber, with Cl^- ions exhibiting a higher density within the membrane channel compared to Na^+ ions (Fig. 8g and h). These findings establish 3D-OH-COF as a promising desalination material and provide insights into the underlying molecular mechanisms. Additionally, the imine-linked 3D COF-300 exhibited remarkable water stability, indicating its potential for long-term water treatment applications. For example, Qin et al. [10] synthesized a high-quality COF-300 membrane on NH_2-modified porous ceramic supports. The resulting membrane exhibited an excellent flux of 395.3 L m^2 h^{-1} at 5 bar, considerably exceeding the performance of contemporary NF membranes, and achieved a 97.4 % rejection rate for Chrome black T. Additionally, the COF-300 membrane exhibited exceptional stability, preserving its performance for up to 90 h.

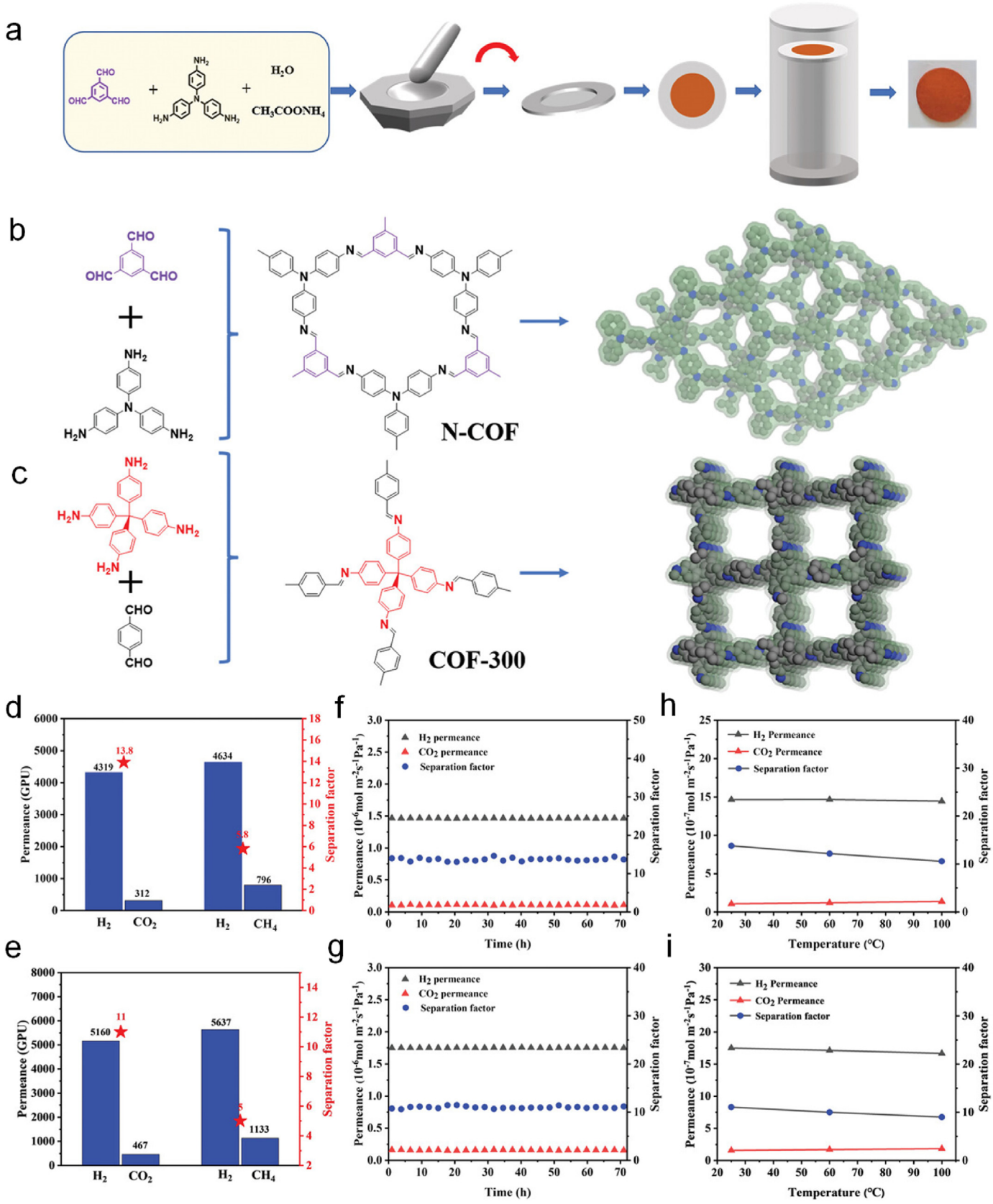


Fig. 6. (a) Diagram illustrating the fabrication process. (b–c) Structure and composition. (d–e) Separation performance of an equimolar binary gas mixture using N-COF membrane and COF-300 membrane. (f–g) Long-term testing with an equimolar H_2/CO_2 mixture at room temperature. (h–i) Selectivity and permeance as functions of temperature [42].

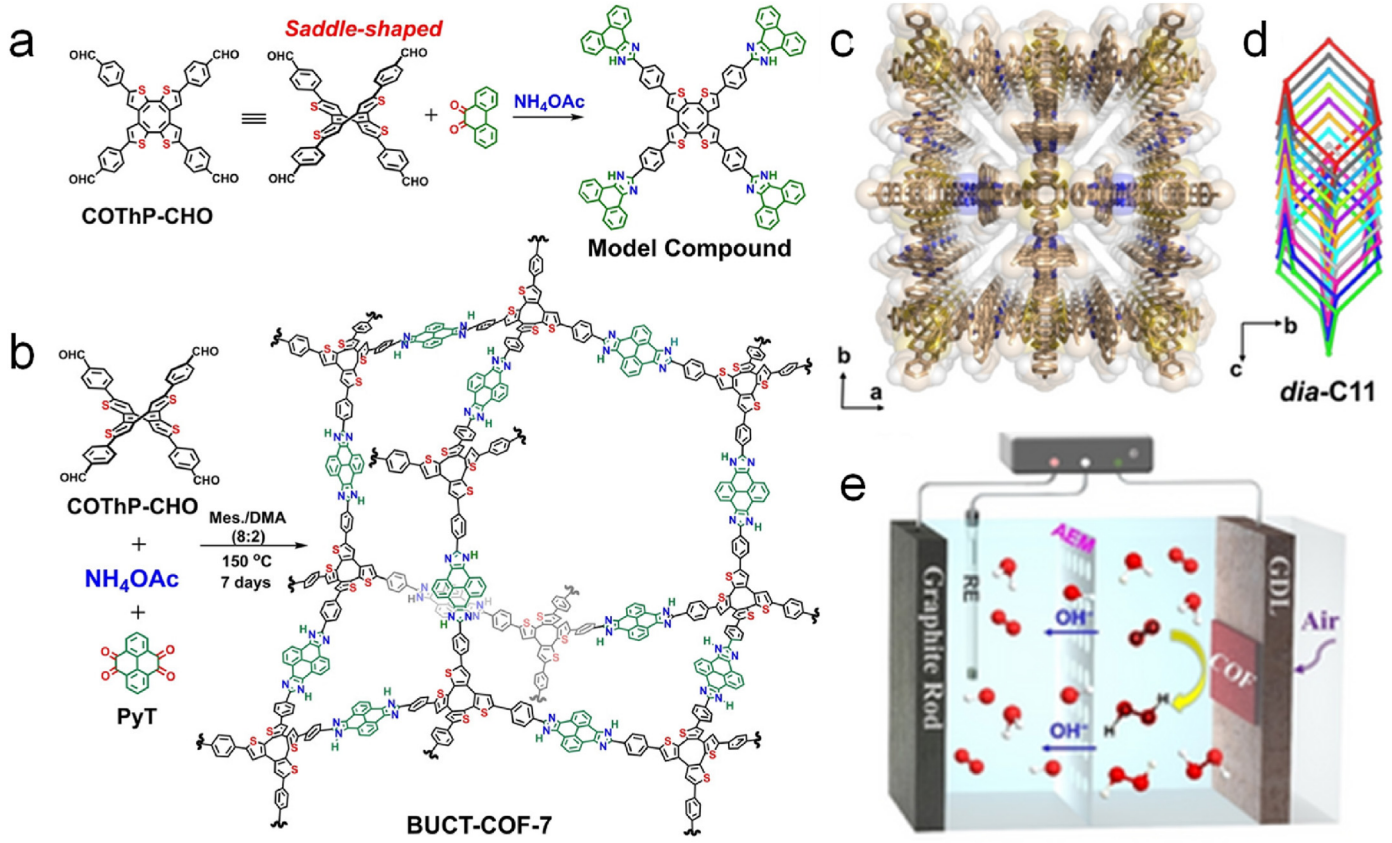


Fig. 7. Synthetic pathway for (a) the imidazole-linked Model Compound and (b) the fully conjugated BUCT-COF-7. (c) Space-filling model. (d) Model depicting 11-fold interpenetration. (e) Diagram of the electrolyzer for the synthesis of H_2O_2 [46].

4.3. Organic solvent nanofiltration

Organic solvents are indispensable in diverse industries such as petroleum, chemicals, and pharmaceuticals, with over 80 % of material consumption in active pharmaceutical ingredient manufacturing attributed to their use. The escalating global demand for organic solvents has necessitated the development of sustainable and efficient methods for solvent recovery. In this context, OSN has emerged as a promising solution due to its environmental benefits, low energy consumption, and minimal carbon footprint [50,51]. Unlike aqueous system NF, OSN membranes require exceptional stability in organic solvents to maintain pore structure and sizes. However, conventional OSN membranes face challenges in achieving persistent selective separation of fine molecules due to non-ideal pore uniformity and polymer swelling in solvents. The unique characteristics of 3D-COFs, including their ultrafine, interconnected pores, offer the potential for overcoming these challenges and creating high-selective OSN membranes. Wang et al. [15] established a 3D COF-based membrane in 2022, simultaneously achieving stability for both OSN and material integration with membranes. This innovative approach employed controlled interfacial crystallization and nanostructured supports to create 3D COF-based membranes with sub-nanometer channels, significantly enhancing methanol permeance and demonstrating an exceptional stability under high-concentration conditions, thus validating their industrial applicability. The OSN performance of the TFPM-HZ/PAN membrane, synthesized over 48 h, was assessed through dead-end filtration at a trans-membrane pressure of 1 bar. The membrane exhibited a high permeance for various organic solvents, with methanol achieving ≈44 L m^{-2} h^{-1} bar^{-1}, four times higher than that for water, due to its hydrophobic nature, which impedes water transport while facilitating methanol movement.

4.4. Pervaporation

Pervaporation is a cost-effective separation method-based membrane that is applicable to biorefining, petrochemicals, and pharmaceuticals. In pervaporation, the membrane initially absorbs components from the feed mixture and followed by evaporation on the other side. Separation of different components is achieved through differential adsorption and diffusion rates. While pervaporation is effective for dehydrating organic solvents, removing volatile organic compounds from aqueous solutions, and separating organic-organic solvent mixtures, developing high-performance membranes with reliable selectivity and productivity remains a challenge. The unique pore structure of 3D COFs has a significant impact on pervaporation. Precisely designing pore sizes allows for the effective separation of substances with different molecular weights, while simultaneously improving both selectivity and permeability. In pervaporation, adsorption and diffusion are closely related to the intrinsic properties of the material, and 3D COFs are well-suited to meet these requirements. Li et al. [31] applied the imine-linked COF membranes (COF-LZU1 and COF-300) for differentiating azeotropic mixtures. The pervaporation performance of COF-300 membranes was evaluated using different azeotropic mixtures. Notably, COF-300 membranes exhibited high separation factors due to their smaller pore size compared to COF-LZU1. In the acetone/n-hexane system, COF-300 enriched acetone from 59 wt% to 97.7 %, achieving a separation factor of 30.0. The membranes also demonstrated a high separation efficiency for other azeotropic mixtures, indicating their potential for industrial applications. The composite membranes achieved high solvent fluxes and significant separation factors, confirming the technical viability of 3D COF-based membranes for azeotropic solvent mixture separation. Qin et al. [52] proposed a novel strategy to improve organic permeation while reducing water permeation by incorporating organophilic porous particles, such as

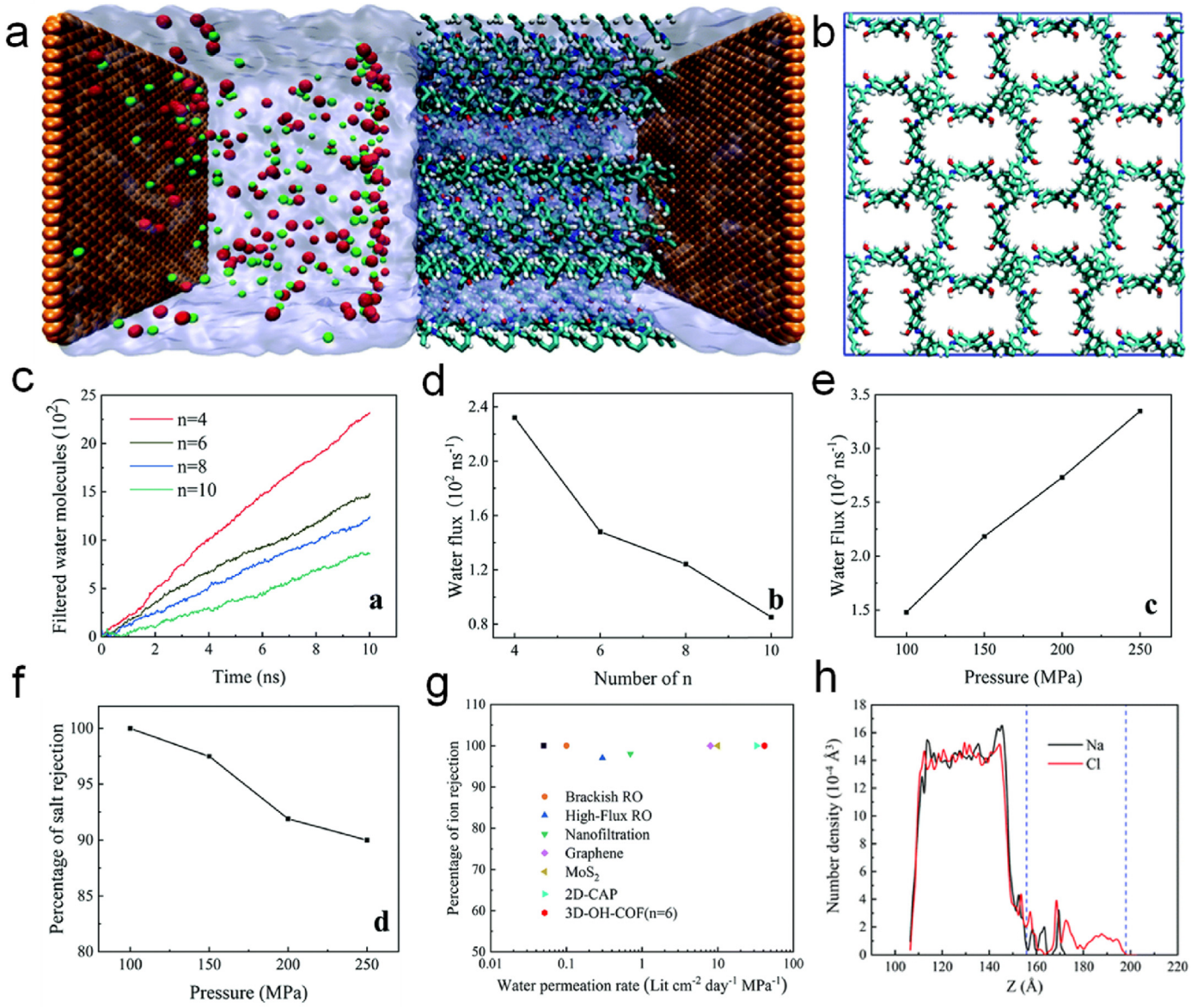


Fig. 8. (a) The desalination model. (b) Topological representation of the 3D-OH-COF membrane. (c) Number of water molecules filtered through the membranes. (d) Relationship between water flux and membrane thickness. (e) Water flux through the n = 6 membrane at various pressures. (f) Salt rejection rate of the membrane (n = 6) at various pressures. (g) Comparison of desalination performance for different nanomembrane materials versus the 3D-OH-COF (n = 6) in this work. (h) Profile of Na^+ and Cl^- ions along the Z axis [49].

COF-300. The impact of COF-300 on the pervaporation performance was evaluated using a 1.0 wt% furfural aqueous solution at 80 °C. Increasing the COF-300 content from 0 to 8 wt% enhanced the separation factor from 32.8 to 49.1, while decreasing the flux from 1701.6 to 1524.2 g m^{-2} h^{-1}. The 8 wt% COF-300/PDMS MMM presented a 14.1 % lift in furfural permeability and a 20.0 % decrease in water permeability, resulting in a 42.7 % improvement in furfural/H_2O selectivity, thereby demonstrating the feasibility of this approach (Fig. 9a–c).

4.5. Fuel cells

Proton exchange membranes (PEMs) are essential in fuel cells, promoting rapid proton transport to the cathode while serving as a barrier to reactants. High proton conductivity is essential for PEM performance. Conductivity and selectivity synergistically determine the power density and energy efficiency in electrochemical systems. However, there is a trade-off between conductivity and membrane selectivity, with increased selectivity typically requiring smaller pores that reduce conductivity. Recently, various densely structured polymer membranes with small pore channels have been fabricated to enhance the transportation of selective ion. These membranes exhibit a high performance of ion selectivity due to size exclusion. For instance, precisely engineered nanopores in these membranes can effectively filter specific ions while blocking others, thereby enhancing the selectivity and efficiency of fuel cells. Furthermore, advanced materials such as nanocomposites and functionalized polymers have been used to further enhance the performance of PEMs. By incorporating nanoparticles or functional groups into the polymer matrix, the resultant modified membranes demonstrated substantial improvements in proton conductivity, mechanical strength, and chemical resistance. These improved properties allow PEMs to maintain an excellent performance under high-temperature and high-humidity conditions, thereby extending the lifespan of fuel cells. For example, Wu et al. [53] synthesized 3D-COOH-COF, a thin COF film with functionalized 3D COOH to stabilize Zn anodes. To a certain extent, the

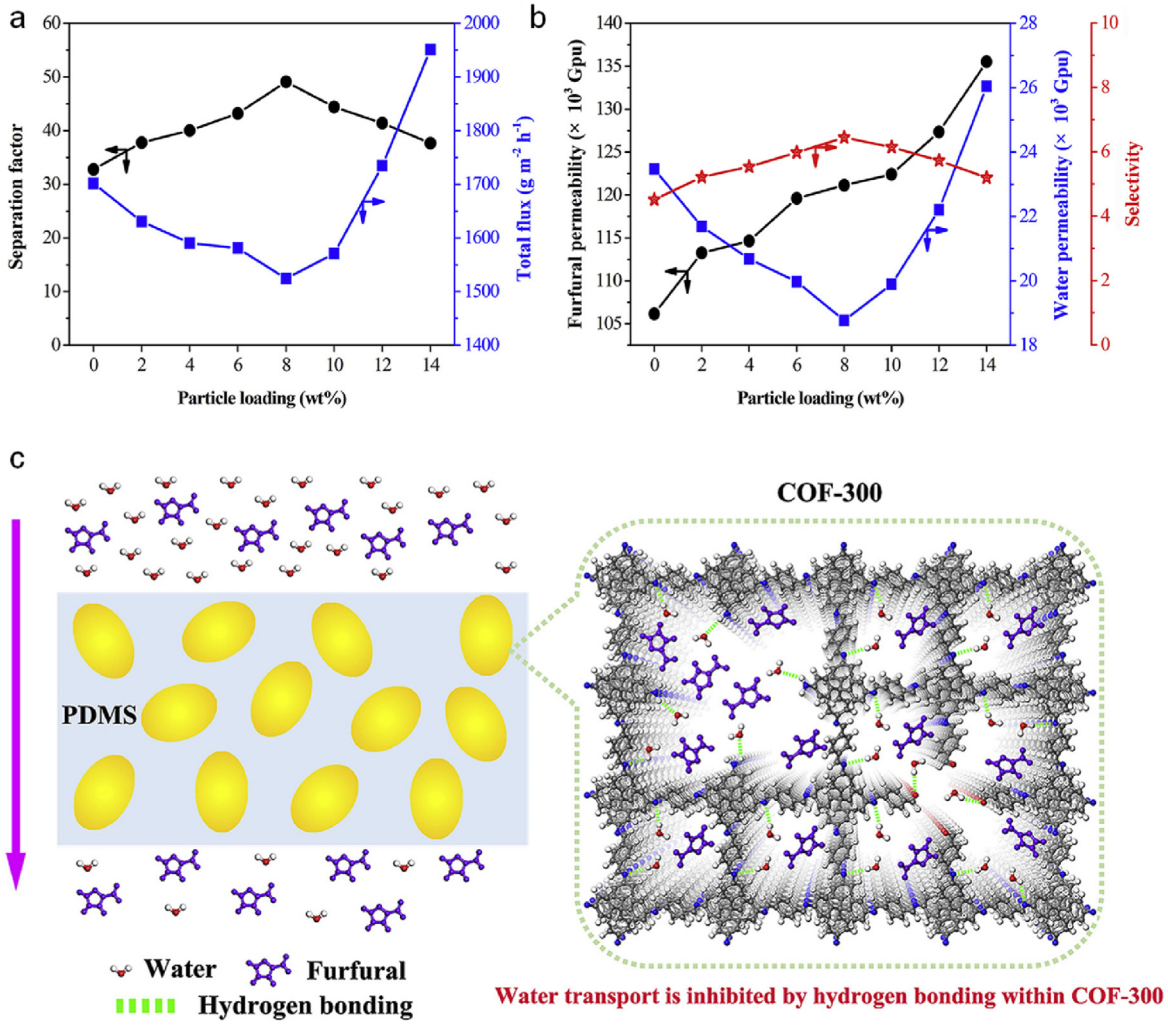


Fig. 9. (a, b) The PV of the samples. (c) Hypothesized mechanism of water transport [52].

3D-COOH-COF protective film improves the deposition of zinc and mitigates corrosion, resulting in superior electrochemical performance. In symmetric Zn||Zn cells, the 3D-COOH-COF@Zn demonstrates stable cycling performance for over 2000 h while operating at 1 mA cm^{-2} and 1 mA h cm^{-2}. In contrast, the bare Zn electrodes experience short-circuiting after 112 h due to the growth of zinc dendrites. At higher current densities and areal capacities (3 mA cm^{-2} and 3 mA h cm^{-2}, 3D-COOH-COF@Zn exhibits exceptional stability for more than 1200 h (Fig. 10a–e) with the average Coulombic efficiency of 99.5 % over 1000 cycles (Fig. 10f–g), representing a promising approach for controlling Zn deposition in aqueous electrolytes. Liang et al. [54] proposed the solvent-free, *in situ* method for synthesizing 3D-COF films using thermal evaporation, including TAM-Tp and TAM-BPDA. Compared to TAM-BPDA, TAM-Tp thin films demonstrated an enhanced hydroxide ion transport and effectively suppressed Zn dendrites. Quasi-solid-state and aqueous Zn-air batteries (ZABs) employing TAM-Tp thin films showed the power densities high to 63.8 mW cm^{-2} and 111.6 mW cm^{-2}. Jiang et al. [11] presented a freestanding 3D COF-based membrane using an IP technique. The membrane demonstrated an excellent swelling resistance and dynamic performance. The rapid proton conduction was ascribed to the interconnected nanochannels that have a low energy barrier. This work advanced 3D COF membrane fabrication and their potential in both membrane separation and stimulus-response applications. In another research, Jiang et al. [7] introduced a 3D COF membrane functionalized with sulfonic acid groups via a dual acid-mediated IP strategy for ion transport. The resulting membranes featured ultramicroporous pore sizes (0.97 nm) and a high density of sulfonate groups, which attributes enabled a proton conductivity up to 843 mS cm^{-1}(90 °C). When applied to the application of osmotic energy conversion, the 3D SCOF membranes exhibited a power density of 21.2 W m^{-2}and a selectivity of 0.976.

5. Conclusion and outlook

COFs are crystalline, porous polymers constructed entirely from all organic building blocks, renowned for high surface area, well-defined pore structures, tunable functionality, and excellent chemical stability. Among them, 3D COFs gradually stand out due to their exceptional properties, including abundant open sites, and interconnected ultrasmall channels and cages. The successful development and post-synthetic modification of 3D COFs into 3D COF-based membranes have expanded their applications in gas separation, catalysis, and liquid separation. One key advantage of 3D COF-based membranes lies in their tunable porosity, enabling precise control over pore sizes and interconnectivity for enhanced selectivity and permeability. The interconnected nanochannels facilitate rapid mass transfer while maintaining selectivity for target molecules or ions. This review starts with categorizing 3D COFs and identifying their key properties (e.g., pore size, topology, stability, hydrophilicity/hydrophobicity and surface charge) relative to membrane development and functionality. Various synthetic methods, including blending, *in situ* growth, and interfacial

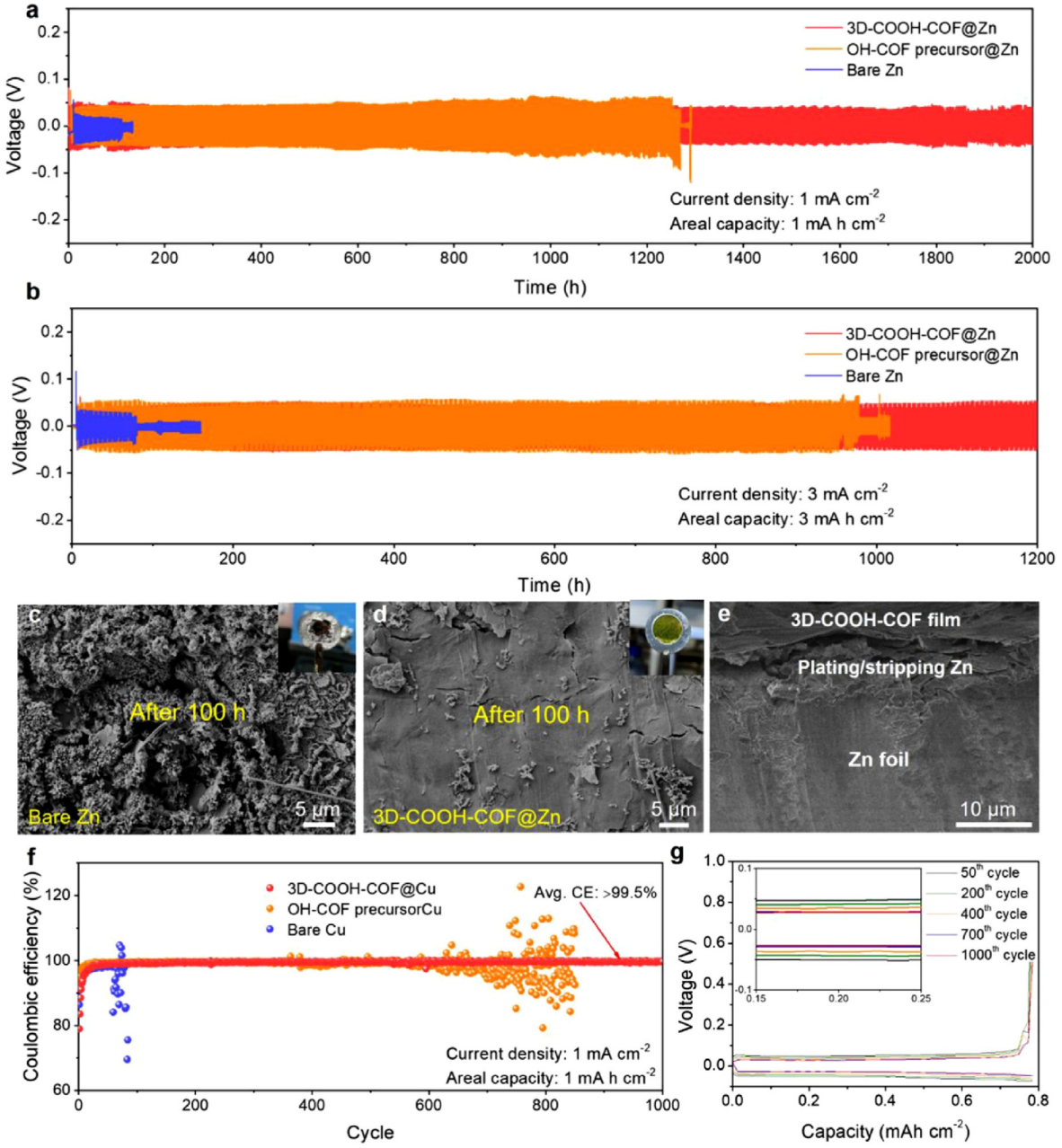


Fig. 10. The cycling performance of Zn plating/stripping using different samples including bare Zn, OH-COF precursor@Zn, and 3D-COOH-COF@Zn at current densities of (a) 1 mA cm^{-2} with 1 mA h cm^{-2}, and (b) 3 mA cm^{-2} with 3 mA h cm^{-2}. (c–e) After 100 h at 1 mA cm^{-2} and 1 mA h cm^{-2}, SEM images of bare Zn (Top view), 3D-COOH-COF@Zn electrode (Top view) and 3D-COOH-COF@Zn electrode(cross-section). (f) Coulombic efficiency of Zn plating/stripping on different conditions at 1 mA cm^{-2}, and (g) the corresponding voltage profiles on 3D-COOH-COF@Cu [53].

polymerization, have been employed to construct 3D COF membranes, which exhibit excellent performance in different applications (e.g., gas separation, water treatment, OSN, pervaporation, and proton exchange), showcasing the potential of these membrane materials.

Despite significant advancements in the synthesis of 3D COFs, several challenges remain in developing high-performance COF-based membranes. The limited number of reported 3D COFs and difficulties in fabricating defect-free membranes are key obstacles. Their complex topology often leads to pore collapse and structural degradation, particularly under high pressure or temperature conditions. Additionally, the low mechanical strength of 3D COFs makes them susceptible to fracture under stress, compromising their long-term durability. Improving the chemical resistance of 3D COFs to withstand harsh operating environments, such as acidic or alkaline conditions, complex organic solvent systems, and elevated temperatures, is also critical for their practical application in various separation processes. While 3D COF-based membranes hold significant potential, challenges like scalability, reproducibility in synthesis, and high production costs continue to hinder their broader application. Moreover, incorporating green chemistry principles to develop environmentally friendly synthesis routes is essential for sustainable manufacturing. To promote industrial adoption, cost-effective design strategies for producing well-defined 3D COF-based membranes with high separation performance must be prioritized. Enhancing the structural stability of 3D COFs through optimized topology design and molecular engineering will be crucial for ensuring long-term performance under demanding conditions, such as high pressure and temperature. Additionally, developing chemically resistant COF frameworks and employing surface modifications to enhance chemical

durability will broaden their applicability across various chemical environments. In conclusion, the development of 3D COF-based membranes offers great promise for advancing membrane technology. By addressing current limitations and leveraging their unique properties, researchers can drive significant advancements in gas and liquid separation processes, unlocking new opportunities in the field.

CRediT authorship contribution statement

Kai Sheng: Writing – review & editing, Writing – original draft, Investigation. **Junyong Zhu:** Writing – review & editing, Supervision, Funding acquisition. **Lei Ge:** Investigation. **Jiale Du:** Investigation. **Tingting Luo:** Investigation. **Lei Jiang:** Investigation. **Wenheng Jing:** Supervision. **Shi-Peng Sun:** Supervision. **Yatao Zhang:** Writing – review & editing, Supervision, Funding acquisition. **Bart Van der Bruggen:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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