Secondary growth of covalent organic frameworks (COFs) on porous substrates for fast desalination

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ABSTRACT
Covalent organic frameworks (COFs) has emerged as a highly promising platform material for the manufacturing of molecule-separating membranes. However, COF membranes are predominantly used in the separation of dyes from water or organic solvents and there are very few reports on COF-enabled membranes for desalination. In this work, the secondary growth approach based on unidirectional diffusion synthesis is developed to grow continuous thin films of a COF with an intrinsic pore size of 0.8 nm on macroporous substrates to prepare COF membranes for desalination. The amino-modified polymer microfiltration substrate is fixed in a diffusion cell to separate the oil phase containing the aldehyde precursor (1,3,5-triformylphloroglucinol, Tp) and the aqueous phase containing both the amino precursor (hydrazine, Hz) and the catalyst. Because of the immiscible bi-phase solutions and the high molar ratio of Hz to Tp, the unidirectional diffusion of Hz molecules in the pore channel of the substrate is achieved and the polycondensation between the two precursors occurs at the phase interface. The unidirectional diffusion synthesis is sequentially performed for two times and the secondary growth is essential to ensure the formation of a defect-free, continuous thin film of COF (TpHz) on the top surface of the substrate. Cladding COF coatings are also formed along the skeleton in the near-surface region of the substrate. Such an asymmetric structure ensures both a good permselectivity and a strong adhesion between the grown COF layers and the substrate. The continuous COF thin film grown on the substrates serves as the selective layer, and the COF membrane prepared under the optimized condition exhibits an appreciable Na$_2$SO$_4$ rejection of 58.3% and a water permeance of 40.5 L·m$^{-2}$·h$^{-1}$·MPa$^{-1}$ which are ~ ten times higher than other membranes with similar rejections. This study not only demonstrates the potential of COFs in desalination but also showcases an efficient strategy to grow continuous thin films of COFs on porous substrates which are desired in diverse applications.

1. Introduction

As an emerging crystallized organic porous materials, covalent organic frameworks (COFs) [1,2] constructed with molecular building units via strong covalent bonds have attracted much interest in a diversity of fields [3–5]. Features including sub-5 nm intrinsic uniform pores [6], versatile chemical design and functionalization [7], and chemical robustness [8] make COFs a highly promising platform material for the preparation of advanced membranes for gas separations [9,10] and molecular separations in liquids [11,12].

Liquid separations based on COF membranes are predominantly concentrated on dye separation from water or organic solvents [5]. The first research on dye removal from water was reported by Banerjee and coworkers using self-standing COFs membranes prepared by a solid-state mixing approach [11]. Their COF membranes showed a pure water permeance of ~92 L·m$^{-2}$·h$^{-1}$·bar$^{-1}$ and a rose Bengal rejection as high as 99%. Later on, Caro et al. [12] and our group [13] applied the high-temperature solvothermal synthesis approach to in situ synthesize intergrown COF layers on nanoporous alumina substrates in the form of tubes and flat chips, respectively, and both membranes exhibited excellent rejections to various dyes. Interfacial polymerization (IP) has been demonstrated an excellent strategy to fabricate thin film composite (TFC) membranes with relatively high permeability [14,15]. Hence, a number of studies based on the liquid/liquid or liquid/air interface were conducted to prepare COF thin films. Banerjee et al. [16], Mariitas et al. [17] and Dichtel et al. [18] adopted the IP approach to synthesize COF thin films at the interface formed by the immiscible bi-phasic solutions and the obtained COF thin film was transferred onto porous substrate for...
dye separations. Besides, the IP occurred at the liquid/air interface was also explored to fabricate ultrathin COF films by Lai et al. [19]. COF membranes with controllable thickness were prepared by layer-by-layer stacking of thus-produced ultrathin COF film and was applied to remove dyes from organic solvents. In order to avoid the tedious transfer process and to enhance the mechanical robustness of the resultant COFs-based membranes, we reported the interfacial polymerization [20] and unidirectional diffusion synthesis [21] for the preparation of COF thin films directly on porous polymeric substrates at room temperature. The obtained membranes exhibited excellent mechanical strength, good stability, and appreciable performances in dye removal.

Most COFs carry intrinsic pores with sizes typically in the range of ~1–3 nm, and such sized pores are particularly suitable for dye separation [5, 22]. This is the reason why most efforts on COF membranes for molecular separations are adsorbed by applications in dye removal and separations. However, by delicate design of monomers, COFs with sub-1 nm aperture can also be synthesized [23–25]. Moreover, staggered stacking of COF monolayers will significantly reduce the effective pore sizes down to several angstroms [26, 27]. Therefore, there should be plenty of chances to use COFs as building blocks to prepare membranes for desalination. Moreover, efforts put in the development of COF membranes for dye separations are very helpful for the design of COF membranes targeted to removing ions from water.

It should be noted that there are a number of reports on COF-embedded mixed matrix membranes (MMMs) for desalination [28–30]. However, in these works, the intrinsic pores in COF nanosheets dispersed in the polymer matrix did not deliver an ion sieving function. Therefore, they should not be considered as COF desalination membranes. The feasibility of COFs for desalination has been demonstrated by simulations. By molecular dynamic simulations, Grossman et al. [31] found that the single-layered CTF-1 with suitably modified groups exhibited a salt rejection higher than 91% and a tremendous water permeance which was 2–3 orders of magnitude higher than conventional polyamide reverse osmosis membranes. Subsequently, Jiang, et al. [32] investigated desalination performance of seven TpPa-X membranes with various functional groups. The computationally designed COFs with suitable aperture size and hydrophilicity were found to display excellent NaCl rejection of over 95% and unexpected water permeance ranged from 1216 to 3375 L·m⁻²·h⁻¹·bar⁻¹. Most recently, our group applied the nonequilibrium molecular dynamics simulation to investigate the desalination behavior of multilayered COF (TpPa-1, CTF-1 and CTF-2) [33, 34], and developed a series of equations to predict water permeance of different types of multilayered COFs based on resistance analysis. It was found that multilayered COFs in the offset-eclipsed stacking model or staggered-stacked model exhibit complete rejection toward inorganic salts and high water permeance (>408 L·m⁻²·h⁻¹·bar⁻¹). However, experimentally, there are very few studies on COF membranes for desalination. Maríñas et al. [17] and Lai et al. [35] used interfacial synthesis to prepare COF membranes and examined their desalination performances. The membranes showed water permeance lower than 9 L·m⁻²·h⁻¹·MPa⁻¹ and a moderate salt rejection less than 75% mainly because the synthesized COFs were nearly amorphous. Very recently, Huang et al. [36] employed the post-synthesis method to prepare continuous COF films on inorganic substrates and the obtained composite membranes exhibited a relatively high salt rejection (>80%) but unfortunately suffered also from low permeance (<7 L·m⁻²·h⁻¹·MPa⁻¹). The rare studies on COF for desalination demonstrated desalination performance from reported COF membranes can be mainly attributed to the following two reasons. First, the apertures of most COFs are too large for ion sieving. Second, the synthesis of defect-free COFs selective layer with thin thickness still remains a huge challenge.

Keeping this understanding in mind, we turn to an imine-based COF (TpHz) with excellent water stability and a narrow aperture down to 0.8 nm. We use the secondary growth approach based on our previously reported unidirectional diffusion synthesis [21] to grow TpHz selective layer on macroporous polymer substrates to prepare composite membranes for desalination. Benefiting from the unidirectional diffusion synthesis, the single side growth of TpHz on the top side of the substrate was achieved. As a result, thus-formed TpHz selective layers are defect-free and thin in thickness, enabling fast permeation of water while tight rejection to ions. Under optimized conditions of secondary growth, the TpHz membrane exhibits an appreciable Na₂SO₄ rejection of 58.3% and a water permeance of 40.5 L·m⁻²·h⁻¹·MPa⁻¹ which is one order of magnitude higher than other COF membranes with similar salt rejections [17, 35, 36]. This study demonstrates the strong possibility of COFs in desalination on one hand and provides a highly controllable strategy to grow high-quality continuous COF thin films on porous substrates on the other hand, which are highly desired in many important applications in addition to membrane separations.

2. Experiments

2.1. Materials

The substrates of polyethersulfone (PES) microfiltration membranes with a nominal pore size of 100 nm were ordered from Haiyan Xindongfeng Plastic Chemical Corporation in the form of round coupons with a diameter of 25 mm. The COF precursors, hydrazine hydrate (H₂H₂O, 98 wt%) and 1,3,5-triformylphloroglucinol (Tp, 98 wt%), were purchased from Aladdin and Tongchuanhyuang Pharmaceutical, respectively. Poly(ethylene imine) (PEI, ~50 wt% in H₂O, M₀ = 600,000–1,000,000) was obtained from Sigma-Aldrich. Ethanol (EtOH, 99.5 wt%), dimethylacetamide (DMAc, 99.0 wt%), p-toluene sulfonic acid monohydrate (PTSA·H₂O, 99.5 wt%), deionized water (DI water, conductivity: 8–20 μs cm⁻¹, pH: 6.8) and inorganic salts (including Na₂SO₄, MgSO₄, CaCl₂, MgSO₄ and NaCl, AR) were received from local suppliers. All the solvents and reagents in this work were used without further purification.

2.2. PEI modification of PES substrate

We followed the literature [37] with some modifications to modify the PES substrates with PEI. The PES substrate was immersed in the PEI aqueous solution (1 g PEI in 200 mL water) for 10 min and subsequently dried at 60 °C for 10 min. This procedure was repeated five times to ensure the deposition of a uniform PEI layer on the substrate surface (Fig. 1a).

2.3. Preparation of TpHz/PES membrane

For the organic phase solutions, 0.06 mmol of Tp (12.6 mg) was fully dispersed in 80 mL of n-hexane. For the water phase solutions, 9 mmol of H₂H₂O (~440 μL) and PTSA·H₂O (1712.0 mg) were dissolve in 80 mL DI water. The bi-phasic solutions were treated with a long-term (>30min) ultrasonication treatment to ensure getting uniform solutions. As shown in Fig. 1b, the PEI-modified PES substrate was vertically fixed on a diffusion cell, and then 10 mL of organic solution and aqueous solution were concurrently added into the corresponding side of the diffusion cell [21]. The setup was kept at room temperature for 6 h in undisturbed condition for the first growth. Afterwards, the solutions in the two side of diffusion cell were removed by a syringe and the TpHz/PES membrane after first growth was dried at 60 °C overnight. To obtain the intended COF-based membrane, the as-synthesized membrane was subjected to a secondary growth in the same condition as the first growth with designed growth durations (12, 24 and 48 h). Thus-produced TpHz/PES membrane was thoroughly washed with ethanol and water several times, and then stored in water.

2.4. Characterization

The fourier transform infrared (FT-IR) spectra of samples (including
precursor, PEI-modified PES substrate and the synthesized COF-based membrane) were recorded on a Nicolet 8700 spectrometer with a scanning range of 4000–600 cm\(^{-1}\). The X-ray diffraction (XRD) pattern of samples was recorded on a Rigaku SmartLab X-ray diffractometer with the 2θ range of 2–40° and a scanning rate of 1.2° min\(^{-1}\). The microscopical morphologies of samples were investigated by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) operated at an accelerating voltage of 5 kV. All the samples for SEM characterization were sputter-coated with a thin layer of platinum to enhance their conductivity. The surface topographies of substrate and COF-based membranes were examined by an atomic force microscope (AFM, XE-100, Park Systems) at non-contact mode. The surface zeta potential of the resultant membrane was tested by an Anton Paar SurPASS electrokinetic analyzer using 1 mmol L\(^{-1}\) potassium chloride (KCl) aqueous solution as the background electrolyte solution and 0.1 mol L\(^{-1}\) NaOH and HCl solution as the pH values conditioners. The Krüss PASS electrokinetic analyzer was employed to examine the surface wettability of membranes. A S230-K electrical conductivity meter (Mettler-Toledo) was employed to measure the concentration of inorganic salts solutions during the rejection test.

2.5. Nanofiltration performance test

Before testing, inorganic salts including Na\(_2\)SO\(_4\), MgSO\(_4\), CaCl\(_2\), MgSO\(_4\) and NaCl were separately dissolved in DI water at the concentration of 1000 ppm and then the salt solutions were used as feeds to test the performance of TpHz/PES membranes. The performance test was carried out on a stirred filtration cell (Amicon 8003, Millipore) at room temperature with a stirring speed of 500 rpm. In order to reach a steady state, the membranes were compacted for more than 30 min at 0.4 MPa prior to testing. The solution permeance (\(P\), L·m\(^{-2}\)·h\(^{-1}\)·MPa\(^{-1}\)) and rejection (\(R\), %) were tested at 0.4 MPa and calculated by Equations (1) and (2), respectively.

\[
P = \frac{V}{S \times t \times \Delta P}
\]

\[
R = \frac{1 - C_p}{C_f} \times 100\%
\]

where \(V\) (L), \(S\) (m\(^2\)), \(t\) (h), \(\Delta P\) (MPa) \(C_p\) and \(C_f\) are volume of the permeate, effective filtration area, testing duration, and testing pressure, permeate concentration, and feed concentration, respectively.

3. Results and discussion

The imine-based COFs were usually synthesized by the Schiff base condensation reaction between aldehyde monomers and amine monomers. Thus, the surface amination modification of substrate can effectively promote the nucleation and growth of the imine-based COF (TpHz) to form a thin and uniform film composited with the substrate. As shown in Fig. 1a, the commercial PES substrate was treated five times with the PEI aqueous solution via dip-coating to form a uniform PEI layer. The PEI layer was adsorbed on the substrate surface through H-bonding interactions and provided abundant active NH\(_2\)-groups for the TpHz growth, thus enhancing the adhesion between the COF layer and the substrate. Afterwards, the PEI-modified PES substrate was vertically fixed on a diffusion cell (Fig. 1b, Fig. S1) to synthesize TpHz on the top side of substrate via the method of unidirectional diffusion synthesis [21]. Finally, the membrane was subjected to a secondary growth to form a denser COF selective layer for ions separation. As reported in our previous work [21], the immiscible solution pair (water and n-hexane) and much higher molar ratio of two monomers (Hz: Tp = 150) in this work enables the unidirectional diffusion of amine monomer through the macropores of the substrate to produce TpHz as a conformal selective layer on the substrate surface (Fig. 1c). It should be noted that PTSA can react with amine monomer to form amine salt and slow down the polymerization and crystallization processes in terms of the common imine-based COFs [11,16]. However, we noted that the reaction activity of Hz and Tp is lower than the reaction activity of the other common amines and Tp on one hand. TpHz synthesized on the similar condition exhibits a weaker orderliness [24] on the other hand. Hence, we adopted the partially protected strategy to obtain a suitable reaction rate by halving the PTSA-H\(_2\)O dosage in this work.

As shown in Fig. 2a, the top side of the synthesized membrane exhibits a darker color than the bottom side, suggesting that TpHz is predominantly formed on the top side. The formation of crystalline TpHz on the top side of substrate was further confirmed by FT-IR and XRD analysis. The stretching bands of the aldehyde groups (-CHO, 2892 cm\(^{-1}\) and -C=O, 1643 cm\(^{-1}\)) of aldehyde monomer Tp appear in the monomers and are absent entirely in the TpHz/PES membrane (Fig. 2b), which indicates the complete conversion from the monomers to the resultant product. After synthesis, two characteristic peaks (-C=–C, 1562

**Fig. 1.** Schematic illustration of the preparation process of TpHz/PES membranes by secondary growth based on unidirectional diffusion synthesis. (a) Flowsheet of the secondary growth synthesis of the TpHz/PES membrane on the PEI-modified PES substrate. Inset is the synthetic scheme of TpHz synthesized by the Schiff base condensation reaction between Tp (blue) and Hz (red). (b) Schematic illustration of diffusion cell for TpHz growth on the substrate by unidirectional diffusion synthesis. (c) Schematic illustration of the formation of the TpHz selective layer on the substrate top side via unidirectional diffusion of Hz and PTSA (catalyst) molecules through the pores of substrate to react with Tp molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
cm\(^{-1}\) and -C-N, 1278 cm\(^{-1}\)) of TpH are present in the spectrum of the resultant membrane, indicating the successful formation of TpH with a keto form on the substrate surface [23]. In order to eliminate the masking effect of polymeric substrate to the XRD analysis of COF, the amorphous anodic aluminum oxide (AAO) substrate [13,38] with nominal pore size of 20 nm was selected to replace PES substrate to fabricate TpH/AAO membrane for XRD characterization. The XRD pattern of the TpH/AAO membrane shows two distinct characteristic peaks located at around 6.9° and 27° (Fig. 2d), corresponding to the intrinsic pore (100 lattice plane) and interlayer distance (001 lattice plane) of TpH (Fig. 2c), respectively [39,40]. This result fits well with the XRD pattern of simulated TpH in the eclipsed stacking model. The appreciable crystallinity of TpH endows the selective layer with good structural stability and high porosity, which are highly desired for molecular separation of a membrane.

As shown in the SEM images in Fig. 3, the PEI-modified PES substrate maintains a macroporous surface morphology, while it turns to be nonporous and dense after the secondary growth of TpH, indicating that a continuous and dense TpH separation layer is formed on the PES substrate. A closer SEM examination (inset in Fig. 3b) reveals that there are no pinholes, cracks, or other defects on the surface of the grown TpH layer. In contrast, the bottom side of the PES substrate still keeps a macroporous morphology (Fig. 3c), indicating that TpH hardly grows on the bottom side of the substrate. Hence, we can conclude that the experiment design of single side growth for the sake of decreasing the mass transfer resistance for separation was achieved. The cross-sectional SEM image of the TpH/PES membrane clearly confirms the existence of a tight TpH separation layer (Fig. 3d). Besides, the formation of TpH on the PES substrate was further examined by the AFM characterization. As shown in Fig. S2, the AFM image of the PEI-modified PES substrate shows a clear skeleton structure, while particulate-like TpH structures can be observed on the surface of the membrane subjected to first and secondary growth. To verify the necessity of amination modification to substrates, we also synthesize the COF membrane on the pristine PES substrate. However, there are just some TpH particles synthesized on the unmodified PES substrate (Fig. S3) since lacking of the essential interaction.

To further explore the formation process of the TpH separation layer, the TpH/PES membrane prepared with a growth duration of 6 + 24 h was soaked in DMAc at room temperature to etch away the PES substrate [20] based on the solubility difference of imine-based COFs [11,41,42] and PES [43,44] in DMAc. Interestingly, we obtained a continuous and flexible thin film of TpH in red color (inset in Fig. 4a) after the removal of the PES substrate. As shown in Fig. 4a, b, SEM examinations reveal that the TpH thin film exhibits a dense morphology similar to that of the top surface of the as-synthesized TpH/PES membrane. However, we can easily find that the TpH thin film possesses an asymmetric structure from the cross-sectional SEM image (Fig. 4c). There is a dense top layer with a thickness of around 500 nm (Fig. 4c and d), which is expected to serve as the selective layer. The thin thickness of the selective layer ensures the high permeation of the synthesized COF membrane. The bottom layer with a thickness of around 12 μm (Fig. 4c) shows a sponge-like pore structure composed of hollow nanotubes (Fig. 4e), which should be attributed to the conformal growth of TpH along the skeleton of PES substrate.

Based on the asymmetric structure of the TpH thin film, we can...
understand the formation process of the TpHz layer on the substrate. In the initial stage of TpHz growth, the nucleation of TpHz occurs at the skeleton of PES substrate and a TpHz cladding layer is formed along the substrate skeleton. As a result, the TpHz cladding layer could be transformed into the sponge-like pore structure after removal of the PES substrate. With increasing reaction time, the polymerization of the two precursors continues, producing more TpHz. Consequently, a relatively dense TpHz layer was formed at the phasic interface, which cuts off the supplies of precursors and terminates the further growth of TpHz along the skeleton of the PES substrate. Eventually, such an asymmetric structure with a dense top layer and a porous bottom layer of TpHz is formed in the PES substrate. We note that although TpHz is mainly grown on the top surface of the substrate, its growth also takes place in the near-surface interior region of the substrate as indicated by the ~12 μm thickness of the interconnected tubular structure formed in the PES substrate with a total thickness of around 100 μm. Obviously, this asymmetric structure is highly desired not only to ensure good permselectivity but also to enhance the adherence between TpHz selective layer and substrate as the bottom layer is embedded into the substrate.

Secondary growth has been widely applied in the synthesis of porous materials membranes, such as metal-organic framework (MOF) membranes [45], zeolite membranes [46]. By depositing the seeds of porous materials on the substrates with subsequent secondary growth, highly permselective porous materials membranes with controllable microstructure can be obtained. The outstanding performance of the porous materials membranes should be attributed to the pre-deposited seeds inducing the oriented secondary growth [47]. In this work, we employed the secondary growth to synthesize the COF-based membrane for desalination. In the first growth, there are some gap-like defects on the surface of the COF-based membrane due to the inadequate growth (Fig. S4a). As a result, the TpHz/PES membrane prepared by 6 h’s first growth shows a relatively low Na₂SO₄ rejection (26.8%) and high permeance (87.7 L·m⁻²·h⁻¹·MPa⁻¹) (Fig. 5c). However, the defects seemingly could not be avoided by simply extending the growth duration (Fig. S5). In order to eliminate the defects and further improve membrane selectivity, the secondary growth was applied to prepare COF-based membranes.

After secondary growth, the anticipated membranes with dense, defect-free selective layers (Fig. 5a, Fig. 5b) were obtained and these membranes were used in the separation of inorganic salts from water (Fig. 5b). The membranes with various duration of secondary growth (6 + 12, 6 + 24, 6 + 48 h) all exhibited a hydrophilic surface property (Fig. S6). With prolonged duration of secondary growth, the permeance of the TpHz/PES membranes is slightly declined from 47.3 to 40.5 L·m⁻²·h⁻¹·MPa⁻¹ and then keeps constant at 41.7 L·m⁻²·h⁻¹·MPa⁻¹. On the contrary, the Na₂SO₄ rejection is increased from 45.6% to 58.3% and then decreased to 52.0% (Fig. 5c). The improvement in salt rejection should be attributed to the formation of a complete and defect-free TpHz layer after secondary growth (Fig. S7). With the growth duration of 6 +
24 h, the membrane exhibits a water permeance of 40.5 L·m⁻²·h⁻¹·MPa⁻¹ and Na₂SO₄ rejection of 58.3%. Compared to membranes with comparable ion rejection rates [18,35,36], the water permeance of our COF membrane is one order of magnitude higher. Because the TpHz/PES membrane prepared with a growth duration of 6 + 24 h exhibits a well-balanced permeance and ion rejection, we further test its rejections towards different monovalent and bivalent salts with the same concentration of 1000 ppm. As shown Fig. S5d, the salt rejection rate of this TpHz/PES membrane towards Na₂SO₄, MgSO₄, CaCl₂, MgCl₂ and NaCl are 58.3%, 45.3%, 25.1%, 21.0% and 6.7%, respectively. The discrepancy in rejection rate to these salts can be explained by the differences in the size of the intrinsic apertures of TpHz (0.8 nm) [3,24] and the size of the hydration radius of Cl⁻ (0.864 nm), Na⁺ (0.716 nm), Ca²⁺ (0.829 nm), Mg²⁺ (0.856 nm) and SO₄²⁻ (1.000 nm) (Table S1) [12,48]. As a result, the membrane possesses a higher rejection for sulfate salts than chloride salts as the hydration radius of SO₄²⁻ is bigger than that of Cl⁻. In addition, the zeta potential test indicates that the membrane is nearly electrically neutral at test conditions (1000 ppm salt solution: pH = 5.8–6.2 [49]) (Fig. S8). Hence, we conclude that its ion rejection is mainly due to the molecular size sieving effect of the TpHz layer. Consequently, we believe the appreciable desalination performances of the TpHz/PES membranes should be attributed to the intrinsic apertures small enough to be close to ions, and the complete and defect-free nature of the TpHz layer tightly adhered to the substrate obtained by the delicate synthesis strategy of secondary growth. We note that there is still room for further improving the desalination performance of COF membranes to compete with polyamide nanofiltration membranes [50]. We believe that the desalination performance of COF membrane can be improved from two aspects. On one hand, the surface charge modification of COF membranes should be an effective strategy since the electrostatic repulsion is regarded as an important factor for the desalination technology by membrane process. On the other hand, the apertures of COFs should be further decreased to be smaller than the kinetics size of component to be separated by suitable monomers design and graft modification.

4. Conclusions

In summary, this work reports the preparation of COF-enabled membranes for desalination with high permeance. We perform secondary growth of a type of COF with an intrinsic pore size down to 0.8 nm on a porous substrate based on unidirectional diffusion synthesis. The synthesis takes place on one side of the substrate as the two monomers dissolved respectively in water and oil are separated by the substrate. Second growth eliminates defects existing in the COF layer obtained in the first growth, leading to a defect-free, continuous COF thin film on top of the substrate as well as a cladding COF layer grown along the skeleton in the near-surface region of the substrate. Thanks to the asymmetric composite structure of microporous COF and the macroporous substrate, thus-synthesized membrane exhibits appreciable salt rejection and remarkably high water permeance. This study demonstrates the strong capability of COFs in desalination and provides a controllable and extendable strategy to grow various continuous COF thin films on porous substrates which are desired in many important applications.

Declaration of competing interest

There are no conflicts to declare.

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Appendix A. Supplementary data

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