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Supporting Information

ABSTRACT: Covalent organic frameworks (COFs) are expected to provide exceptional permselectivity in molecular separations because of their stable, uniform, molecular-sized pore channels. To realize the superior performances of COF-based membranes, it remains strongly desired for the rapid and controllable growth of COFs on substrates under mild conditions. Herein, we report on the layer-by-layer (LbL) strategy for the rapid synthesis of imine-linked COFs on porous polymeric substrates in ethanol at room temperature. This strategy exploits the alternative availability of each COF monomer to endow a self-limiting nature to the reaction, thus resulting in conformal growth of COFs along the pore wall of the substrate. The grown COFs with thicknesses tunable by LbL cycles reduce the effective pore sizes, while the inherent ∼2 nm channels in COFs allow additional water to permeate. Thus-produced membranes exhibit significantly enhanced selectivity (>99% rejection to dyes) and unprecedentedly high water permeances, which are ∼3−20 times higher than other membranes with similar rejections. This work potentially presents a new and general methodology to prepare imine-based COF membranes for molecular separations.

KEYWORDS: covalent organic frameworks (COFs), layer-by-layer (LbL) synthesis, membranes, molecular separations, nanofiltration

INTRODUCTION

Covalent organic frameworks (COFs) are a new class of covalently bound crystalline network structures with well-defined inherent nanoporosities.1−4 They are attracting tremendous interests in a broad range of applications.5−8 Because of (1) ordered pores with monodispersed pore diameters, (2) small pore sizes down to ∼1−5 nm, (3) designable pore wall chemistry, and (4) excellent chemical and much better thermal stability than many other framework materials, COFs are particularly considered as unique building blocks for advanced separation membranes. Very recently, a few simulating and experimental works on COF-based membranes appeared.9−15 Banerjee et al. synthesized continuous COF films either in the form of free-standing thick films12 or sub-100 nm thin films,13 which can be transferred onto porous substrates. Caro, Fan, and co-workers synthesized thin layers of intergrown COF crystals on surface-activated porous ceramic supports.14 Thus, produced COF membranes exhibited enhanced permeabilities in molecular separations. However, the reported synthesis of COF membranes were all performed in aggressive solvents for long durations and usually at elevated temperatures, significantly hampering their large-scale preparation and widespread applications. For example, polymeric substrates extensively used in membrane separation cannot be integrated into these synthetic processes because they cannot tolerate the aggressive solvents and high temperatures. Moreover, COFs are currently synthesized by simultaneous mixing of monomer pairs in solutions and reactions burst in the bulk solutions, leading to inhomogeneous nucleation and consequently insufficient control on the morphology and positioning of COFs if they are intended to be grown on substrates. Therefore, to maximize the permeselectivity and to realize the practical production of COF membranes, it is essential to develop a strategy for the rapid synthesis of COFs with controllable structures under mild conditions.

Considering that COFs are generally synthesized via step condensation reactions between two multifunctional monomers (e.g., amines and aldehydes for imine-based COFs), we expect that the reactions may be performed in a cyclic mode by alternatively introducing two monomers into the reacting system. The synthesis of COFs is thus endowed a self-limited nature controlled by the availability of each monomer, leading to precise and continuous control on the growth of COFs on the substrate. The cyclic synthesis of COFs can be realized by the layer-by-layer (LbL) process, which is a versatile method based on alternative reactions between two or more precursors on substrates.16−19 This method enables the deposition of...
different materials on various substrates with morphology, thickness, and surface composition precisely controllable at the molecular scale. Imine-linked COFs are highly water stable, and possess a high structural regularity and crystallinity. Moreover, the imine groups provide an inherent hydrophilicity to these COFs, favoring the fast permeance of water through the frameworks. These alluring features inspire us to develop imine-linked COF membranes for water treatment based on the principle of LbL process.

In this work, COFs are synthesized on hydrolyzed polyacrylonitrile (HPAN) ultrafiltration membranes at room temperature using ethanol as the solvent. The COFs are grown with precisely tunable thicknesses along the pore walls of the HPAN substrates. Thus-produced composite membranes are highly selective in molecular separations and exhibit water permeance remarkably higher than other membranes with similar rejections. This work realizes LbL synthesis of COFs on porous substrates for the first time, and establishes a highly controllable route to produce ultrapermeable COF-functionalized membranes for molecular separations.

■ RESULTS AND DISCUSSION
To perform the LbL synthesis of imine-linked COFs, we should first find a suitable substrate, which has a strong interaction with COF monomers to initiate the LbL synthesis. We believe that HPAN with rich carboxyl groups on the surface would be a good choice because the amine monomers can be first incorporated onto the HPAN substrate by interactions between amine groups and carboxyl groups. Also importantly, the carboxyl groups may also work as catalysts to facilitate the Schiff-base reaction between COF monomers, thus avoiding the use of additional catalysts. The extensively used monomer pairs for imine-linked COFs, benzidine (BD), and 1,3,5-triformylphloroglucinol (Tp), were first investigated in the LbL synthesis. They were dissolved in ethanol, respectively (Figure S1a, b). HPAN substrates were immersed in the BD solution for 10 min, followed by ethanol rinse, and then immersed in the Tp solution for another 10 min followed by another ethanol rinse, which completes one LbL cycle. All the immersion and rinse were performed at room temperature. This process was repeated until the designated number of LbL cycles was achieved (Scheme 1a).

We denote the membrane with X cycles of LbL synthesis as the TpBDX-HPAN membrane. The successful preparation of TpBD on the HPAN substrate is vividly demonstrated by the change in the physical appearance of the HPAN substrate, which was turned to dark red after 11 cycles in line with the color of TpBD powders. The color became increasingly darker with rising LbL cycles, implying more TpBD was formed on the substrate. Fourier transform infrared (FTIR) spectroscopy confirms the formation of TpBD on the HPAN substrate. A total consumption of the monomers is clearly observed (Figure S2a), evidencing by the disappearance of C = O stretching bands (1639 cm\(^{-1}\)) of Tp and N–H stretching bands (3300–3100 cm\(^{-1}\)) of BD. Furthermore, the synthesized TpBD were found to be in the keto form as there is a strong peak at 1578 cm\(^{-1}\) arising from the C=O stretching. Moreover, the peak intensity of the C=O stretching bands is gradually enhanced with rising LbL cycles (Figure S2b).

Under scanning electron microscopy (SEM), we found that the pristine smooth surface of the HPAN substrate (Figure S3) was covered with densely packed fine particulates after LbL synthesis of TpBD on the HPAN substrate. A total consumption of the monomers is clearly observed (Figure S2a), evidencing by the disappearance of C = O stretching bands (1639 cm\(^{-1}\)) of Tp and N–H stretching bands (3300–3100 cm\(^{-1}\)) of BD. Furthermore, the synthesized TpBD were found to be in the keto form as there is a strong peak at 1578 cm\(^{-1}\) arising from the C=O stretching. Moreover, the peak intensity of the C=O stretching bands is gradually enhanced with rising LbL cycles (Figure S2b).

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confirms the distribution of TpBD throughout the membrane. We performed thermogravimetric analysis on the HPAN substrates before and after COF growth. The results showed that COFs remained stable at the temperature up to $\sim 300^\circ$C, and after 5 cycles of LbL synthesis, there is about 2.5% TpBD crystallites developed on the HPAN membranes, demonstrating a small amount of COFs generated on the substrates (Figure S4).

The growth behavior of COFs on the HPAN substrate is dependent on the porous structure and surface property of the substrate. The pore wall of the HPAN substrate is covered with poly(acrylic acid) (PAA) as a result of the hydrolyzation of PAN chains. Upon immersion in the BD ethanolic solution, BD molecules are chemisorbed to the surface PAA chains because of the strong interactions between the amine groups on BD and the carboxyl groups on PAA. Subsequent ethanol rinse removes free BD molecules not absorbed to the PAA chains. Upon exposure to the Tp ethanolic solution, the Schiff-base reaction between Tp and BD takes place, producing TpBD primary crystallites. In contrast to the synthesis in bulk solutions where both monomers are nearly unlimited available, BD is only available in the substrate pores, consequently, the growth of TpBD predominantly takes place along the pore walls. Moreover, because of the limited availability of BD and also the confinement effect of the pores, TpBD is formed as small crystallites along the pore. In subsequent cycles of alternative exposure to the monomer pairs, the TpBD crystallites are progressively grown in sizes, leading to TpBD layers with increasing thicknesses along the pore walls (Scheme 1b). Because of the stabilization effect of the surface PAA chains the TpBD particles are expected to be tightly attached to the pore walls. We note that the TpBD nanoparticles were also formed and attached on the top surface of the HPAN substrate, and because the confinement effect of the free surface the growth of TpBD was much weaker, bigger particles were also produced on the top surface as evidenced by Figures 1b and S5.

As the HPAN substrate has a three-dimensionally interconnected porosity, TpBD grown along the pore wall will correspondingly form a continuous phase replicating the porous structure of the substrate. To demonstrate the growth of TpBD inside the porosity of the HPAN substrate, we treated the TpBD11-HPAN membrane in dimethylacetamide (DMAc) to dissolve away the HPAN substrate. The TpBD layer remained intact on the polypropylene (PP) nonwoven backing and became semitransparent with the removal of HPAN (Figure S6). SEM reveals that the TpBD layer maintains a continuous morphology and was composed of aggregated nanoparticles. Its thickness was significantly reduced to $\sim 6\mu m$ from the initial $\sim 60\mu m$ for the HPAN substrate (Figure S7). Bigger pores, for example, the finger-like macrovoids initially in the HPAN substrate, are not maintained in the TpBD replica as a result of collapse of the ultrathin TpBD layer along the pore wall with the removal of the HPAN substrate. That is, upon the depletion of PAN the TpBD particulates previously along the pore walls were coalescent with their neighbors and assembled to form a much thinner but denser layer. Therefore, the remaining continuous TpBD layer after removal of the substrate evidence the conformal coating layer of TpBD along the pore wall of the HPAN substrate. We note that the hydrolyzed surface of the HPAN substrate is essential for the growth of TpBD along the pore wall and the carboxyl groups not only anchor the diamine monomers but also catalyze the Schiff-base reactions between Tp and BD. Alternative exposure

Figure 2. Separation performances of TpPa-HPAN membranes. (a) Photographs of the membranes prepared with various LbL cycles. (b) PWPs and CR rejection rates of membranes prepared with various LbL cycles. Inset shows the appearance of the feed (Fe), filtrate (Fi), and retention (Re) solution involved in the filtration of the CR solution using the TpBD11-HPAN membrane. (c) AF, CR, and MB rejection rates of membranes prepared from different LbL cycles. (d) 3D models of AF, MB, and CR dye molecules. (e) UV–vis spectra and solution appearance change of the selective recovery of AF from a mixture containing AF and CR.
of the monomer pairs to pristine PAN substrates without the hydrolysis treatment did not result in any noticeable growth of TpBD on the substrate as the substrate remained the initial pore size and particles can rarely be observed on the surface (Figure S8).

This LbL strategy can be extended to synthesize other imine-linked COFs. By replacing BD with p-phenylenediamine (Pa) (Figure S1c),26 we successfully prepared TpPa-HPAN membranes by alternatively exposing HPAN substrates to Pa and Tp ethanolic solutions. As shown in Figure 2a, similar to the case of TpBD, the membrane took increasingly darker color with rising LbL cycles. Likewise, FTIR analysis also presents a total consumption of monomers and increased intensity of its characteristic peak with rising LbL cycles (Figure S9). Also, DMAC treatment removed the HPAN supports, leaving behind an intact COF layer composed of nanoparticles adhered on the PP backing (Figure S10). That is, TpPa was also grown along the pore walls of the HPAN substrate. However, TpPa was grown on the pore walls with a lower rate than TpBD as evidenced by the much thicker skeleton of the TpBD$_x$-HPAN membrane than the TpPa counterparts (Figure S11).

We did not observe any noticeable characteristic crystalline diffraction peaks of the COFs grown on the substrate because the peaks originated from crystalline COFs have been shielded by the strong peaks of the HPAN substrates with a PP backing. We synthesized TpPa and TpBD powders in ethanol at room temperature which was similar to the condition of the LbL synthesis on HPAN substrates. XRD analysis reveals that the synthesized TpPa and TpBD powders present a moderate crystallinity evidenced by peaks at 4.7° and 3.3°, respectively, which is in line with other works (Figure S12).22,27 Therefore, we conclude that the COFs synthesized on HPAN substrates are also crystalline. Considering that the LbL synthesis is performed at room temperature for short durations, it is reasonable for COFs to be moderately crystallized under this mild condition.26

As shown in Figure S13, the HPAN substrate exhibits a negatively charged surface, which should be attributed to the presence of carboxyl groups.28 After LbL synthesis, the membrane remains a negatively charged surface in a wider pH range. Moreover, the pristine HPAN substrate exhibited a water contact angle (WCA) of ~23°. After growth of TpPa, WCAs of the composite membranes were slightly varied in the range from ~23° to ~34° depending on the LbL cycles (Figure S14), indicating that the TpPa-HPAN membranes remain strongly hydrophilic.14 The negatively charged and strongly hydrophilic surface, as well as the nanoporous nature of COFs, implies that the COF-grown membranes may deliver fast water permeation.

The pristine HPAN substrate showed a pure water permeability (PWP) of ∼500 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, which was decreased to ∼332 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ after 3 LbL cycles. The water permeance was further decreased to ∼276 and ∼187 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ after LbL synthesis for 7 and 11 cycles, respectively (Figure 2b). This decrease in permeance is due to the increasing thickness of the TpPa layer along the pore walls, which reduces the effective pore sizes in the composite membrane. The selectivity of the membranes was then evaluated by filtrating aqueous dye (Congo red, CR) solutions. The rejection to CR was remarkably enhanced from ~19.4% for the pristine HPAN substrate to ~91.2% after merely 3 LbL cycles. The rejection was steadily increased to about ~99.8% after 11 LbL cycles. The change in the color of the dye solutions (insets in Figure 2b) and the static adsorption results (Figure S15) clearly indicate that adsorption plays a negligible role in the removal of dyes from the solution as adsorption only removes <5% dyes from the solution. Therefore, the excellent dye removal of the TpPa-HPAN membrane is predominantly due to the mechanism of rejection of the TpPa-functionalized membrane pores. To further identify the effect of size discrimination and electrostatic repulsion in the dye rejection, we used the membranes to treat solutions of other dyes including acid fuchsin (AF) and methyl blue (MB) (Figure 2c). The rejection rates for these two dyes were also steadily increased with rising LbL cycles. All the three dyes are negatively charged and the different rejection rates should be originated from the changing effect of size discrimination of the membrane to them. A simple comparison of molecular weights of these dyes does not explain the difference as CR having the second largest molecular weight always exhibits the largest rejections for membranes prepared from various LbL cycles. Instead, it depends on the molecular dimensions of the dyes. As shown in Figure 2d, AF molecule presents the smallest lateral size of 1.26 nm × 1.04 nm, and correspondingly shows the lowest rejection. CR has the biggest size of 2.63 nm × 0.73 nm although its molecular weight is not the largest among the three dyes, and gives the highest rejection. MB with a size of 2.22 nm × 2.12 nm displays a medium rejection rate. This observation implies the significant role of pore size discrimination on dye rejection.13

Considering that there is a significant difference in rejection rate to CR and AF of the composite membranes (e.g. ~96% vs ~19% for the TpPa$_x$−HPAN membrane), we expect that...
the membrane can be used to separate the two dyes. The TpPa$_3$–HPAN membrane was used to treat a solution containing 50 ppm of AF and 50 ppm of CR. As shown in insets in Figure 2e, CR and AF solutions present a red and rose pink color, respectively. After passing through the membrane, only the rose pink color can be observed in the filtrate solution, clearly demonstrating that CR molecules are mostly rejected by the membrane, which is further confirmed by the absence of the characteristic peak at $\sim$345 nm of CR in the UV–vis spectroscopy of the filtrate (Figure 2e). These results indicate thus prepared COF-functionalized membranes can effectively recover specific dyes from solutions of mixed dyes with similar molecular weights, implying their great potential in dye recovery and separation.\textsuperscript{12}

To reveal the long-term stability of the composite membranes, a continuous testing of PWP and selective separation performance were carried out for 6 h (Figure S16). The TpPa$_3$–HPAN membrane displayed a slightly declined PWP in the early stage and reaches a plateau during following testing. The initial PWP decline about $\sim$20.6% is likely caused by the compaction of the HPAN substrate. Almost negligible decline in the rejection to CR over 6 h demonstrates the durability of the membrane, and also confirms that the adsorption only plays a very minor role in the removal of dyes otherwise rejection will drop in the continuous filtration tests as a result of adsorption saturation. Besides, the membrane maintained its prominent performance after being challenged with 2 M HCl for 48 h (Figure S17), evidencing its superior stability under acidic conditions.\textsuperscript{22,29–31}

Next, the performances of the TpBD–HPAN membranes were evaluated. As shown in Figure 3a, the PWPs of the TpBD membranes are sharply decreased from $\sim$415 to $\sim$2 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ with the LbL cycles increased from 3 to 11. Accordingly, the rejection for CR is increased to $\sim$98.6% after 5 LbL cycles and remains almost unchanged with further increased cycles. In addition, the TpBD–HPAN composite membranes exhibited gradually increased rejection to AF and MB (Figure 3b). Compared to TpPa$_3$–HPAN membranes prepared with the same LbL cycles, the TpBD–HPAN membranes always exhibited higher rejections to AF and MB. That is, the LbL synthesis of TpBD is more effective in tuning the effective pore size of the HPAN substrates because TpBD is grown faster in the membrane pores compared to TpPa. Moreover, the TpBD$_{2}$–HPAN membrane exhibited $\sim$96.6% rejection to 2 nm gold nanoparticles (Table S2), further demonstrating their outstanding size discriminating performance.

To highlight the excellent performance, we compared our COF-functionalized membranes via the LbL strategy with membranes prepared by other methods (Figure 4, Table S3). In general, COF-based membranes exhibit a higher PWP and comparable dye rejection as compared to other membranes. Particularly, the TpPa$_9$ and TpBD$_{2}$–HPAN membranes prepared in this work present PWPs up to $\sim$265 and $\sim$339 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, respectively, which is $\sim$3–20 times higher than that of other membranes including reduced graphene oxide (rGO) and metal–organic framework (MOF) based composite membranes\textsuperscript{32,33} while the high dye rejection rates ($\sim$99%) are maintained. In addition to the initial high water permeance of the HPAN substrates, the ultrahigh permeability of our COF-functionalized membranes should be attributed to the highly porous, sub-2 nm, and water-affinitive pore channels of COFs, which provide additional accessible channels to accelerate water permeation.\textsuperscript{34}

![Figure 4](image)

**Figure 4.** Performance of the COF-functionalized membranes prepared by the LbL route in comparison with other reported membranes. The detailed information for each membrane is given in Table S3.

### CONCLUSIONS

In summary, rapid synthesis of imine-linked COFs is realized by the LbL process at room temperature. Hydrolyzed PAN ultrafiltration membranes are used as the porous substrates and are alternatively exposed to the ethanolic solutions of the aldehyde and amine monomers. Both TpBD and TpPa are grown along the pore wall of the substrate, producing a conformal coating on the substrate skeleton with the coating thickness adjustable by LbL cycles. Thus-produced COF-functionalized membranes efficiently reject Congo red molecules and 2-nm gold particles from water. Remarkably, the membranes exhibit $\sim$3–20 times higher water permeance than other membranes with similar dye rejections and also excellent acid resistance and long-term stability. We expect these COF-functionalized membranes to find important applications in fast separation (e.g., dye separation and removal of pharmaceutical wastes from water), and this LbL synthesis strategy can extend to synthesize other types of COFs on various substrates targeted for specific applications.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.8b01537.

Experimental procedures, characteristics of the dyes for filtration tests, hydrolysis mechanism of the PAN substrates, appearance of the ethanolic solutions of COF monomers, FTIR spectra of the monomers, the HPAN substrate and the TpBD, FTIR spectra of the TpBD–HPAN membranes, surface SEM morphology of the pristine HPAN substrate, thermogravimetric analysis of the HPAN substrate and the TpBD$_3$–HPAN membrane, surface morphology of the TpBD–HPAN membranes, photographs of the TpBD$_3$–HPAN membrane, cross-sectional SEM images, surface SEM image of the TpBD$_3$–HPAN membrane, ATR-FTIR spectra of the TpPa–HPAN membranes, XRD pattern of COF powders, zeta potential of the HPAN substrate and the TpPa–HPAN membranes, water contact angles of the HPAN substrate and the TpPa–HPAN membranes, adsorption of CR by the pristine and COF-grown...
HPAN membranes, change in pure water permeance and rejection to CR of the TpPz2-HPAN membrane, PWP and rejection of TpPz2-HPAN membrane, gold concentrations in the filtration and retention solutions obtained in the separation of gold particles, and comparison of dye removal performance (PDF)

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Notes

The authors declare no competing financial interest.

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