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# Synthesis of Ultrathin Zeolitic Imidazolate Framework ZIF-8 Membranes on Polymer Hollow Fibers Using a Polymer Modification Strategy for Propylene/Propane Separation

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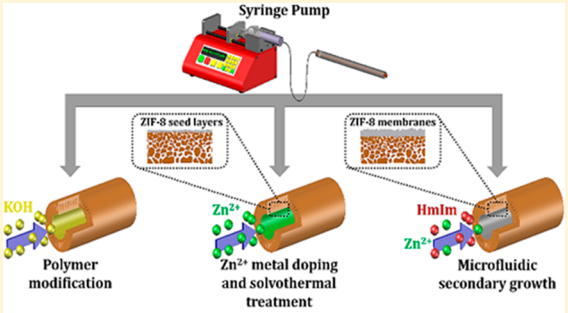
Supporting Information

**ABSTRACT:** Polycrystalline zeolitic imidazolate framework ZIF-8 membranes have shown great potential for energy-efficient propylene/propane separation. Their large-scale applications are, however, hampered by the lack of facile and cost-effective processing technologies for ultrathin ZIF-8 membranes on scalable substrates. Here, we report facile preparation of ultrathin ZIF-8 membranes on the bore side of Matrimid hollow fibers based on a polymer modification strategy. Site-selective nature of the method enables a positional control over locations (i.e., bore or shell side) of active ZIF-8 layers on the hollow fibers. The ZIF-8 membranes grown on the bore side of Matrimid hollow fibers with polydimethylsiloxane coating displayed an average propylene permeance and a separation factor of ∼152 × $10^{-10}$ mol·$m^{-2}$·$Pa^{-1}$·$s^{-1}$ and ∼55, respectively. Optimization of ZIF-8 seeding step resulted in an improvement in propylene permeance (∼369 × $10^{-10}$ mol·$m^{-2}$·$Pa^{-1}$·$s^{-1}$) while maintaining relatively high separation factor (∼40).



Polycrystalline ZIF-8 Membrane on Polymer Hollow Fiber via Polymer Modification Strategy

## 1. INTRODUCTION

Polycrystalline zeolitic imidazolate framework ZIF-8 membranes (mostly grown on planar substrates) have shown excellent kinetic separation of propylene from propane due to its effective aperture of ∼4.0 Å, which is in between the van der Waals diameter of propylene (∼4.0 Å) and propane (∼4.2 Å).[1,2] Currently, there have been no commercial polycrystalline ZIF-8 membranes. This is ultimately due to the cost of polycrystalline membranes being prohibitively high (e.g., ∼$1,000 per $m^2$ for polycrystalline zeolite membranes vs ∼$20 per $m^2$ for polymer membranes).[3] It is, therefore, critical to reduce the cost of ZIF-8 membranes by increasing membrane productivity by (1) using cost-effective scalable substrates with high surface-to-volume ratio and (2) reducing the membrane thickness (<1 μm).[4]

Despite successful preparation of polycrystalline ZIF-8 membranes on inorganic substrates with high surface-to-volume ratio (i.e., hollow fiber, capillary, tubular),[5−8] inorganic substrates are not considered cost-effective. For example, ceramic hollow fibers, in particular, can provide high packing density but they are fairly expensive. Moreover, ceramic hollow fibers are in general quite difficult to handle due to their inherently poor mechanical properties. In contrast, polymer hollow fibers are inexpensive and easily form modules with high packing density, and thereby are more attractive as cost-effective substrates for polycrystalline ZIF-8 membranes.[9]

Hou et al.[10] explored the formation of ∼1 μm thick ZIF-8 membranes on the shell side (i.e., outer side) of polyvinylidene fluoride (PVDF) hollow fiber functionalized with 3-amino-propyltriethoxysilane−titania by immersing the hollow fiber in ZIF-8 synthesis solution. Biswal and co-workers[11] demonstrated a facile room temperature synthesis of ZIF-8 membranes on either the shell or bore side of polybenzimidazole-based hollow fibers (o.d., 780 μm) using an interfacial synthesis method for helium separation. Venna et al.[12] utilized a simple continuous flow processing method to prepare ZIF-8 membranes on the shell side of Torlon polyamide−imide hollow fibers (o.d., 400 μm) for postcombustion $CO_2$ capture application. Finally, Li and co-workers[13] reported the synthesis of ultrathin ZIF-8 membranes on the shell side of Zn-based gel coated PVDF hollow fibers via gel−vapor deposition. The 87 nm thick ZIF-8 membranes showed a high separation factor of 73 and remarkable propylene permeance of 840 GPU (1 gas permeation unit, GPU = 3.35 × $10^{-10}$ mol·$m^{-2}$·$s^{-1}$·$Pa^{-1}$).

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While ZIF-8 membranes grown on the shell side of polymer hollow fibers have slightly a higher surface-to-volume ratio, membranes grown on the bore side have several advantages: (1) where the relatively fragile polycrystalline ZIF-8 membranes are better protected from physical damage during handling, (2) hollow fibers can be packed together in a close proximity to form modules with a high fiber packing, and (3) the module assembly process can be performed without damaging the relatively brittle ZIF-8 layers, especially when membranes are ultrathin (i.e., <1 $\mu$m). However, growing ZIF-8 membranes on the bore side of hollow fibers requires synthesis in a confined space, thereby presenting several challenges such as accessibility, reactant availability, positional control, etc.[14] Coronas et al.[15] were among the first to report synthesis of ZIF-8 membranes on the bore side of polysulfone hollow fibers (i.d., 315 $\mu$m) using a continuous flow processing method for $CO_2/CH_4$ and $H_2/CH_4$ separations. Nair and co-workers[16] prepared ~8.8 $\mu$m thick ZIF-8 membranes on the bore side of Torlon hollow fibers using interfacial microfluidic membrane processing, where the membranes formed at the interface between two solutions (water−octanol). The membranes exhibited propylene permeance and a separation factor of ~27 GPU and ~12, respectively.[16] Later, the same group reported improved ZIF-8 membranes with propylene permeance and a separation factor of 45 GPU and 180, respectively.[17,18] Most recently, Jeong and co-workers[19] prepared ultrathin (~800 nm thick) ZIF-8 membranes on the bore of Matrimid hollow fibers (i.d., 344 $\mu$m) via microwave-assisted seeding followed by microfluidic secondary growth. The membranes displayed an average propylene permeance of ~55 GPU and a propylene/propane separation factor of ~46. With the exception of a few groups (i.e., Nair's[16−18] and Jeong's[19] groups), reports on the synthesis of ZIF-8 membranes on the bore side of polymer hollow fibers intended for propylene/propane separation are quite rare. This is unsurprising considering the challenging nature of preparing high-quality ZIF-8 membranes on the confined space of hollow fibers.

In general, polycrystalline ZIF-8 membranes can be prepared via either in situ or secondary growth.[20,21] Although not as straightforward as the in situ growth, synthesis of ZIF-8 membranes by secondary growth allows for better control over membrane microstructures (i.e., membrane thickness, crystal orientation, crystal grain size, etc.) and therefore better separation performances of the resulting membranes.[22] However, the challenges here lie in obtaining high-quality seed layers prior to membrane growth. Typical high-quality seed layers consist of seed nanocrystals that are densely packed, uniformly distributed on surfaces, and strongly attached to the substrate surfaces.[21] In our recent contribution,[23] we have introduced the "polymer-modification-enabled in situ metal−organic framework formation" (termed as PMMOF) method for the construction of ZIF/polymer composites and/or ZIF thin films on polyimide (Kapton and Matrimid) flat sheets. The method relies on the targeted zinc ion doping on modified polymer substrates (i.e., partially deimidized polyimides) which enables the formation of ZIF nanoparticles at a specific location. As a proof-of-concept, the ZIF-8 nanocrystals deposited on Matrimid substrates by the PMMOF were secondarily grown to form defect-free and well-intergrown membranes.[23]

Herein, we report a successful preparation of ultrathin ZIF-8 membranes with much-improved propylene/propane separation performances on the bore side of Matrimid hollow fibers by using the PMMOF method in combination with microfluidic secondary growth. PMMOF can control the location of where the ZIF-8 polycrystalline layer is grown, owing to the site-selective nature of the process. In this work, Fourier transform infrared spectroscopy was used to identify the chemical bonding environment present on the surface of Matrimid hollow fibers, X-ray diffraction was used to determine the crystallinities and phases of the ZIF-8 crystals, and electron microscopy was used to analyze the microstructures of the ZIF-8 seed layers and membranes. Finally, gas transport properties of the ZIF-8 membranes on Matrimid hollow fibers were determined using a Wicke−Kallenbach technique (Figure S1).

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Matrimid 5218 (Alfa-Aesar, Ward Hill, MA, USA) and *N*-methyl-2-pyrrolidinone ($C_5H_9NO$; 99.5%, Daejung Chemicals & Metals, Siheung, Korea, hereafter NMP) were used to fabricate Matrimid hollow fibers. Potassium hydroxide (KOH; reagent grade, VWR International) was used to hydrolyze the imide rings of Matrimid hollow fibers. 2-Methylimidazole ($C_4H_6N_2$; 99%, Sigma-Aldrich, hereafter HmIm), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$; 98%, Sigma-Aldrich), sodium formate (HCOONa; 99%, Sigma-Aldrich), methanol ($CH_3OH$; >99%, Alfa-Aesar), and deionized (DI) water were used to prepare PMMOF and secondary growth precursor solutions. Polydimethylsiloxane (Sylgard 184, Dow Chemical, hereafter PDMS) and hexane ($C_6H_{14}$; ACS grade, VWR International) were used to seal defective ZIF-8 membranes.

**2.2. Preparation of Matrimid Hollow Fibers.** Porous Matrimid hollow fibers were prepared using a dry−wet jet spinning process. Spinning parameters can be found in Table S1. The pristine hollow fibers were microporous ($N_2$ permeance ~45 594 GPU) with i.d. and o.d. of 465 and 590 $\mu$m, respectively (Figure S2). Preparation of the Matrimid hollow fiber setup (11 cm in length) used for ZIF-8 seeding and secondary growth can be found in our previous work (see also Figure S3 for optical photograph of the setup).[19]

**2.3. Preparation of ZIF-8 Seed Layers on Matrimid Hollow Fibers.** Surface modification and Zn ion doping on the bore side of a Matrimid hollow fiber were performed following a procedure previously reported with a slight adjustment.[23] Briefly, using a syringe pump (Harvard Model 55-4152) setup shown in Figure S3, a 5 M aqueous KOH solution (50 °C) was flowed to the bore side of the hollow fiber at a flow rate of $5.50 \times 10^{-3}$ $cm^3/s$ for different periods of time, followed by a continuous flow of 100 mM aqueous zinc nitrate hexahydrate solution with a similar flow rate for 1 h. Excess KOH and metal solution were purged slowly with air and dried with Kimwipes. To form a ZIF-8 seed layer on the bore side, the $Zn^{2+}$-doped hollow fiber was positioned vertically in a Teflon autoclave containing HmIm linker solution (10.36 g of HmIm and 0.5 g of sodium formate in 120 mL of methanol). Then, the autoclave was kept inside a preheated convection oven at 120 °C for 1 h, followed by 2 h of cooldown to room temperature. The seeded hollow fiber was then washed with fresh methanol for 1 h. Finally, the ZIF-8 seeded hollow fiber sample (hereafter, ZIF-8-S/HF) was dried inside a convection oven at 60 °C for 4 h.

**2.4. Preparation of ZIF-8 Membranes on Matrimid Hollow Fibers.** A ZIF-8-S/HF was grown into a well-


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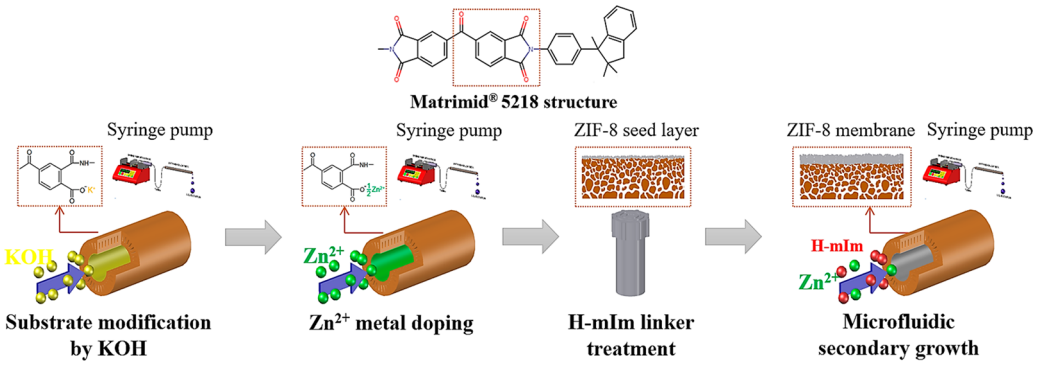


**Figure 1.** Schematic illustration of the synthesis of ZIF-8-M/HFs using combination of the PMMOF process and microfluidic secondary growth.

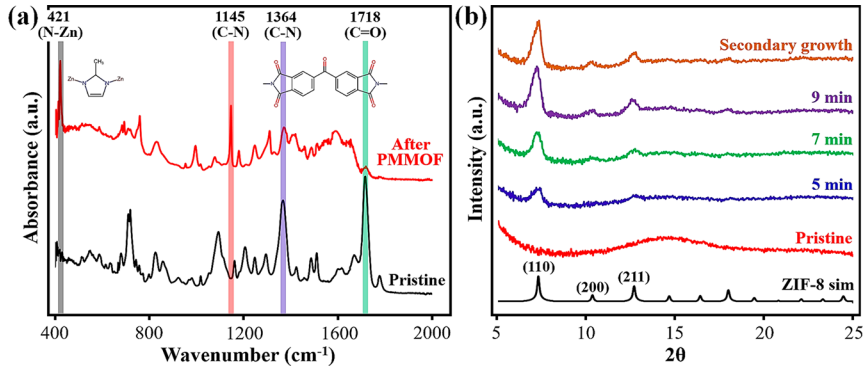


**Figure 2.** (a) ATR-FTIR spectra of the bore side of pristine Matrimid hollow fibers and ZIF-8-S/HFs after PMMOF process and (b) PXRD patterns of ZIF-8-S/HFs synthesized in different hydrolysis times in comparison with the simulated one.

intergrown ZIF-8 membrane using a microfluidic secondary growth method. Preparation of secondary growth precursor solution is described elsewhere.[19,24] A syringe pump (Harvard Model 55-4152) was used to flow the secondary growth solution through the bore side of ZIF-8-S/HF at a flow rate of $8.33 \times 10^{-4}$ $cm^3/s$ for 6 h. The membrane growth was performed inside a vacuum oven at 30 °C. The resulting ZIF-8 membrane (hereafter, ZIF-8-M/HF) was thoroughly washed by flowing methanol through the bore side at flow rate of $1.83 \times 10^{-3}$ $cm^3/s$ for 1 h. Finally, the ZIF-8 membrane was dried at room temperature for 24 h.

**2.5. Defect Sealing of ZIF-8 Membranes Using PDMS.** Defect sealing of ZIF-8-M/HFs was performed while the membrane was in the permeation module. A 5 wt % PDMS/hexane coating solution was prepared by dissolving part A and part B of Sylgard 184 with a 10:1 ratio in hexane under vigorous stirring at room temperature for several hours. Then, the PDMS coating solution was flowed to the bore side of a ZIF-8-M/HF sample at a flow rate of $1.83 \times 10^{-3}$ $cm^3/s$ for 1 min. Excess PDMS solution was slowly removed from the bore side by flowing air at a flow rate of $5.50 \times 10^{-3}$ $cm^3/s$ for 1 min. Finally, the PDMS coated ZIF-8 membrane (hereafter, ZIF-8-M-PDMS/HF) was dried and cured at room temperature under vacuum for 48 h.

**2.6. Characterization.** Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra (wavenumber scan range from 400 to 4000 $cm^{-1}$) were collected using a Thermo Scientific Nicolet iS5 FTIR spectrometer equipped with iD7-ATR diamond accessory. Powder X-ray diffraction (PXRD) patterns were collected using a Miniflex II benchtop X-ray diffractometer (Rigaku) with Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å) scanning in the 2$\theta$ range 5−25°. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7500F operating at an acceleration voltage of 5 keV and a working distance of 15 mm. The gas separation properties of ZIF-8-M-PDMS/HFs were measured using the Wicke−Kallenbach method (see Figure S1). The permeation measurements were performed under atmospheric pressure at room temperature (~22 °C). A 50:50 vol % propylene/propane feed mixture ($3.33 \times 10^{-1}$ $cm^3/s$) was flowed to the bore side, while argon sweeping gas ($3.33 \times 10^{-1}$ $cm^3/s$) was flowed through the shell side of the hollow fiber. The composition of the propylene and propane in the argon sweep gas was analyzed using an Agilent GC 7890 A gas chromatograph equipped with a HP-PLOT Q column.

## 3. RESULTS AND DISCUSSION

Figure 1 illustrates the synthesis of ZIF-8 seed layers by the PMMOF and polycrystalline ZIF-8 membranes by subsequent secondary growth. Details about the PMMOF process were presented in our recent report.[23] Briefly, the imide rings of Matrimid were first hydrolyzed by a strong base (i.e., KOH) forming carboxylates that serve as ion-exchangeable sites and create hydrophilic free volume.[25] The KOH-modified Matrimid hollow fibers were then subjected to a continuous flow of an aqueous zinc solution, thereby initiating the $K^+$−$Zn^{2+}$ ion-exchange reaction and diffusion of free $Zn^{2+}$ into the hydrophilic free volume of the polymer.[23] The $Zn^{2+}$ ion-exchanged layers did not propagate through the entire thickness of the Matrimid hollow fibers as the shell side of the hollow fibers remained unchanged as compared to the bore side (Figure S4). In fact, only a portion (several micrometers thick) of the hollow fibers were hydrolyzed and then ion-exchanged to form $Zn^{2+}$ polyamate salt as evidenced by a clear


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morphological change observed under SEM (Figure S5). Upon in situ solvothermal treatment in an HmIm ligand solution, free $Zn^{2+}$ diffuse from the polymer free volume and then react with HmIm to form ZIF-8 seed layers on the bore side of the hollow fibers. One of the advantages of the PMMOF process is a positional control over ZIF-8 seed layer formation, which depends on the location where substrate modification and zinc ion doping take place. Finally, the seeded hollow fibers prepared by the PMMOF process were then secondarily grown under a continuous flow of a growth solution to form continuous, defect-free, and well-intergrown ZIF-8 membranes.

Figure 2a presents the ATR-FTIR spectra of the bore side of pristine hollow fibers and ZIF-8 seeded hollow fibers (ZIF-8-S/HFs) obtained by the PMMOF process. The pristine Matrimid hollow fibers exhibited characteristic ATR-FTIR peaks at 1364 and 1718 $cm^{-1}$, which were assigned to asymmetric C−N and C═O vibration modes of imide groups, respectively.[26] Upon modification by KOH, the absorption peak corresponding to the C═O imide groups (1718 $cm^{-1}$) almost disappeared, resulting from imide ring cleavage by the KOH solution. The hydrolyzed Matrimid hollow fibers exhibited several overlapping peaks at wavenumbers between 1500 and 1600 $cm^{-1}$, which are a combination of N−H amide (1550 $cm^{-1}$), carboxyl−$K^+$ complex (1500−1600 $cm^{-1}$), and C═O amide (1640 $cm^{-1}$) modes.[27] The ATR-FTIR spectra of the KOH-treated and $Zn^{2+}$ ion-exchanged hollow fibers were mostly indistinguishable (Figure S6). Solvothermal reaction in an HmIm ligand solution led to formation of ZIF-8 seed crystals on hollow fibers, evidenced by the appearance of two new peaks at 421 and 1145 $cm^{-1}$, which were assigned to the Zn−N and C−N absorption bands of ZIF-8, respectively.[28] The corresponding PXRD patterns presented in Figure 2b further confirm the formation of pure-phase ZIF-8 crystals. Interestingly, the intensities of the characteristic diffraction peaks of ZIF-8 increase as the KOH treatment time increases, indicating the formation of ZIF-8 crystals in greater number as the hydrolysis reaction increases. An extended alkali treatment increased the zinc ion content in the hydrophilic polymer layer, which led to an increase in crystal formation. It is noted that Matrimid hollow fibers not subjected to a hydrolysis reaction did not form ZIF-8 crystals as evidenced from weak PXRD reflections as shown in Figure S7e (see also SEM images in Figure S7).[23]

Since the quality of polycrystalline membranes prepared by secondary growth highly depends on the quality of seed layers,[21,22] we attempted to improve the quality of ZIF-8 seed layers on the bore side of Matrimid hollow fibers through systematic optimization of KOH treatment time. Figure 3 and Figure S8 show the surface and cross-sectional electron micrographs of the ZIF-8-S/HFs after the PMMOF process.

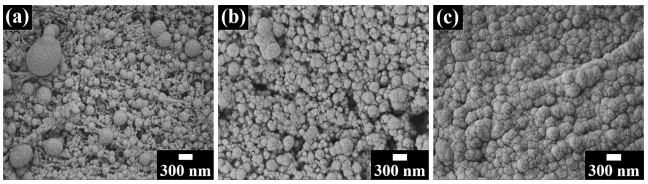


**Figure 3.** SEM images of ZIF-8-S/HFs prepared using Matrimid hollow fibers treated with a 5 M KOH for (a) 5, (b) 7, and (c) 9 min. With the increased KOH treatment time, densely packed ZIF-8 seed layers can be obtained on the bore side of hollow fibers.

KOH treatment for 5 min led to poor-quality ZIF-8 seed layers with low surface coverage. With an increase of KOH treatment time to 9 min, the ZIF-8 seed layer exhibited better surface coverage. As mentioned earlier, a longer KOH treatment time increases the number of $Zn^{2+}$ ions in the polymer free volume as well as in the ion-exchangeable sites, thereby leading to an enhancement in crystal formation.[23] To further confirm the formation of ZIF-8 seed layers on the bore side of Matrimid hollow fibers, a quick acid treatment was performed. After subjecting the seeded hollow fiber to a diluted $HNO_3$ (0.05 M) treatment, the ZIF-8 seed layer that was originally covering the surface of the hollow fibers was removed, exposing bare surfaces of the hollow fibers (Figure S9).

Figure S10 presents the surface and cross-sectional electron micrographs for both the bore and shell sides of ZIF-8-S/HFs after the ZIF-8 seeding optimization step. As opposed to the bore side, few ZIF-8 crystals formed on the shell side even though an HmIm linker solution was provided from the shell side. To show the site-selective feature of the PMMOF process, we attempted to form ZIF-8 seed layers and subsequently ZIF-8 membranes by performing the PMMOF on the shell side. Figure S11 shows the formation of high-quality ZIF-8 seed layers and membranes on the shell side of hollow fibers. Due to the mechanical robustness and handling convenience during membrane synthesis and more importantly during module assembly, we focused on the synthesis of ZIF-8 membranes on the bore side of Matrimid hollow fibers in this study.

An optimized ZIF-8 seed layer on the bore side of Matrimid hollow fibers was then subjected to a continuous flow of growth solution to form high-quality ZIF-8 membranes. As shown in Figure 4a,b, the secondarily grown ZIF-8 membranes

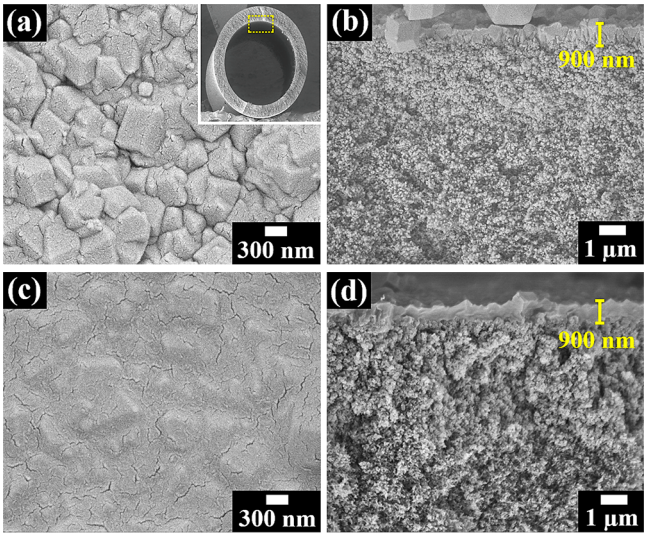


**Figure 4.** Top and cross-section views of ZIF-8-M/HFs (a, b) before and (c, d) after PDMS coating under high magnification. Inset image shows the cross section of the ZIF-8-M/HFs under low magnification.

were continuous, well-intergrown, and absent of any macroscopic defects such as cracks and pinholes. The thickness of the membranes were ~900 nm, comparable to the thickness of ZIF-8 membranes synthesized by our groups under microwaves.[19] Furthermore, the polycrystalline ZIF-8 layers appear to be strongly adhered to the substrates, which is completely opposite to those prepared using ZIF-8 seed layers physically


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deposited on the inner side of the hollow fibers to resemble conventional dip-coating method as presented in our earlier study (see also SEM images in Figure S12).[19] Unlike the conventional dip-coating method, the PMMOF seeding method enables the formation of ZIF-8 seed crystals with strong attachment to substrate surfaces, thereby resulting in the formation of ZIF-8 membranes that are strongly adhered on hollow fibers. We postulate that strong attachment of ZIF-8 membrane layer to the substrate surface is attributed to the possible formation of a chemical bond between $Zn^{2+}$ coordinated to the carboxylic groups of Matrimid and nitrogen of the HmIm linker.

Propylene/propane binary gas separation performances of ZIF-8 membranes (ZIF-8-M/HFs) were determined using a Wicke−Kallenbach setup conducted under atmospheric pressure at room temperature (~22 °C). The membranes unfortunately showed poor separation performances (see Table S2) presumably due to poor membrane microstructure (i.e., ZIF-8 crystal grain boundary).[23] It is well-known that gas transports through polycrystalline membranes are governed by selective diffusion through crystal grains (intracrystalline diffusion) and nonselective diffusion through grain boundary (i.e., intercrystalline diffusion). Sheng et al.[29] demonstrated that these intercrystalline grain boundary defects could be minimized or blocked by applying a thin layer of PDMS on top of a polycrystalline ZIF-8 film, resulting in an improvement of the propylene/propane separation performances of the membranes. Furthermore, since PDMS is extremely permeable toward propylene, thin PDMS coating is not expected to compromise the propylene flux through ZIF-8 membranes.[30]

To coat a thin PDMS layer onto ZIF-8-M/HFs, a PDMS coating solution was flowed through the bore sides of ZIF-8-M/HFs that were already packaged into test modules. Figure 4c,d shows the surface and cross-section microstructures of the PDMS-coated ZIF-8 membranes (ZIF-8-M-PDMS/HFs), showing a smooth and uniform PDMS layer coating the top of polycrystalline ZIF-8 layer. The thickness between the PDMS coated and as-synthesized ZIF-8 membranes were identical (~900 nm), owing to the extremely thin PDMS layer. After the PDMS curing process, separation performances of the ZIF-8-M-PDMS/HFs were again tested under equimolar propylene/propane feed. Figure 5a and Table S2 present the separation performances of the ZIF-8-M-PDMS/HFs, showing the average propylene/propane separation factor and propylene permeance of ~55 and ~152 × $10^{-10}$ mol·$m^{-2}$·$Pa^{-1}$·$s^{-1}$ (~45 GPU), respectively. This performance is comparable to those reported in the literature and within the "commercially attractive" region for commercial propylene-selective membranes as proposed by Colling et al.[31] (Figure S13). The ability to in situ seal or heal defective ZIF-8 membranes inside membrane modules using a facile flow processing method is important for practical application as it provides a new means to either improve or restore separation performances of the membranes after module assembly or even during actual operation.

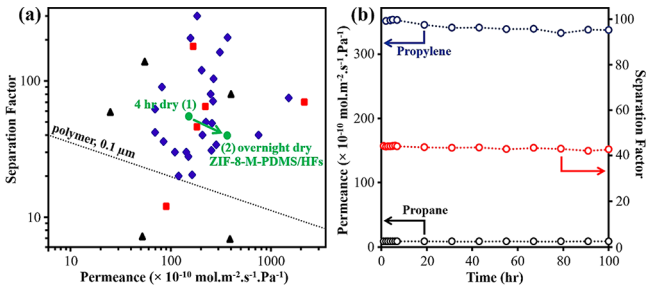


**Figure 5.** (a) Propylene/propane separation performances of the ZIF-8-M-PDMS/HFs (●) in comparison to those reported in the literature. The data includes ZIF-8 membranes grown on polymer hollow fibers (■),[13,16−19] organic and inorganic flat disks (♦),[4,24,29,32−40] and inorganic tubes, capillaries, and hollow fibers (▲).[5−8] The upper bound for polymer membrane was drawn based on ref 41. (b) Long-term binary propylene/propane permeation test conducted at 22 °C under atmospheric pressure. ZIF-8-M-PDMS/HFs show a relatively stable separation performance over the period of 100 h of continuous operation.

For their practical applications, it is of great interest to enhance propylene permeances of ZIF-8 membranes.[4] We found that the propylene permeance of the ZIF-8 membranes increases dramatically to (~369 ± 17) × $10^{-10}$ mol·$m^{-2}$·$Pa^{-1}$·$s^{-1}$ (~110 GPU) when the seeded hollow fibers (i.e., ZIF-8-S/HFs) are dried at 60 °C for prolonged time (i.e, overnight) prior to secondary growth. The propylene/propane separation factor slightly decreases from 55 to 40, but the separation factor is still within an acceptable value. The enhancement in propylene permeance of our ZIF-8 membranes was surprising. We postulate that the improvement in propylene permeance may stem from the instability of the $Zn^{2+}$ ion-exchanged layer in methanol. As previously mentioned, only a portion of Matrimid (several micrometers thick) hollow fibers were hydrolyzed and then ion-exchanged to form $Zn^{2+}$ polyamate salts, and these $Zn^{2+}$ polyamate salts are believed to be slightly dissolved in methanol solvent.[42] Due to a much shorter drying time (4 h) after the ZIF-8 seeding step, some leftover methanol in the pore of the substrates might cause dissolution of a part of the $Zn^{2+}$ ion-exchanged layer which subsequently densifies, thereby leading to a reduced propylene permeance. As opposed to methanol, the $Zn^{2+}$ polyamate salt layers are insoluble in water as mentioned by Frost et al.;[43] therefore the use of water-based secondary growth solution used during the secondary growth step does not compromise the pore of the substrates.

Finally, long-term stability of the ZIF-8 membranes is essential for their large-scale applications. As shown in Figure 5b, ZIF-8-M-PDMS/HFs exhibit a relatively stable separation performance over 100 h of continuous flow of binary propylene/propane mixture. There was no significant deterioration in membrane performances observed during the long-term permeation measurement test.

## 4. CONCLUSIONS

We have successfully demonstrated the formation of submicrometer thick polycrystalline ZIF-8 membranes on the bore side of Matrimid hollow fibers using a secondary growth method. Nanometer-sized ZIF-8 seed crystals with uniform surface coverage were prepared using a polymer modification process followed by solvothermal reaction in an HmIm ligand solution. Location of ZIF-8 seed layers and membranes (i.e., shell or bore side) were readily controlled by adjusting the location of the polymer modification (i.e., KOH treatment and zinc ion exchange). A subsequent microfluidic secondary growth conducted at room temperature resulted in continuous and well-intergrown submicrometer (~900 nm) thick ZIF-8 membranes on the bore side of the hollow fibers. The optimized ZIF-8 membranes, once coated with thin PDMS layers, displayed a separation performance with an average


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propylene permeance and a separation factor of ~369 × $10^{-10}$ mol·$m^{-2}$·$Pa^{-1}$·$s^{-1}$ (propylene permeability of 99 barrer) and ~40, respectively. Furthermore, the membranes showed stable separation performances over continuous operation for 100 h. The current synthesis is expected to be applicable for facile preparation of ZIF-8 membrane modules by growing ZIF-8 films on off-the-shelf hollow fiber modules, which is a significant step forward toward commercialization of ZIF-8 membranes.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b02969.

Additional SEM images, PXRD patterns, ATR-FTIR spectra, and Robeson plot (PDF)

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### Notes

The authors declare no competing financial interest.

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