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Efficient Propylene/Propane Separation**

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Complete List of Authors:	Ma, Xiao-Hua; King Abdullah University of Science and Technology, Swaidan, Ramy; King Abdullah University of Science and Technology Wang, Yingge; King Abdullah University of Science and Technology, Advanced Membranes and Porous Materials Center, PSE Division Hsiung, Chia-en; King Abdullah University of Science and Technology Han, Yu ; KAUST, Pinnau, Ingo; KAUST,

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**Highly Compatible Hydroxyl-Functionalized Microporous Polyimide-ZIF-8
Mixed Matrix Membranes for Energy Efficient Propylene/Propane
Separation**

Xiaohua Ma^{a,b}, Ramy J. Swaidan^{a,b}, Yingge Wang^b, Chia-en Hsiung^b,
Yu Han^b, and Ingo Pinnau^{a,b*}

^aFunctional Polymer Membranes Group, ^bAdvanced Membranes and Porous Materials Center,
Division of Physical Sciences and Engineering, King Abdullah University of Science and
Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

Corresponding Author

* ingo.pinnau@kaust.edu.sa

Keywords

ZIF-8, intrinsically microporous polyimide, hydroxyl-functionalization, mixed-matrix membrane,
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ABSTRACT

Mixed-matrix membranes composed of mechanically strong, solution-processable polymers and highly selective ultramicroporous fillers (pore size $< 7 \text{ \AA}$) are superior candidate membrane materials for a variety of energy-intensive gas separation applications because of their structural tunability to achieve enhanced gas permeability and gas-pair selectivity. However, their industrial implementation has been severely hindered because inefficient compatibility of the polymer matrices and crystalline fillers results in poorly performing membranes with low filler capacity and interfacial defects. Herein, we report for the first time a unique strategy to fabricate highly propylene/propane selective mixed-matrix membranes (MMMs) composed of a hydroxyl-functionalized microporous polyimide (PIM-6FDA-OH) and an ultramicroporous, strongly size-sieving zeolitic imidazolate framework (ZIF-8). Excellent compatibility between PIM-6FDA-OH and ZIF-8 with selective filler loading up to 65 wt% resulted from N...O-H induced hydrogen bonding as evidenced by Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The newly developed MMMs demonstrated *unprecedented mixed-gas performance* for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation and outstanding plasticization resistance of up to at least 7 bar feed pressure. The reported fabrication concept is expected to be applicable to a wide variety of OH functionalized polymers and alternative tailor-made imidazolate framework materials designed for MMMs to achieve optimal gas separation performance.

INTRODUCTION

Propylene is the second largest produced organic chemical with an annual global production capacity of approximately 100 million tons in 2016.¹ It is primarily used for synthesis of polypropylene, propylene oxide, acrylonitrile, cumene, acrylic acid, isopropanol and others.^{1,2} At a propylene price of ~ 700-1000 USD/ton, propylene represents a total market value of ~100 billion USD/year. The final step in the production of propylene is large-scale distillation from propane in a C3-splitter at ~20 bar and ~50 °C.^{3,4} Because of the small difference in relative volatility between propylene and propane (~1.08-1.12), distillation is performed in columns over 200 ft tall containing over 150 trays and operating at reflux ratios > 10, thereby making it one of the most energy-intensive separation processes in the chemical process industry.⁵⁻⁷ Membrane technology offers a potential alternative to the conventional distillation process for propylene/propane separation. The current sales of membrane-based gas separation systems is in the range of US\$ 1-1.5 billion per year with a 90% market share for: (i) hydrogen recovery from various off-gas streams, (ii) onsite nitrogen production from air, (iii) carbon dioxide removal from natural gas, and (iv) olefin recovery from nitrogen-containing petrochemical vent gas streams.⁸ However, current commercial polymer membrane materials used in these processes suffer from several severe drawbacks for viable propylene/propane separation: (i) low C₃H₆ permeability (< 10 barrer — 1 barrer = 1 x 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹), (ii) low C₃H₆/C₃H₈ selectivity (< 10), and (iii) poor plasticization resistance under challenging high-pressure mixed-gas conditions that leads to reduction of selectivity.^{9,10} One of the most promising membrane materials for propylene/propane separation is based on a chemically and thermally stable ultramicroporous zeolitic imidazolate framework (ZIF-8) with sodalite topology made by synthesis of zinc nitrate hexahydrate and 2-methylimidazole.¹¹ This ultramicroporous material is characterized by external aperture windows of 3.4 Å as determined by single-crystal XRD. Interestingly, recent work reported a significantly larger effective pore size of 4.0-4.2 Å due to some framework flexibility in ZIF-8,¹²⁻¹⁴ providing the material with excellent molecular sieving properties for propylene/propane separation.¹⁵ However, fabrication of defect-free pure ZIF-8 membranes is difficult

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3 due to the crystalline nature of the material which leads to inherent brittleness and intercrystalline packing
4 defects. One approach to overcome these deficiencies is to prepare mixed-matrix membranes (MMMs)
5 which are composed of a solution-processible, mechanically strong polymer with gas transport properties
6 preferably located on or above the permeability/selectivity performance trade-off curve for a specific
7 application and an ultramicroporous filler that can boost both gas permeability and gas-pair selectivity.¹⁶⁻
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14 ¹⁸ This concept has been applied to ZIF-8-based MMMs for a variety of gas separation applications,²⁰⁻²²
15 including propylene/propane separation.^{23,24} The most important challenges in the formation of advanced
16 mixed-matrix membranes are: (i) elimination of interfacial defects that arise from poor compatibility
17 between the polymer matrix and the highly selective ultramicroporous filler and (ii) limitations in the
18 maximum filler loading for MMMs with sufficiently high mechanical strength.²⁵ A recent study
19 demonstrated that ZIF-8 nanoparticles coated with polydopamine (PD) enhanced their compatability with
20 a Tröger's base derived polyimide matrix due to interactions by hydrogen bonding of the ortho-
21 dihydroxyl groups in the PD and the nitrogen of the imidazole in ZIF-8.²⁶ The resulting MMMs
22 demonstrated moderately improved gas separation properties but no propylene/propane permeation data
23 were reported and the ZIF-8 content was limited to only 30 wt%.

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35 This work reports the preparation and exceptional propylene/propane separation properties of a novel
36 MMM type made from a solution-processable microporous dihydroxyl-functionalized polyimide (PIM-
37 6FDA-OH)²⁷ and ZIF-8 as highly permeable and selective ultramicroporous filler (Figure 1a). PIM-
38 6FDA-OH was selected as the matrix material for ZIF-8 nanocomposite membranes because of its
39 hydroxyl-functionality for enhanced compatibility and excellent gas transport properties with propylene
40 permeability of 3.5 barrer combined with C₃H₆/C₃H₈ selectivity of 30, which places its performance
41 above the polymer permeability/selectivity upper bound reported by Burns and Koros.^{28,29}

EXPERIMENTAL SECTION

Materials. Basolite® Z1200 (2-methylimidazole zinc salt, ZIF-8) was obtained from Sigma-Aldrich and dried at 200 °C for 24 h before use. The hydroxyl-functionalized microporous polyimide (PIM-6FDA-OH) was prepared by polycondensation reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5'-diamino-6,6'-diol (SBIDA) as previously reported by our group.²⁷ The monomer 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99% Aldrich-Sigma) was purified by sublimation before use. All materials and solvents for monomer and polymer syntheses, bisphenol A, methylsulfonic acid, dichlorotin hydrochloride solution, sodium carbonate, dichloromethane, ethyl acetate, ligroin, nitric acid, pyridine, anhydrous tetrahydrofuran (THF) and *N*-methylpyrrolidone were also obtained from Aldrich-Sigma. The molecular weight (M_n) and polydispersity index (PDI) of PIM-6FDA-OH obtained by GPC (Agilent 1200) were 8.54×10^4 g mol⁻¹ and 1.94, respectively.

Membrane Preparation. Mixed-matrix membranes (MMMs) reported in this work consisted of a dihydroxyl-functionalized, intrinsically microporous polyimide (PIM-6FDA-OH) and a zeolytic imidazolate framework (ZIF-8). The MMMs were made by the following procedure: First, dried commercial ZIF-8 (30, 60, 80, 100 and 120 mg, respectively) was separately placed in vials and then dispersed in 3 mL anhydrous THF using an ultrasonic horn (Vibra-Cell, Sonics & Materials Inc.) The mixture was sonicated for 30 min with an energy intensity of 50% and 3 s intervals. Second, PIM-6FDA-OH powder (170, 140, 120, 100 and 80 mg, respectively) was slowly added to the mixture and placed on a roller mixer for 24 h. Based on weighted amounts of PIM-6FDA-OH and ZIF-8, the stock suspensions contained 15, 30, 40, 50, and 60 wt% ZIF-8, respectively. Third, the polymer concentration of each suspension was adjusted to ~ 5 wt% by gently flushing with N₂ to partially remove THF. Thereafter, the more concentrated suspensions were placed again on a roller mixer for 24 h to ensure homogeneous mixing of PIM-6FDA-OH and ZIF-8 particles in THF. Finally, isotropic films were obtained by casting the suspensions on glass plates with a doctor blade. The cast films were placed in an oven and the THF

was removed by continuous flushing with nitrogen at room temperature for 8 h. The resulting mixed-matrix membranes were further dried at 250 °C for 24 h. Prior to gas permeation testing, complete solvent removal from the films was confirmed by TGA analysis under N₂ atmosphere. Films with thicknesses of ~40-60 μm were used for gas permeation experiments.

Materials Characterization. Thermal gravimetric analysis (TGA) was carried out with a TGA Q5000 equipped with a thermal analyzer both in N₂ and air atmosphere; the samples were heated from room temperature to 800 °C. Fourier transform infrared spectroscopy (FT-IR) spectra were acquired using a Varian 670-IR spectrometer. Wide-angle X-ray diffraction (WXR) was conducted on a Bruker D8 Advance diffractometer from 6 to 50° at a scanning rate of 0.5° min⁻¹. X-ray photoelectron spectroscopy (XPS) of PIM-6FDA-OH, ZIF-8 and the mixed-matrix membrane containing 33 wt% ZIF-8 was performed with a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 150 W, a multichannel plate, and delay line detector under 1 × 10⁻⁹ Torr vacuum. Energy-filtered transmission electron microscopy (EF-TEM) was performed on a FEI Titan ST electron microscope equipped with a GIF system operated at 300 kV. ZIF-8 particles size distribution was determined by dynamic light scattering measurements using a Zetasizer Nano ZS from Malvern Pananalytical. The BET surface area of ZIF-8 powder was measured by N₂ adsorption at -196 °C (Micrometrics ASAP 2020 with micropore option); the sample was degassed at 150 °C for 12 h before testing. Dynamic mechanical stress-strain curves of PIM-6FDA-OH and the ZIF-8-based MMMs were measured using a dynamic mechanical analyzer (DMA, TA Instruments Q800). The samples were kept at 25 °C for one minute and then ramped at 3 N/min to 18 N.

Pure-Gas Permeation Measurements. The pure-gas permeability values of the membranes for C₃H₆ and C₃H₈ were determined at 2 bar upstream pressure and 35 °C using the constant-volume/variable-pressure method. The membranes were degassed in the permeation system on both sides under high vacuum at 35 °C for at least 24 h. The increase in permeate pressure with time was recorded by a MKS Baratron transducer. The gas permeability was determined by:

$$P = 10^{10} \frac{V_d l}{P_{up} ART} \frac{dp}{dt}$$

where P is the permeability (barrer) – 1 barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹, p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg s⁻¹), V_d is the calibrated permeate volume (cm³), l is the membrane thickness (cm), A is the effective membrane area (cm²), T is the operating temperature (K), and R is the gas constant (0.278 cm³ cmHg cm⁻³(STP) K⁻¹). The diffusion coefficient D (cm² s⁻¹) was calculated by $D = P/S$ using the solubility coefficient S obtained from direct gravimetric sorption measurements at 2 bar and 35 °C. The ideal selectivity of C₃H₆/C₃H₈ was obtained by the permeability ratio, $\alpha = PC_3H_6/PC_3H_8$.

Mixed-Gas Permeation Experiments. Pressure-dependent mixed-gas testing of the mixed-matrix membranes was performed with a C₃H₆/C₃H₈ (50:50 mol%) feed mixture from 2 to 7 bar at 35 °C. A stage-cut (permeate to feed flow rate) of 0.01 was used to avoid concentration polarization. The permeate composition was determined using a calibrated gas chromatograph (Agilent 3000A Micro GC) equipped with thermal conductivity detectors (TCD). The mixed-gas permeability of component i was determined via:

$$P_i = 10^{10} \frac{y_i V_d L}{x_i p_{up} ART} \frac{dp}{dt}$$

where y_i is the molar fraction of component i in the permeate and x_i is the molar fraction of component i in the feed. The mixed-gas permselectivity was calculated by:

$$\alpha_{C_3H_6/C_3H_8} = \frac{y_{C_3H_6}/y_{C_3H_8}}{x_{C_3H_6}/x_{C_3H_8}}$$

Gravimetric Sorption. C₃H₆ and C₃H₈ sorption data of the mixed-matrix membranes were obtained gravimetrically using an IGA-003 (Hiden Isochema) at 2 bar and 35 °C with samples of 30 ~ 50 mg. All samples were degassed for at least 24 h until constant weight was obtained before starting the sorption run. Each sorption run was repeated three times to ensure data reproducibility.

RESULTS AND DISCUSSION

Structural Properties. Commercially available ZIF-8 powder (Basolite Z1200, Sigma-Aldrich) was used for the preparation of PIM-6FDA-OH-based mixed-matrix membranes. The Brunauer-Emmett-Teller (BET) surface area of the Basolite Z1200, measured by nitrogen adsorption at -196 °C up to 1 bar (Figure S1), was 1406 m² g⁻¹. The particle size distribution of ZIF-8 was determined by light scattering of a suspension in ethanol using a Malvern Zetasizer ZS. Two main fractions were identified of which 96.5% contained an average particle size of 309 nm and 3.5% had an average size of 782 nm (Fig S2). TEM images of Basolite Z1200 particles are shown in Figure S3, which confirmed the particles size range of ZIF-8.

Mixed-matrix membranes were obtained with up to 65 wt% ZIF-8 loading in PIM-6FDA-OH by suspension casting as described in the experimental section (Figure 1a). All MMMs were heated to 250 °C for 24 h prior to mechanical and gas permeation testing to ensure complete removal of solvent either trapped in the polymer matrix or inside the ZIF-8 cages as confirmed by thermal gravimetric analysis (TGA). Excellent compatibility between ZIF-8 and the PIM-6FDA-OH polyimide matrix is clearly visible in the TEM cross-section images shown in Figure 1b and Figure S4. The ZIF-8 particles were well distributed in the PIM-6FDA-OH polyimide matrix up to 52 wt% loading; at higher ZIF-8 content of 65 wt%, agglomeration is clearly visible, but no interfacial gaps were detectable by TEM.

The mechanical properties of pure PIM-6FDA-OH polyimide and PIM-6FDA-OH/ZIF-8 mixed-matrix membranes are shown in Table S1. PIM-6FDA-OH showed Young's modulus, tensile strength and elongation at break of 0.51 GPa, 16.9 MPa and 4.6%, respectively. Young's modulus and tensile strength increased for MMMs containing up to 33 wt% ZIF-8, indicating good compatibility between PIM-6FDA-OH and ZIF-8. At higher ZIF-8 loadings, tensile strength decreased significantly, most likely due to agglomeration of ZIF-8 particles in the MMMs. The elongation at break of the MMMs decreased continuously with increasing fraction of ZIF-8, specifically at the highest loading of 65 wt%, demonstrating the mechanical stability limit of the MMMs of this study.

Figure 1. (a) Preparation of PIM-6FDA-OH/ZIF-8-based MMMs; (b) TEM images of PIM-6FDA-OH-based MMMs containing 33 and 65 wt% ZIF-8; (c) TGA of the MMMs in air; (d) XRD patterns of PIM-6FDA-OH, ZIF-8 and PIM-6FDA-OH/ZIF-8 MMMs.

Combustion of the MMMs in air by heating up to 800 °C using TGA (Figure 1c) generated ZnO residue, which was used to calculate the weight content of ZIF-8 in the MMMs.^{23,24} Only small deviations of the ZIF-8 content in the originally prepared casting suspensions were observed in the MMM films (Table S2). XRD patterns of PIM-6FDA-OH/ZIF-8 MMMs (Figure 1d) demonstrated that all characteristic diffraction peaks of pure ZIF-8 were retained in the MMMs, indicating that the crystal structure of the embedded ZIF-8 was not altered by the membrane preparation protocol and the subsequent heat treatment at 250 °C to completely dry and activate the MMMs. In general, interfacial

incompatibility of fillers dispersed in a continuous polymer matrix can be identified by a lower experimental MMM density relative to the calculated MMM values based on pure polymer and filler densities and their MMM weight fractions.^{22,31,32} Lower MMM density can result from either large macroscopic interfacial defects or increased polymer matrix chain spacing induced by filler nanoparticles.³² In both cases, MMM permeability is expected to increase combined with a reduction in permselectivity due to loss of the size-sieving diffusion selectivity. The experimental densities of the PIM-6FDA-OH/ZIF-8-based MMMs were essentially identical to the theoretical values calculated based on pure-component density values by: $\rho_{\text{MMM}} = \rho_{\text{P}}\Phi_{\text{P}} + \rho_{\text{ZIF-8}}\Phi_{\text{ZIF-8}}$, where ρ_{P} and $\rho_{\text{ZIF-8}}$ are pure-component densities of PIM-6FDA-OH ($\rho = 1.30 \text{ g cm}^{-3}$) and ZIF-8 ($\rho = 0.95 \text{ g cm}^{-3}$), respectively; Φ_{P} and $\Phi_{\text{ZIF-8}}$ are the volume fractions of polymer and ZIF-8 (Table S2, Figure S5). This result implies that the pure-component gas transport properties of ZIF-8 and PIM-6FDA-OH were preserved in the MMMs, which is of utmost importance for the estimation of gas permeabilities and selectivities of the MMMs by the Maxwell model (Table S3 and Table S4).^{7,18}

Interaction between ZIF-8 and PIM-6FDA-OH was qualitatively identified by FT-IR and XPS spectra, as shown in Figure 2. The C-N band of pure PIM-6FDA-OH and ZIF-8 are located at 1100 and 1146 cm^{-1} , respectively (Figure 2a). A continuous decrease in C-N band intensity and gradual shifts in peak positions from 1100 to 1105 cm^{-1} and 1137 to 1140 cm^{-1} for the MMMs at different ZIF-8 loadings compared to pure polymer PIM-6FDA-OH, all indicative of favorable materials interaction, were observed after normalization of the MMM FT-IR spectra with respect to the C-N band of pure ZIF-8.

Further evidence for the interaction between PIM-6FDA-OH and ZIF-8 was provided by comparing their XPS spectra with PIM-6FDA-OH/ZIF-8 MMMs (Figure S6). High resolution Zn 2p spectra of ZIF-8 show the binding energies for Zn 2p_{3/2} and Zn 2p_{1/2} core levels centered at 1021.3 and 1044.4 eV, respectively. However, clear shifts to higher energy values (about 0.6 eV) for both Zn 2p_{3/2} and Zn 2p_{1/2} core levels in the MMM sample containing 33 wt% ZIF-8 suggest the change of local chemical bonding environment around Zn resulting from the interaction between ZIF-8 and PIM-6FDA-OH (Figure 2b).

Moreover, high resolution XPS spectrum of N 1s (Figure 2c) in the MMM sample (centered at 400.3 eV) reveals a major shift of 1.7 eV to a higher energy value compared to pure ZIF-8 (398.6 eV, Figure 2c), and a minor shift (~ 0.2 eV) to a lower energy value compared to PIM-6FDA-OH (400.4 eV), indicating possible electron transfer from ZIF-8 to PIM-6FDA-OH in the MMM. Such effects are most likely induced by the $N\cdots H-O$ hydrogen bonding between the nitrogen moiety of the 2-methylimidazole in ZIF-8 and the hydroxyl groups in PIM-6FDA-OH (Figure 2d).

Figure 2. a) FT-IR spectra of PIM-6FDA-OH, ZIF-8 and PIM-6FDA-OH/ZIF-8 mixed-matrix membranes in the range of C-N bond from 1050 to 1175 cm^{-1} ; b) Zn 2p_{1/2} and 2p_{3/2} XPS spectra of ZIF-8 and PIM-6FDA-OH/ZIF-8 (33 wt%) mixed-matrix membrane; c) N 1s XPS spectra of PIM-6FDA-OH, ZIF-8 and PIM-6FDA-OH/ZIF-8 (33 wt%) mixed-matrix membrane; d) Possible mechanism for shifting of Zn- and N-signal of the MMM.

Gas Separation Performance. The C_3H_6 and C_3H_8 pure-gas permeation properties of the PIM-6FDA-OH/ZIF-8 mixed-matrix membranes measured at 2 bar and 35 °C are reported in Table S2; the intrinsic properties of pristine PIM-6FDA-OH²⁸ and pure ZIF-8³⁰ are listed for comparison. A propylene permeability of ~130 barrer and C_3H_6/C_3H_8 selectivity of ~100 were calculated from recently reported experimental permeation data of 2 μ m-thick pure ZIF-8 composite membranes.³⁰ Clearly, an increase in ZIF-8 loading resulted in significant enhancement in C_3H_6 permeability and C_3H_6/C_3H_8 selectivity in the PIM-6FDA-OH-based MMMs. The propylene permeability soared 11-fold from 3.5 barrer for the pristine PIM-6FDA-OH to 38 barrer for the MMM containing 65 wt% ZIF-8. Furthermore, an increase in pure-gas C_3H_6/C_3H_8 selectivity from 30 to 43 was observed, which is the highest selectivity of all MMMs reported to date for propylene/propane separation.

Propylene and propane sorption coefficients were determined by gravimetric sorption experiments at 2 bar and 35 °C and the diffusion coefficients were then obtained from the relationship $D = P/S$ (Table S2). The C_3H_6 solubility coefficient increased from 0.22 for PIM-6FDA-OH to 0.52 $\text{cm}^3(\text{STP}) \text{cm}^{-3} \text{cmHg}^{-1}$ for the MMM containing 65 wt% ZIF-8 combined with an even more significant ~4-fold increase in the C_3H_6 diffusion coefficient from 0.16×10^{-8} to $0.73 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$. As expected from their pure-gas solubility properties, incorporation of ZIF-8 to PIM-6FDA-OH had essentially no effect on the C_3H_6/C_3H_8 solubility selectivity of ~1.1. Hence, the boost in C_3H_6/C_3H_8 permselectivity of the MMMs can be attributed almost entirely to enhanced C_3H_6/C_3H_8 diffusion selectivity due to the strong molecular sieving effect of the ultramicroporous ZIF-8 filler (Table S2).

The pure-gas performance of the PIM-6FDA-OH/ZIF-8 mixed-matrix membranes is compared to the propylene/propane trade-off curve in Figure 3a. Clearly, their performance is located significantly above the upper bound line and higher than the calculated *theoretical* performance of hypothetical mixed-matrix membranes based on polymer matrices located on the upper bound line with 30, 40, and 50 wt% loading of ZIF-8 with $PC_3H_6 = 130$ barrer and $\alpha_{C_3H_6/C_3H_8} = 100$ (Table S3) using the Maxwell equation (Data and calculations are included in the Supporting Information, Table S3).

Figure 3 a) Pure-gas C_3H_6 permeability and C_3H_6/C_3H_8 selectivity for PIM-6FDA-OH/ZIF-8 membranes with different ZIF-8 loadings and the theoretical performance of mixed-matrix membranes with 30 vol% (red), 40 vol% (blue) and 50 vol% (green) ZIF-8 loading dispersed in polymers located on the 2003 polymer upper bound line²⁹; b) Pure- and mixed-gas C_3H_6/C_3H_8 separation properties of PIM-6FDA-OH/ZIF-8 and 6FDA-DAM/ZIF-8²³ mixed-matrix membranes at 2 bar; c) Pressure dependence of C_3H_6 permeability of PIM-6FDA-OH and MMMs containing 33 and 65 wt% ZIF-8; d) Pressure dependence of C_3H_6/C_3H_8 selectivity of PIM-6FDA-OH and MMMs containing 33 and 65 wt% ZIF-8; e) Pressure dependence of C_3H_6 permeability of PIM-6FDA-OH/ZIF-8 MMMs and 6FDA-DAM-based MMMs

containing 28.7 and 48 wt% ZIF-8; f) Pressure dependence of C_3H_6/C_3H_8 selectivity of PIM-6FDA-OH/ZIF-8 MMMs and 6FDA-DAM-based MMMs containing 28.7 and 48 wt% ZIF-8.

In their seminal work, Zhang and Koros reported excellent propylene/propane separation performance of ZIF-8-based MMMs using a non-hydroxyl-functionalized 6FDA-DAM (1,3,5-trimethyldiaminobenzene) polyimide as the polymer matrix with the maximum loading of 48 wt%.²³ Based on pure-gas experiments the 6FDA-DAM (48 wt%) MMM displayed a propylene permeability of 56.2 barrer with C_3H_6/C_3H_8 selectivity of 31. In a similar approach using a 9:1 copolymer matrix of 6FDA-TMPD (2,3,5,6-tetramethyl-p-phenylenediamine) and 6FDA-DABA (3,5-diaminobenzoic acid) containing 41.9 wt% ZIF-8, Askari and Chung reported pure-gas MMM properties of $PC_3H_6 = 47.3$ barrer and C_3H_6/C_3H_8 selectivity of 27.4 measured at 3.5 bar and 35 °C.²⁴ Because of its higher intrinsic C_3H_6/C_3H_8 selectivity (30 vs. 12.4) and higher ZIF-8 loading capacity (65 vs 48 wt.%), PIM-6FDA-OH-based MMMs exhibited better overall pure-gas performance than the 6FDA-DAM-derived MMM analogues (Figure 3b). Mixed-gas permeation properties measured at 4 bar pressure and 35 °C with a 50:50 propylene/propane feed showed a drop in propylene permeability and C_3H_6/C_3H_8 selectivity for both membrane types (open symbols, Figure 3b), most likely due to competitive sorption effects.^{10,28,33} Nevertheless, the highest loading PIM-6FDA-OH/ZIF-8 (65 wt%) membrane maintained excellent mixed-gas performance with a propylene permeability of 30 barrer and C_3H_6/C_3H_8 selectivity of ~31.

Previous work showed that the C_3H_6/C_3H_8 selectivity of pure ZIF-8 membranes was severely pressure dependent and declined rapidly with increasing pressure when tested under mixed-gas conditions (Figure S7) due to a decrease in propylene permeability and, more importantly, a significant increase in propane permeability.^{30,34} This result indicated that pure ZIF-8 is susceptible to plasticization-like effects possibly due to stretching of its highly size-selective aperture by sorption of large, condensable hydrocarbons.^{30,34} The mixed-gas propylene permeability (Figure 3c) and C_3H_6/C_3H_8 selectivity (Figure 3d) pressure dependence was evaluated up to 7 bar for the pristine PIM-6FDA-OH polyimide and the MMMs containing 33 and 65 wt% ZIF-8, respectively. Interestingly, more stable propylene/propane mixed-gas

performance was observed for the MMMs. The PIM-6FDA-OH/ZIF-8 MMMs demonstrated outstanding plasticization resistance with only ~6-8% decrease in mixed-gas selectivity by increasing the feed pressure from 2 to 7 bar (Figure 3d). Even at a feed pressure of 7 bar ($p/p_{\text{sat}} \sim 0.5$) membranes with ZIF-8 loading of 33 and 65 wt% exhibited mixed-gas selectivity of 21.1 and 28.7, respectively (Table S5). On the other hand, the mixed-gas $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity of the pristine PIM-6FDA-OH membrane decreased by 40% from 21 to 12.7 by raising the feed pressure from 2 to 7 bar (Figure 3d). The more significant decrease in mixed-gas $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity of the pure PIM-6FDA-OH membrane could have resulted from more significant effects of polymer plasticization on gas transport properties as compared to the OH-functionalized ZIF-8-based MMMs. Over the same pressure range, the non-functionalized 6FDA-DAM/ZIF-8 mixed-matrix membranes also displayed a larger relative decline in permeability and selectivity than the PIM-6FDA-OH/ZIF-8 membranes (Figure 3e and Figure 3f). Our results suggest that the strong molecular interaction of the hydroxyl-functionalized polyimide and nitrogen-containing ZIF-8 by N $\cdots$ O-H hydrogen bonding stabilized the structural flexibility of the individual components in the MMMs. Consequently, our approach provides a new platform for development of highly plasticization-resistant mixed-matrix membranes including imidazolate-derived metal-organic frameworks other than ZIF-8.

CONCLUSIONS

The growing need for more energy-efficient gas separations has dramatically increased interest using membrane systems. In this work, a series of high-performance, plasticization-resistant mixed-matrix membranes for propylene/propane separation was successfully developed based on ultramicroporous ZIF-8 and a dihydroxyl-functionalized polyimide (PIM-6FDA-OH). Hitherto, unmatched mixed-gas propylene/propane performance was demonstrated for MMMs containing up to 65 wt% ZIF-8 under challenging high-pressure feed conditions. Strong interactions between the OH-functionalized polyimide and the N-containing imidazolate framework by hydrogen bonding were detected by FTIR and XPS spectra and resulted in formation of defect-free, high-performance MMMs. Our approach provides

therefore a promising route for investigation of MMMs based on alternative OH-functionalized polymers and tailor-made ZIFs for other energy-intensive separations, such as ethylene/ethane and butane isomer purification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Mechanical properties, ZIF-8 nitrogen adsorption isotherm, ZIF-8 particles size distribution, TEM, XPS, Maxwell model predictions, experimental gas transport data.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ingo.pinnau@kaust.edu.sa (I.P.).

ORCID

Ingo Pinnau: 0000-0003-3040-9088

Notes

The authors declare no competing financial interest.

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