Title

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Journal

Advanced Materials, 37(45)

ISSN

0935-9648

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Publication Date

2025-11-01

DOI

10.1002/adma.202509150

Generalizable Porous Aromatic Framework-Included Polymer Membranes for Diffusion-Enhanced Gas Separations

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Funding: This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Separation Science in the Chemical Sciences, Geosciences, and Biosciences Division, under Award Number DE-SC0019992. The U.S. National Science Foundation is thanked for providing graduate fellowship support for A.A.U., K.E.E., and E.O.V, and the Philomathia Foundation is thanked for providing additional graduate fellowship support for A.A.U.

Keywords: gas separations, porous polymers, mixed-matrix membranes, permeability

Industrial separation processes account for 10–15% of global energy consumption. Membrane-based processes are less energy intensive than traditional gas separation technologies; however, enhanced material separation performance and stability for numerous gas mixtures are needed for widespread industrial adoption. This work presents a generalizable strategy for preparing mixed-matrix gas separation membranes exceeding the performance upper bounds of existing polymer membranes for a wide variety of industrially relevant gas mixtures. By incorporating robust porous aromatic framework (PAF) filler particles into dense commercial polymer matrices (6FDA-DAM, Matrimid®, and cellulose acetate), gas diffusivity and solubility can be enhanced. For diverse industrially relevant gas mixtures (e.g., CO_2/N_2, O_2/N_2, He/CH_4, H_2/N_2, and C_2H_4/C_2H_6), the resulting composite membranes exhibit enhanced gas permeabilities—by as much as 520%—and largely unchanged selectivities even after 6 years of aging under simulated flue gas conditions. These improvements arise from the ultrahigh porosity, exceptionally high permeability, excellent chemical compatibility, and unique physicochemical properties of the embedded PAF particles. In addition, functionalizing the PAFs with polyamines enables composite membranes that achieve among the highest reported performances against plasticization, a common obstacle in the commercialization of gas separation membranes. Significantly, the PAF-1 particles are readily dispersible in a range of common membrane casting solvents, suggesting their broader utility as a filler for the design of high-performance membranes for a variety of industrially relevant gas separations.

1. Introduction

Chemical separations account for as much as 45–55% of U.S. industrial energy consumption and are a major contributor to global greenhouse gas emissions.[1] As such, the wide-spread adoption of energy-efficient alternatives to traditional separation processes (e.g., distillation) is urgently needed to advance a more sustainable energy future.[1, 2] In the context of gas separations, polymer membrane-based technologies are a promising alternative to thermal or adsorption-based separation methods and have been in use on small scales commercially for several decades.[1, 3] Membrane technologies have been shown to be associated with lower operating costs than distillation methods and can be operated with far greater energy efficiencies (up to 10 times greater).[1, 3] Further, membranes can be continuously operated, in contrast to many adsorptive separation processes. However, the widespread implementation of membranes has been limited by the well-known selectivity-permeability trade-off.[3] Transport of gases in glassy polymers is governed by a solution-diffusion mechanism, with selectivity generally being determined by differences in diffusivities of permeating species through the membrane.[4] Diffusivities can be dramatically altered by disrupting polymer chain packing through the addition of bulky side groups or stiff backbones, and this approach has led to the creation of hundreds of new polymers with high permeabilities resulting from increases in statistical free volume.[5] However, over time the permeability is drastically reduced as a result of polymer chain dynamics that decrease the non-equilibrium free volume, a phenomenon known as aging.[6] Additionally, these polymers typically still suffer from a selectivity-permeability trade-off.

Mixed-matrix membranes (MMM)—which comprise nanoparticle fillers such as carbon molecular sieves, metal–organic frameworks, or zeolites dispersed in a polymer matrix—have been shown to exhibit improved separation performances relative to traditional polymer membranes as a result of size-sieving or adsorption solubility enhancements.[2, 7–10] In some cases, these composites have also been shown to exhibit improved chemical and mechanical stability[10, 11] Despite the potential of the mixed-matrix approach, filler/polymer incompatibility and poor nanoparticle dispersion within the membranes are common challenges limiting the performance of many of the materials studied to date.[12, 13] Furthermore, most examples utilize a filler that can preferentially interact with only one adsorbate, whereas a filler that is generalizable to many different separations could dramatically advance MMM technology.[2, 9, 10, 14]

In an effort to address these issues, we chose to investigate the use of porous aromatic frameworks (PAFs) as fillers in dense polymer membranes. These highly porous network

polymers are made up of organic nodes and aromatic linkers connected via strong covalent linkages, which afford exceptional physical and chemical stability.[10] The PAFs typically feature diamondoid-like structures with static voids that could potentially support high gas diffusion rates in composite membranes. Furthermore, as a result of their organic makeup, we expected that PAFs might exhibit superior polymer compatibility relative to rigid, inorganic fillers (e.g., zeolites), which can cause composite membrane embrittlement and reduce mechanical stability.[15] Indeed, the use of PAFs as fillers in MMMs has recently been shown to diminish polymer aging while improving performance in gas separation,[16–20] pervaporation,[21] and water purification[15] applications.

Here, we show that the prototypical material PAF-1 can be incorporated into the glassy polymers 6FDA-DAM, Matrimid®, and cellulose acetate to generate dense composite membranes that exhibit increased free volumes, owing to the ultrahigh porosity of the framework filler. Gas diffusivities are enhanced in these composites as a result, and polymer selectivities are simultaneously retained owing to the excellent chemical compatibility between the PAF and polymer matrix. Furthermore, we identify unique physiochemical properties of PAF-1 that suggest its promise as a universal filler in the design of MMMs for various gas separations. More broadly, our results reveal that the utilization of PAFs with high permanent porosity allows tuning of gas diffusivity in composite membranes without the need for exotic polymers with highly rigid backbones or bulky side chains.

2. Results and Discussion

2.1 Fabrication of 6FDA-DAM-Based PAF-1 Membranes

Composite membranes were initially fabricated with 10 and 20 wt% PAF-1 (**Figure S1**) in 6FDA-DAM (**Figure S2**; 6FDA = 4,4'-(hexafluoroisopropylidene)diphthalic anhydride; DAM = 2,4,6-trimethyl-1,3-phenylenediamine), a polymer known to exhibit excellent selectivities and permeabilities approaching the theoretical upper bounds for pure polymer membranes for a variety of gas pairs.[22] Critical to our fabrication process is a "priming" step. This step involves the slow addition of a small portion of polymer solution to a solution of dispersed PAF nanoparticles while stirring, before the addition of the remaining polymer solution (see the SI for details). This initial step coats the PAF particles with a thin layer of polymer and supports the formation of defect-free membranes (see below), which are imperative for high-selectivity gas transport.[6, 20]

Helium pycnometry and nitrogen gas adsorption measurements revealed that the filler volume percentage of the 20 wt% PAF-1 in 6FDA-DAM membranes is approximately 50%

(**Table S1**). This high volume-based loading results from the low measured density of 0.33 g/mL of the highly porous PAF-1 particles (Brunauer-Emmett-Teller (BET) surface area of 4640 m^2/g; **Figures S3** and **S4**). The measured density notably agrees closely with predicted densities (0.31–0.34 g/mL) for models of the expected *dia* structures proposed for amorphous PAF-1.[23–25] Both the PAF-1 particles and 6FDA-DAM exhibit high thermal stability (decomposition temperatures >500 °C), which is maintained in the composite membranes (**Figure S8**).

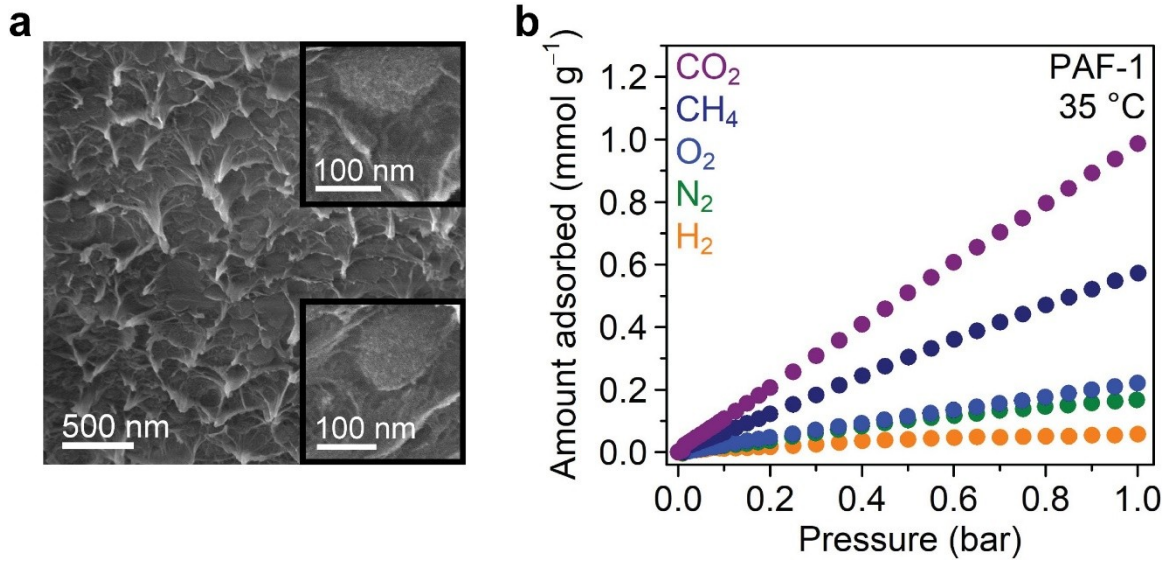

Figure 1. (a) Cross-sectional SEM images (expanded views in insets) of a 20 wt% PAF-1 in 6FDA-DAM membrane indicate high dispersity and strong compatibility between the organic PAFs and polymer. (b) Gas adsorption isotherms at 35 °C for bulk PAF-1 powder.

A comparison of cross-sectional scanning electron microscopy (SEM) images of the neat polymer and 6FDA-DAM loaded with 10 and 20 wt% PAF-1 revealed high volume-based loadings of PAF-1 in the composites and good PAF dispersibility (**Figures 1a** and **S9–S10**). Consistent with our prior work, the imaged PAF-1 particles typically exhibit particle size diameters between 100 and 200 nm (**Figure S7**).[15] Importantly, expanded views of the SEM images revealed strong interactions at the interface between the PAF particles and membrane polymer matrix without apparent defects, agglomerations, or sieve-in-a-cage morphologies (**Figure 1a**, insets). Consistent with this evidence of high PAF/polymer compatibility, the glass transition temperatures (T_g) of the PAF-loaded membranes were several degrees higher than for the pure polymer membranes (**Table S2**). We attribute the high uniformity of the PAF composite membranes and excellent PAF/polymer compatibility to favorable π–π stacking and van der Waals interactions between the framework and polymer membrane, as well as polymer filling within the PAF mesopores.[20]

2.2. Gas Permeation Testing

We next investigated the gas transport properties of six gases—H_2, He, CH_4, N_2, O_2, CO_2—through the neat and composite membranes using single-component permeation measurements. These gases were chosen given their ubiquity in industrial gas separations and diverse chemical properties, kinetic diameters, and condensabilities (**Table S3**).[3, 26–28] Of note, bulk PAF-1 exhibits linear adsorption profiles for all six of these gases (**Figure 1b**), indicative of physisorptive uptake and a low affinity for each adsorbate.[29] Considering this, we postulated that the highly porous PAF-1 filler would facilitate non-selective but high-diffusivity gas transport pathways not available in conventional neat polymer membranes, therefore giving rise to composite membranes exhibiting enhanced gas permeabilities. Indeed, in the 20 wt% PAF-1 membrane, the permeabilities of all six gases were found to be ~500% greater than in the neat 6FDA-DAM membrane (**Figure 2** and **Table S4**). Comparative analysis of the 20 wt% PAF-1 membrane against previously reported membranes demonstrates a remarkable increase in permeability without sacrificing selectivity (**Table S6**), highlighting excellent compatibility between the filler and polymer phase, a critical factor in MMM development.

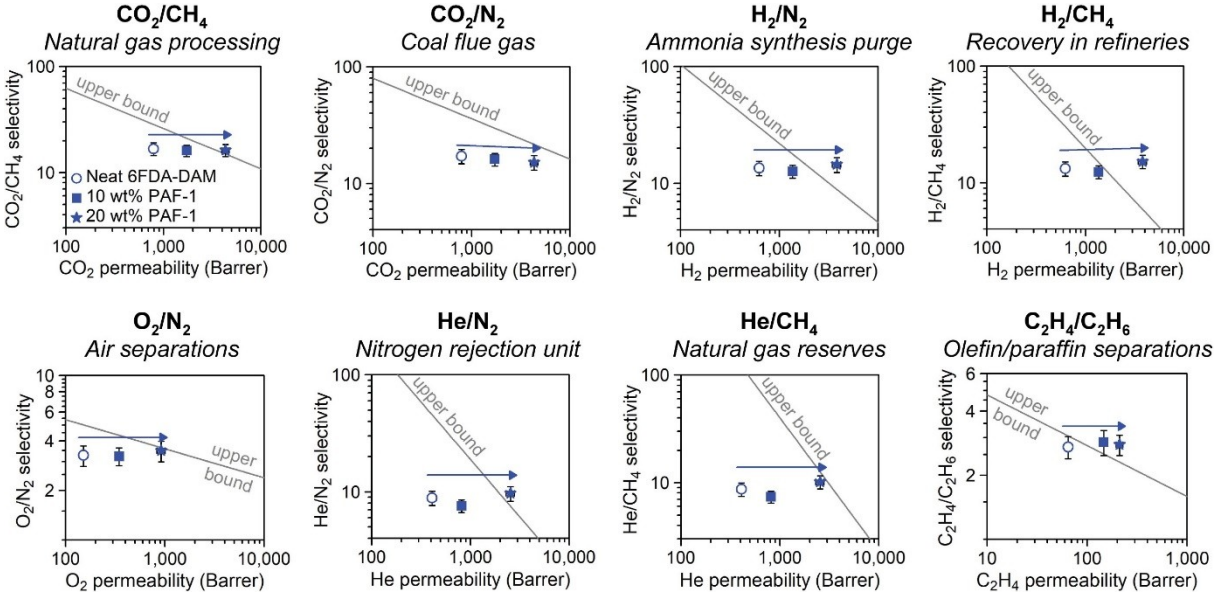

Figure 2. Performances of 6FDA-DAM-based PAF-1 membranes relative to the polymer upper bounds (gray lines) for various gas pairs: CO_2/CH_4 (natural gas processing[24, 25]), CO_2/N_2 (carbon capture from power plant flue gas[26, 27]), H_2/CH_4 (off-gas processing in refineries[28, 29]), H_2/N_2 (hydrogen purification from ammonia synthesis purge gas[28]), He/CH_4 (purification of natural gas reserves[22]), He/N_2 (purification of off-gas from the nitrogen rejection unit in natural gas processing plants[22]), O_2/N_2 (air separations[28]), and C_2H_4/C_2H_6 (olefin purification from hydrocarbon mixtures[21]). Open circles represent the neat polymer membrane without PAF-1; closed squares represent 10 wt% PAF-1 membranes; closed stars represent 20 wt% PAF-1 membranes. Permeabilities and selectivities were averaged over at least two independent

membranes and measured by single-component tests at 35 °C and 2 bar feed pressure. Error bars correspond to propagation of error from uncertainty in the film thickness and area.

The gas permeation selectivity can be computed as the ratio of the permeabilities of each gas.[3] We calculated the gas permeation selectivities of the neat and composite membranes for eight gas pairs highly targeted in industrial gas separations (**Table S5**).[11, 28, 30–34] The measured permeabilities and selectivities of the fabricated membranes for each gas pair are plotted in **Figure 2**, along with the predicted upper bound performances established for the pure polymer membranes.[3] In each of the plots, there is a favorable right horizontal shift corresponding to an increase in permeability with increasing PAF-1 loading, such that the performance of the composite approaches or even surpasses the pure polymer upper bounds. The selectivity in all cases, which should be dictated by the polymer matrix, remains relatively unchanged. We also tested the membranes for the separation of ethylene and ethane, as olefin/paraffin separations remain among the most challenging yet sought-after membrane separations.[1, 26] In these permeation tests, the 10 and 20 wt% PAF-1 membranes again exhibited performances that surpassed the upper bound for this gas pair, [26] as a result of enhanced gas permeability and stable selectivities. For all gases, the membrane performance also remained approximately constant at all pressures tested (**Figures S11** and **S12**). Similar trends were maintained when testing under mixed gas feed conditions, using equimolar CO_2/N_2 feed mixtures as a representative mixture (**Figures S13–S15**).

2.3. Diffusivity and Solubility Measurements

To better elucidate the gas transport mechanisms of the composite membranes, we collected gas adsorption isotherms for the membrane samples (**Figure S16**) and calculated gas solubilities based on the membrane densities (**Table S1**) and quantities of gas adsorbed at 1 bar. We then applied the solution-diffusion model[4] to determine diffusivities, which were calculated as the ratio of the measured gas permeability to solubility. The solubility of each gas studied remained relatively constant in the membranes regardless of PAF-1 loading, while the gas diffusivity dramatically increased with increased PAF-1 loading (**Figure 3**). These trends confirm that the enhanced gas permeabilities in the composite membranes are a consequence of enhanced diffusive gas transport through the PAF-1 pores. These static pores are large enough (~1.5 nm diameter, **Figures S5** and **S6**) to easily accommodate gas molecules and provide transport pathways through the membranes for rapid Knudsen diffusion. Importantly, the gas adsorption isotherms also revealed that approximately all PAFs embedded in the membranes

remain accessible for gas transport. Indeed, the measured gas uptake in the composite membranes matched that expected from the weighted-average uptake between the neat 6FDA-DAM membrane and bulk PAF-1 (**Figure S17)**.

We further modeled gas transport in the PAF-1-based MMMs using a Maxwell equation that assumes that the fillers have extremely high permeability within the composite membranes, representing the scenario of maximum achievable permeability by a composite membrane (see Experimental Section). This model also assumes that the fillers are spherical, non-interacting, rigid, and uniformly dispersed in the polymer matrix with negligible sorbate accumulation or interfacial defects.[35] These assumptions uniquely align closely with the properties of the PAF-1 fillers, including the weak physisorption behavior observed for PAF-1 (**Figure 1b**) and ultra-permeable transport channels expected in the highly porous fillers. Predicted permeability values using this Maxwell model aligned remarkably closely with measured permeability values of the MMMs across each gas tested, indicating that these favorable properties and exceptionally high-permeability channels for all gas pairs are present in the composite membranes (**Figure S18**).

2.4. Synthesis and Characterization of Matrimid® 5218- and Cellulose Acetate-Based PAF-1 Membranes

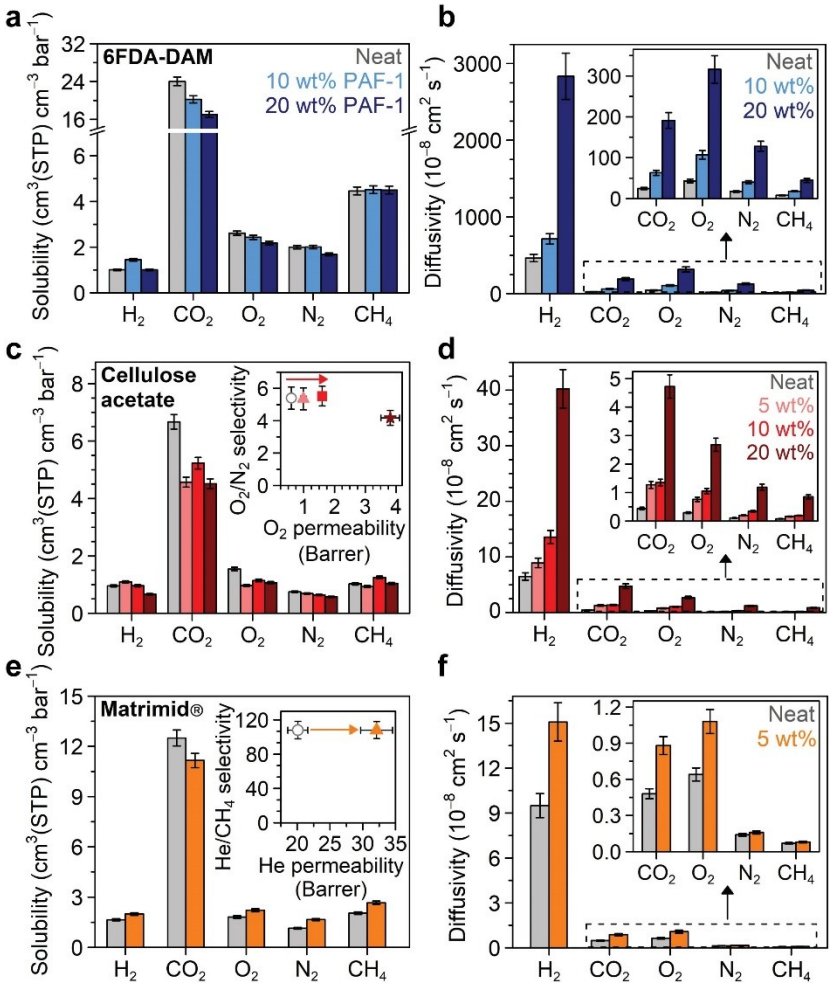

Figure 3. Gas solubilities (left) and diffusivities (right) measured at 1 bar and 35 °C in (a, b) 6FDA-DAM, (c, d) cellulose acetate, and (e, f) Matrimid® membranes with varied PAF loadings. Solubilities were measured from equilibrium adsorption isotherms (see SI), while diffusivities were determined using the solution-diffusion model. (c, inset) O_2/N_2 separation performances of the cellulose acetate membranes, based on single-gas permeation tests averaged over at least two independent membranes at 35 °C and 2 bar feed pressure. (e, inset) He/CH_4 separation performances of the Matrimid® membranes, based on single-gas permeation tests averaged over at least two independent membranes at 35 °C and 2 bar feed pressure. Error bars correspond to propagation of error from uncertainty in the gas isotherm measurements and film thickness, area, and density.

To assess the broader utility of PAF-1 as a porous filler capable of increasing membrane permeability without affecting selectivity, we synthesized composite membranes using Matrimid® 5218 or cellulose acetate as the polymer matrix (**Figure S2**). These polymers were chosen due to their diversity in chemical structures (for example, cellulose acetate does not contain aromatic groups), higher selectivities for various gas pairs relative to 6FDA-DAM, and prevalent use in industrial membrane separations.[11, 27, 36] The resulting composite membranes exhibited favorable trends similar to those observed for the 6FDA-DAM-based composite membranes: the permeability for all six gases dramatically increased with PAF loading—nearly

doubling upon just 5 wt% PAF-1 loading—while the selectivity for the same eight gas pairs remained largely constant (**Figures S21, S22, 3c,** and **3e** and **Tables S4** and **S5**). This performance was maintained at all feed pressures tested (**Figures S25–S28**). However, we note that membranes prepared with 20 wt% PAF-1 in cellulose acetate exhibited decreased selectivity for every gas pair, along with a dramatic increase in the permeability of each gas (**Figures 3c** and **S27**). This behavior is indicative of the formation of PAF-1 percolation networks spanning across these densely loaded membranes.[37]

To confirm that the performance enhancements achieved with the Matrimid® and cellulose acetate-derived composites arise from high-diffusivity transport pathways created by the embedded PAF-1 particles, we again collected gas adsorption isotherms for each membrane (**Figures S23** and **S24**). Solubility and diffusivity analyses using the solution-diffusion model[4] revealed that the solubility of each gas remained approximately constant regardless of PAF-1 loading (**Figures 3c** and **e**), while the diffusivity of each gas dramatically increased with increasing PAF-1 loading (**Figure 3d** and **f**). The relative diffusivity increases also mirror the relative permeability increases observed in the membranes with increased PAF-1 loading.

2.5. Solvent Dispersion of PAF-1 Particles

Of note, during composite membrane fabrication, we found that PAF-1 can be successfully dispersed in eight different common membrane casting solvents with diverse boiling points, polarities, and dielectric constants, namely chloroform, toluene, tetrahydrofuran, dichloromethane, acetone, *N*-methyl-2-pyrrolidone, ethanol, and water (**Table S7**). In particular, dynamic light scattering measurements (**Figure 4a**), particle SEM images (**Figure S7**), and Tyndall scattering (**Figure S29**) revealed that PAF-1 remains well dispersed in each solvent as 100-200-nm particles following the mixing and sonication steps used for membrane fabrication. Additionally, no PAF-1 agglomerates were observed in any of the particle size distributions. These results suggest that PAFs may potentially be used as fillers for an even larger selection of dense membrane materials, which often require specific casting solvents according to their solubility, the chosen casting process, and desired film properties.[38, 39]

We attribute the excellent PAF-1 dispersibility across a range of solvents to the solvent-accessible nature of the framework pores and corresponding attractive interactions between bulk solvent and pore-filled solvent. Indeed, differential scanning calorimetry experiments revealed that PAF-1 samples soaked with water exhibit a melting point peak around −24 °C, consistent with melting point depressions observed for water nanoconfined in other materials with pore sizes similar to those of PAF-1 (**Figure 4b**).[40–42] Proton nuclear magnetic resonance

(NMR) spectroscopy was used to further corroborate solvent accessibility within the PAF pores. The ^{1}H spectrum of a sample of PAF-1 soaked with water features a broad signal with a noticeable shoulder, and this signal could be deconvoluted into two peaks at 4.33 and 4.26 ppm (**Figure S30**), which we assign to water confined in the framework pores and water residing between PAF particles, respectively (see the SI and **Figure S31** for additional details). Interestingly, this pore filling with water occurs despite the high hydrophobicity of PAF-1, and we are currently exploring other potential applications that might exploit this unusual property.

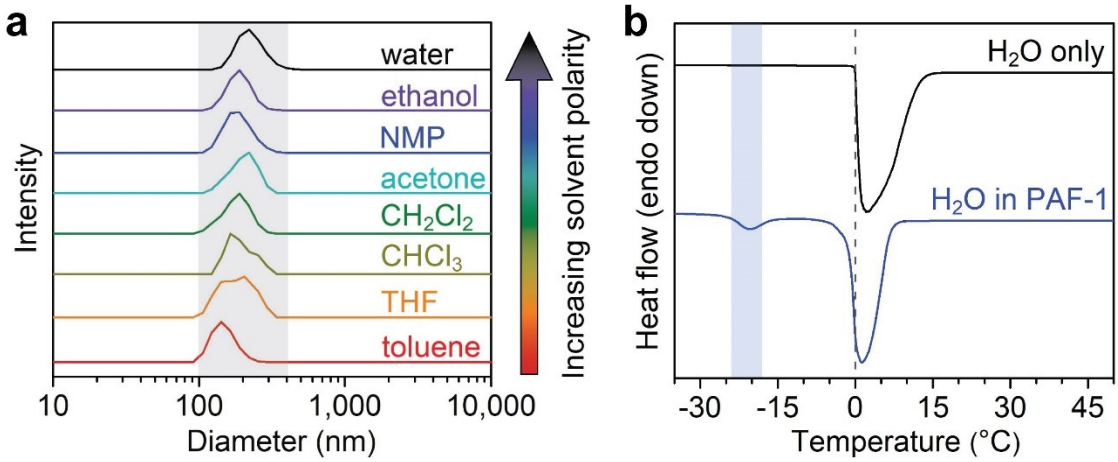

Figure 4. (a) Number-averaged particle size distributions of PAF-1 dispersed in solvents with varied boiling points and polarities, as measured by dynamic light scattering. The data were compiled from at least three independent measurements. (b) Melting point determination via differential scanning calorimetry of bulk water (black) and water-loaded PAF-1 (blue). The same profiles were obtained over five replicate temperature scans. The expected melting onset of bulk water at 0 °C (gray dotted line) is included for reference. The large peak around 0 °C in the water-loaded PAF-1 spectrum corresponds to bulk water between PAF-1 particles in the sample.

2.6. Plasticization Resistance, Anti-Aging, and Functionalized PAF-1 Fillers

We also functionalized the PAF-1 fillers with CO_2-selective, hydrogen-bonding polyamines (ethylenediamine (EDA) and diethylenetriamine (DETA)), to assess how gas transport would be impacted upon adding such stabilization, gas selectivity, and functional group effects. Single-gas permeation measurements revealed that the polyamine-functionalized PAF-1 composite membranes exhibited trends similar to those of the unfunctionalized PAF-1 membranes: retained gas selectivity and elevated gas permeabilities (by 54% and 28% upon 20 wt% PAF-1-EDA and PAF-1-DETA incorporation, respectively; **Figures 5a** and **S33**). These lower permeability enhancements relative to 20 wt% PAF-1 are attributed to the decrease in PAF-1 porosity upon functionalization, in agreement with BET surface area trends (4640, 930, and 430 m^2/g for PAF-1, PAF-1-EDA, and PAF-1-DETA, respectively). The high CO_2

capacities and selectivities of PAF-1-EDA and PAF-1-DETA (**Figures S32, S36,** and **S37**) suggested that their incorporation would increase CO_2/N_2 and CO_2/CH_4 selectivities, effects not observed. In view of the high recent interest in using polyamines to promote CO_2 selectivity in membranes,[43, 44] we investigated the CO_2–polyamine thermodynamics in the PAFs to better understand the gas transport mechanisms. Isosteric heats of adsorption ($-Q_{st}$) were calculated using the Clausius–Clapeyron relationship, based on single-component CO_2 adsorption isotherms fitted using dual-site Langmuir–Freundlich models (**Figures S37** and **S38** and **Table S9**). The $-Q_{st}$ values calculated for PAF-1-EDA (87 kJ/mol) and PAF-1-DETA (74 kJ/mol) fall within the 60–100 kJ/mol range associated with CO_2 chemisorption,[45] indicating that a significant amount of energy would be required to desorb the CO_2. Given that gas permeation is a continuous process, we hypothesize that the polyamines strongly immobilize the first CO_2 molecules that permeate across the membranes. This immobilization prevents additional CO_2 molecules from replacing the bound CO_2 and favorably interacting with the polyamines, thereby not significantly impacting CO_2 permeation during steady-state conditions after all polyamine groups in the membranes are bound to CO_2.

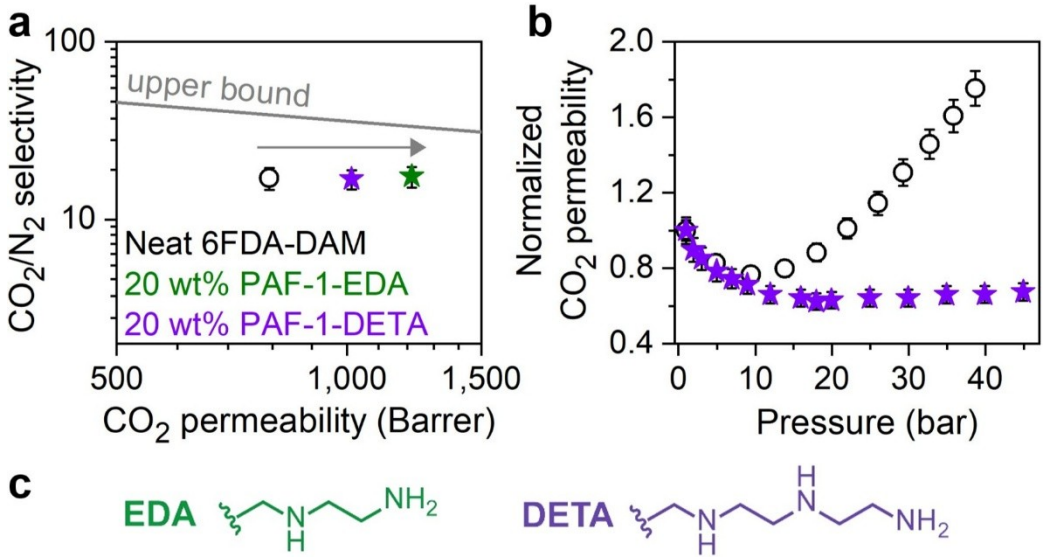

Figure 5. (a) Gas permeability increases with retained CO_2/N_2 selectivity and (b) dramatic enhancements in plasticization resistance are obtained upon appending (c) ethylenediamine (EDA) and diethylenetriamine (DETA) hydrogen-bonding moieties onto the PAF-1 pore walls. Permeabilities were averaged over at least two independent membranes and measured by single-component tests at 35 °C. Permeabilities shown in (a) were collected using a 2-bar feed pressure. Permeabilities shown in (b) are normalized to the permeability measured at 1 bar. Error bars correspond to propagation of error from uncertainty in the film thickness and area.

Plasticization, or polymer swelling at high pressures of polarizable gases, leads to selectivity loss and remains a major hurdle in the commercialization of membranes for many applications (e.g., natural gas processing).[10, 11, 27, 30, 46] We performed high-pressure CO_2 permeation measurements on the polyamine-appended PAF membranes (**Figures 5b** and **S35**) to assess potential plasticization resistance arising from hydrogen-bonding interactions between the polyamines and membrane polymers. The plasticization pressure, marked as the pressure at which permeability begins to increase due to swelling, for neat 6FDA-DAM was found to be ~10 bar. In contrast, the 20 wt% PAF-1-DETA membranes did not exhibit a plasticization pressure outside of measurement error even up to 45 bar of testing, achieving one of the highest reported anti-plasticization performances among mixed-matrix membranes (**Table S10**). Likewise, the neat 6FDA-DAM membranes readily redissolved when submerged in $CHCl_3$ casting solvent, as expected, whereas the robust 20 wt% PAF-1-DETA membranes remained insoluble, with only 10% mass loss observed after submersion in chloroform for 24 h (**Table S11**). These findings suggest that the amine groups in the PAFs provide stabilizing cross-linking interactions to the polymer chains, offering impressive stabilization capabilities even under high gas pressures and plasticizing conditions.

Aging, or the collapse of free volume transport pathways over time that deleteriously results in permeability loss, similarly remains a significant challenge in the commercialization of membranes, especially high-permeability and glassy polymers.[16, 20, 47] As a dense, glassy polymer, neat 6FDA-DAM membranes exhibited aging with a nearly 20% loss in CO_2 permeability after slightly over 2 years of aging. In comparison, highly permeable composite membranes containing 20 wt% PAF-1 or 20 wt% PAF-1-EDA in 6FDA-DAM exhibited dramatic anti-aging improvements, showing only 2% and 0.7% losses in CO_2 permeability after over 4 years and nearly 2 years of aging, respectively (**Figure S39**). Similar to anti-plasticization enhancements, the incorporation of PAF fillers offers a simple strategy to stabilize dense membrane polymers and drastically reduce unfavorable aging effects.

2.7. Industrial Applicability of PAF MMMs

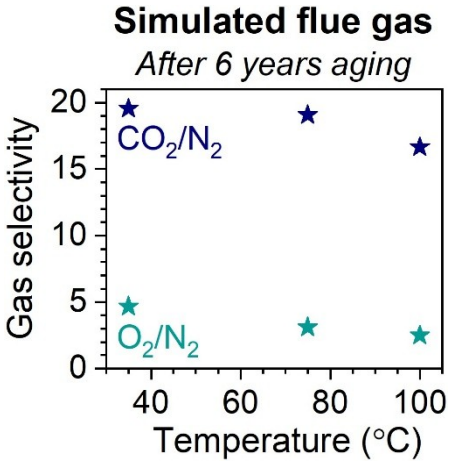

Figure 6. Gas separation performances are retained for 20 wt% PAF-1 in 6FDA-DAM membranes as a representative PAF-MMM when tested under simulated flue gas mixtures (81:15:4 N_2:CO_2:O_2; total pressure: 6.7 bars) at varied temperatures after 6 years of aging.

The composite nature of MMMs combines advantages from their constituent phases, making them highly attractive for industrial gas separation membranes. The polymeric phase enables scalable fabrication via common commercial-scale methods such as blade/rod or slot-die casting, while the filler enhances permeability and selectivity and, in the case of PAFs, industrially practical anti-plasticization, anti-aging, and chemical stability enhancements. Metal–organic frameworks, commonly used as fillers, often suffer degradation when exposed to open air and/or humid conditions due to their relatively weak coordination bonds, suggesting that the resulting MMMs would have a limited shelf life.[48] In contrast, the covalent, organic structures of PAFs also open new opportunities for MMMs to maintain robustness in humid conditions, improve compatibility with the organic polymer phase and various casting solvents, and potentially lower production costs compared to metal-containing fillers such as metal–organic frameworks. We also note that our membrane "priming" step is readily completed prior to solution casting, enabling this step to be likewise adopted prior to casting in roll-to-roll manufacturing systems.

To demonstrate the superior durability and industrial applicability of PAF-based membranes, we evaluated the transport performance of a six-year-old 20 wt% PAF-1/6FDA-DAM membrane stored under ambient conditions (exposed to air, humidity, and temperature fluctuations). The membrane was tested with realistic conditions using a ternary gas mixture (N_2:CO_2:O_2 = 81:15:4), simulating flue gas at elevated pressures (total pressure of 6.7 bar) and temperatures (up to 100 °C). Remarkably, the membrane maintained excellent performance, exhibiting a CO_2/N_2 separation factor of 19.5 (**Figure 6**) and a CO_2 permeability of 979 Barrer

(**Figure S40**) at 35 °C, consistent with selectivities obtained from CO_2/N_2 (50:50) mixed gas testing (**Figure S15**) and single-component gas testing (**Figure 2**).

3. Conclusion

We have described an approach for fabricating composite gas separation membranes that exploit the ultrahigh porosity and permeability of PAF fillers to achieve drastically enhanced gas permeabilities and anti-aging behavior relative to the corresponding pure polymer membranes. The selectivities of these composite membranes are dictated by the choice of nonporous, glassy polymer matrix material used and are maintained upon incorporation of up to at least 20 wt% PAF-1 in the case of 6FDA-DAM, 10 wt% PAF-1 in the case of cellulose acetate, and 5 wt% PAF-1 in the case of Matrimid®. Calculations based on measured permeabilities, gas adsorption isotherms, and material densities confirm that the unique separation properties of the membranes arise from the high diffusivity of different gases through the highly porous PAF-1 particles, rather than through specific solubility enhancements. Dramatic stabilization to plasticization (e.g., at high CO_2 partial pressures) can further be introduced to polymer membranes through incorporation of hydrogen-bonding, polyamine-appended PAFs. Advantageously, PAF-1 particles can also be well-dispersed in a variety of potential casting solvents, regardless of their polarities, most likely facilitated by solvent nanoconfinement in the PAF pores. Overall, our results suggest that PAFs are promising as versatile fillers in gas separation membranes for a diverse variety of gas mixtures.

Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Separation Science in the Chemical Sciences, Geosciences, and Biosciences Division, under Award Number DE-SC0019992. The U.S. National Science Foundation is thanked for providing graduate fellowship support for A.A.U., E.O.V, and K.E.E., and the Philomathia Foundation is thanked for providing additional graduate fellowship support for A.A.U. We thank Membrane Technology and Research, Inc. for generously supplying the Matrimid® polymer used in this work. We also thank Dr. Elena Kreimer and the Microanalytical Facility for assistance with elemental analyses, Dr. Kristofer Gleason for helpful discussions regarding mixed-gas permeation measurements, Dr. Markita Landry and Dr. Francis Cunningham for dynamic light scattering instrument use, Arun Jonhson for discussions regarding solvent nanoconfinement, Jim Breen for assistance with custom glassware used for membrane casting, the University of California Berkeley Electron Microscope Laboratory for advice and assistance

in electron microscopy sample preparation and data collection, and Dr. Katie R. Meihaus for helpful discussions, writing, and editing contributions.

Conflicts of interest

The authors declare the following competing interests: the University of California, Berkeley has applied for a provisional patent on some of the technology discussed herein, on which E.O.V., A.A.U., and J.R.L. are listed as co-inventors. A.A.U., E.O.V., and J.R.L. have a financial interest in ChemFinity Technologies, Inc., which is developing membrane materials for various separations.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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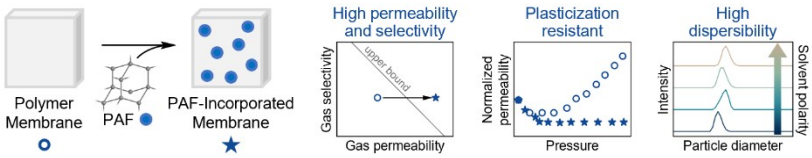
Generalizable Porous Aromatic Framework Membranes for Diffusion-Enhanced Gas Separations



This work contains a generalizable procedure for enhancing the gas permeability of polymer membranes without compromising selectivity by incorporating robust porous aromatic frameworks (PAF). The PAF fillers are highly dispersible in a wide range of solvents, and amine-functionalization of the PAF enhances the plasticization resistance of the mixed-matrix membranes.