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Enhanced CO₂ Capture and Hydrogen Purification by Hydroxy Metal–Organic Framework/Polyimide Mixed Matrix Membranes

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In modern industry, separation of chemical mixtures in the production of gases, petrochemicals, and other commodities is an extremely energy-intensive process, predominantly relying on thermal-driven processes such as distillation.^[1] Membrane technology can mitigate the intensive energy demands associated with conventional separation approaches, potentially consuming less than 10 % of the energy used in distillation.^[2] Despite such promise, membrane separations confront numerous hurdles, including the inadequate separation performance of established membranes and the high cost of scaling up new membranes.^[2,3] Indeed, the currently employed polymeric membranes face a tradeoff between separation productivity and efficiency (i.e., Robeson upper bounds),^[4] which has retarded the growth of membrane technology in the realm of gas separations. For example, CO₂ removal from natural gas represents the largest industrial gas separation application,^[5] but membrane processes account for less than 5 % of the natural gas separation market, owing to their unsatisfactory per-

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formance compared with other competing technologies, such as amine adsorption. Likewise, high-performing membranes, exemplified by thermally arranged polymers and metal-organic frameworks (MOFs), exhibit performances above the Robeson upper bounds but often suffer from challenges in large-scale fabrication, owing to issues like the brittleness of the membranes.^[3,6]

To address the aforementioned obstacles and improve the competitiveness of membrane separation technology, mixed-matrix membranes have been heavily investigated to substantially boost the separation productivity and efficacy.^[7] Mixed-matrix membranes comprising a polymer (i.e., the continuous phase) and inorganic fillers (i.e., the disperse phase) simultaneously utilize the easy processability of polymers and molecular sieving properties of nanomaterials, enabling unprecedented gas separation performance.^[8] More importantly, since membrane manufacturing industries primarily employ polymer solutions to prepare membrane products (i.e., hollow fiber membrane bundles), it is technologically facile to incorporate nanocrystals into polymer solutions to fabricate mixed-matrix membranes.^[9] Thus, mixed-matrix membranes are immediately compatible with state-of-the-art membrane fabrication processes and are inherently more scalable and cost-effective than other types of membranes that

require aggressive annealing or sophisticated processing steps.

Extensive research into materials for mixed-matrix membrane formation has been carried out in recent decades.^[7c,e,10] As a new generation of inorganic fillers for membranes, nano-sized MOFs possess customizable pore sizes similar to gas molecules with high surface areas, providing fast and efficient molecular sieving of gas mixtures with Angstrom-level size differences. Furthermore, the organic ligands of MOFs promote the formation of intimate interfacial interactions between MOF particles and polymer chains, reducing the propensity of interphase defects caused by the inhomogeneous nature of the mixed matrix. The exotic features of MOFs have stimulated keen interests in studying a rich spectrum of MOF-based mixed-matrix membranes with broad applications including CO₂ capture,^[11] H₂S removal^[6d] and paraffin/olefin separations.^[7b,12] Despite virtually unlimited combinations of MOFs and polymers, only a small fraction of MOF-based mixed-matrix membranes perform beyond the current Robeson upper bounds.^[7b,c] Surprisingly, a close examination of the few successful cases reveals that those high-performing membranes predominantly rely upon polymers of intrinsic microporosity (PIMs) or on aggressive thermal annealing processes.^[11,13] Nevertheless, PIM-based membranes can undergo a

rapid loss of permeability owing to their notoriously accelerated physical aging.^[6a,14] Likewise, previously reported mixed-matrix membranes have ubiquitously been annealed at temperatures above 200 °C.^[13b,15] Albeit with a handful of such membranes exceeding the Robeson upper bounds, aggressive annealing creates hurdles for scale-up, since it adds complexity of membrane manufacturing alongside the increased brittleness of membranes. Other rarely studied approaches, such as introducing moisture into the feed gas,^[7b,16] are also difficult to scale-up since moisture tends to condense and block gas permeation in membranes at low operation temperatures. To our knowledge, reports of MOF-based mixed-matrix membranes that exceeding the Robeson upper bounds without involving the aforementioned challenges are scarce.

Herein we report a new class of MOF-based mixed-matrix membranes with synergistically enhanced performance beyond present Robeson upper bounds and compatibility with the current membrane manufacturing platform. Such high performance results from the precise interfacial engineering of MOFs and polymers through tailoring and matching the reciprocal functional groups of MOF ligands and polymer chains. A family of zirconium-based MOFs—UiO-66—has emerged as a promising nanocrystal for mixed-matrix membrane formulations, arising from its appealing stability against high temperatures and moistures.^[17] Mixed-matrix membranes based on UiO-66 and its derivatives have been reported with superior performance.^[15a,7b,11,18] We previously reported membranes based on amino-functionalized UiO-66 (i.e., UiO-66-NH₂) with dramatically improved gas permeability.^[19] To assess how functionalization of the ligands independently affects the properties of membranes, herein, we focus on another type of frameworks derived from UiO-66 but with distinct pore functionalities from UiO-66-NH₂. We judiciously altered the pore functional groups by pursuing hydroxy Zr-based MOFs made from li-

gands different from those in UiO-66-NH₂. The MOF examined here, defined as UiO-66-(OH)₂, was synthesized through coordination of hexanuclear zirconium clusters and 2,5-dihydroxy-1,4-benzenedicarboxylic acid,^[20] which forms a pore aperture size of a similar magnitude to most gas molecules. The abundant hydroxy groups are uniquely suited to serve as active sites to interact with functional groups in the polymers. UiO-66-(OH)₂ displays preferential sorption for a particular gas pair, such as CO₂/CH₄.^[21] More crucially, the OH groups afford potential to extend the functionalization by forming chemical bonds with specific polymers under certain conditions (e.g., UV exposure). To our knowledge, these unique features of UiO-66-(OH)₂ have not been fully explored and this MOF has never been reported as a molecular filler to fabricate mixed-matrix membranes for gas separation. We fabricated mixed-matrix membranes from UiO-66-(OH)₂ and a polyimide, called 6FDA-DAM:DABA (3:2) (6FDA = 4,4'-(hexafluoroisopropylidene)diphthalic anhydride; DAM = 2,4,6-trimethyl-1,3-diaminobenzene; DABA = 3,5-diaminobenzoic acid) (6FDD), which incorporates desirable carboxylic moieties in the polymer chains^[22] (Figure 1 a). The carboxylic groups in the polymer form direct hydrogen bonds with the hydroxy groups in UiO-66-(OH)₂, thereby promoting intimate interphase adhesion in the mixed matrices. These O–H–O hydrogen bonds are formed between the OH groups in UiO-66-(OH)₂ and the carboxylic groups in 6FDD polyimide, whereas in UiO-66-NH₂/6FDD mixed membranes, O–H–N hydrogen bonds are formed.^[19] To our knowledge, this is the first report of mixed-matrix membranes containing UiO-66-(OH)₂ nanoparticles with performance exceeding the present Robeson upper bounds for multiple gas separation applications, including CO₂ capture and hydrogen purification.

UiO-66-(OH)₂ was synthesized following a similar procedure to that reported in ref. [20] and incorporated into the 6FDD polyimide to prepare mixed-matrix membranes (Figure 1 a, b).

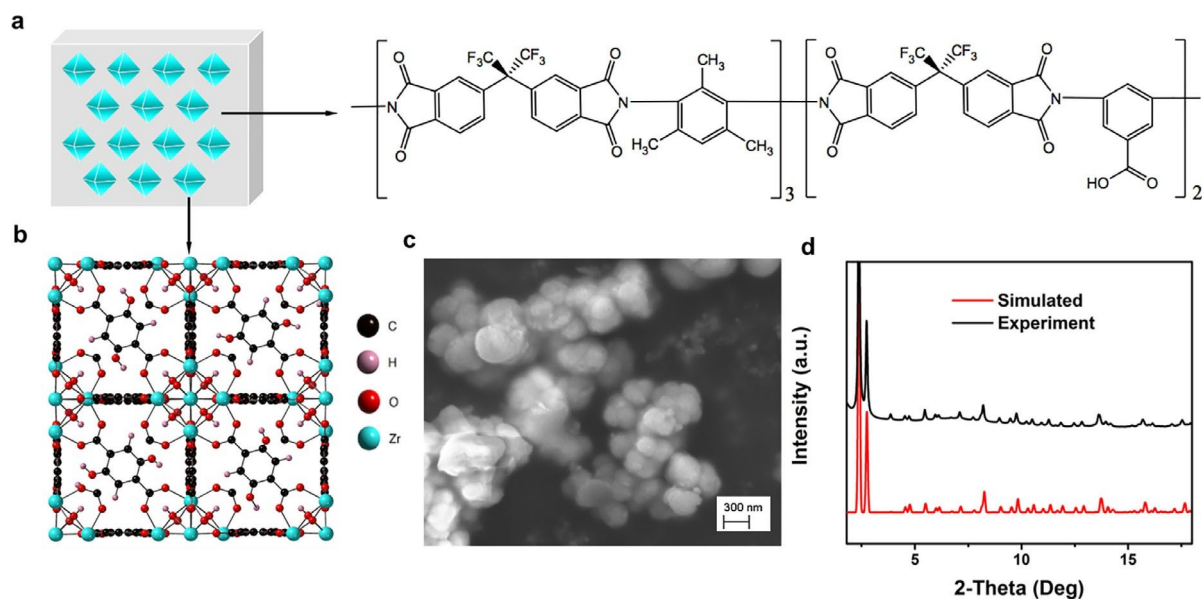


Figure 1. Formation of UiO-66-(OH)₂/6FDD mixed-matrix membranes: a) Schematic showing components of UiO-66-(OH)₂/6FDD mixed-matrix membranes. b) Crystal structure of UiO-66-(OH)₂. c) Scanning electron microscope image of UiO-66-(OH)₂ nanocrystals. d) Powder X-ray diffraction of UiO-66-(OH)₂ from experiment and simulation.

Dynamic light scattering (DLS) results revealed the mean particle size of UiO-66-(OH)₂ to be 324 ± 99 nm (see the Supporting Information, Figure S1). Scanning electron microscopy (SEM) provided further evidence of the particle size of UiO-66-(OH)₂ of approximately 300 nm (Figure 1 c), in accordance with the results from the DLS measurements. Powder X-ray diffraction (XRD) experiments unveiled the characteristic peaks of UiO-66-(OH)₂, in strong agreement with simulation results, suggesting the desirable crystal structure was achieved (Figure 1 d). Further fundamental characterizations of UiO-66-(OH)₂ particles were conducted with thermogravimetric analysis (TGA) and nitrogen physisorption studies. TGA results proved the strong resilience of UiO-66-(OH)₂ against high temperatures, as no noticeable degradation of UiO-66-(OH)₂ was observed until 300 °C (Figure S2). From nitrogen physisorption, UiO-66-(OH)₂ was found to have a BET surface area of 537 m² g⁻¹ (Figure S3 and Table S1), in accordance with the reported value of 560 m² g⁻¹.^[20] Pore size distribution modeling of UiO-66-(OH)₂ demonstrated a medium pore width of around 7 Å, in a similar range to gas molecules (Figure S4 and Table S1). The physicochemical characterizations indicate the utility of UiO-66-(OH)₂ as an ideal candidate for preparing mixed-matrix membranes, owing to its nanoparticle size, amenable pore apertures, and robustness at high temperatures.

The cross-sections of the prepared membranes were examined by using SEM, clearly revealing the integral morphologies of membranes in the absence of interfacial macro-voids (Figures 2 and S5). Indeed, UiO-66-(OH)₂ nanocrystals exhibit significant adhesion with polymers in the mixed-matrix membranes, since no gap or delamination occurs at the MOF-polymer boundary. Further characterization of the membranes was conducted with FTIR spectroscopy, TGA, and differential scanning calorimetry (DSC; Figures S6 and S7 and Table S2). FTIR spectroscopy is an effective means to probe filler-polymer chemical interactions in the mixed-matrix membranes as the characteris-

tic peak for a particular covalent bond is highly susceptible to shift once a strong electrostatic force of attraction is established in its proximity. The membranes gave an adsorptive peak at 1603 cm⁻¹ (Figure S6), which is likely associated with the C=C stretching of benzene rings conjugated with the COOH groups in the polymer. This peak is redshifted upon incorporating MOFs, indicating the formation of hydrogen bonds between the OH groups of UiO-66-(OH)₂ and the COOH groups of the polymer.^[23] DSC characterization gave further evidence of the strong polymer-filler interactions. The glass transition temperatures (*T*_g) of the mixed-matrix membranes showed direct dependence on the MOF loading, whereby *T*_g increased upon incorporation of MOFs, which is likely due to the polymer-MOF interface rigidification (Table S2).^[7d] Following a similar trend to the neat MOFs, TGA results indicated that the mixed-matrix membranes tolerate high temperatures and undergo no significant weight loss until 300 °C (Figure S7), proving their robustness against elevated temperatures.

We further examined the intrinsic gas transport properties of the membranes by using a house-customized pure gas permeation system based on a constant volume/variable pressure approach. Pure gas permeation has been widely used as a valid technique to quantify the gas separation performance of membranes, which also serves as the basis of Robeson upper bounds.^[4] Indeed, prior studies have shown that mixed gas permeation could yield better performance than the case of pure gas permeation.^[7a,24] Gas permeation results (Figure 3) were compared with previously reported polymeric membranes and mixed-matrix membranes (Tables S3– S6).^[6d,7b,c,11,13b,15a,25] The addition of MOFs improves the gas permeabilities appreciably while maintaining an intrinsic gas selectivity with a loading up to 50 wt% for all four gas pairs examined here (CO₂/CH₄, CO₂/N₂, H₂/CH₄ and H₂/N₂; Figure 3 and Table S3). In particular, with 50 wt% MOF loading, the H₂ permeability was enhanced by a factor of five, from 191 Barrers

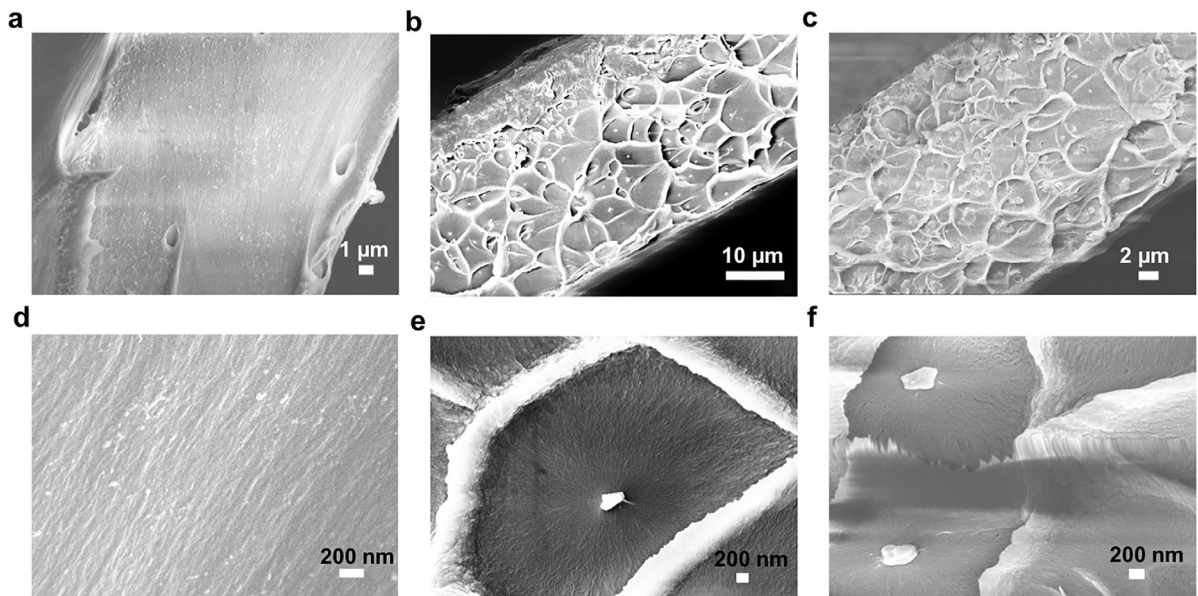


Figure 2. Cross-sectional morphologies of neat polymer and UiO-66-(OH)₂/6FDD mixed-matrix membranes by scanning electron microscopy: a, d) Neat polymer membranes; b-f) UiO-66-(OH)₂/6FDD mixed-matrix membranes with 10 wt% (b, e) and 20 wt% (c, f) UiO-66-(OH)₂ loadings in 6FDD polyimide.

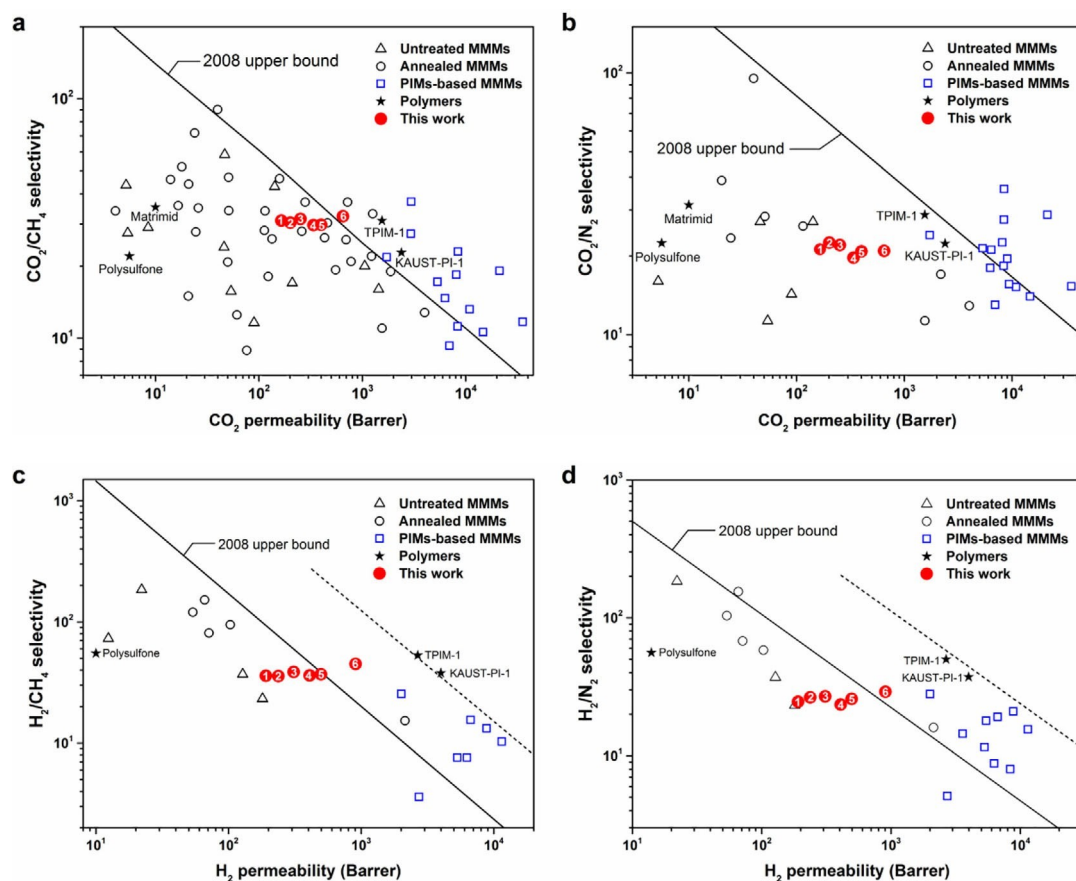


Figure 3. Gas separation performance of UiO-66-(OH)₂/6FDD mixed-matrix membranes: a) CO₂/CH₄; b) CO₂/N₂; c) H₂/CH₄; d) H₂/N₂. UiO-66-(OH)₂ loadings of 0, 10, 20, 30, 40, and 50 wt% are denoted by red solid circle symbols 1, 2, 3, 4, 5 and 6 respectively, alongside previously reported membranes (Tables S3–S6). Gas transport properties in this work were calculated by averaging at least two membrane samples from duplicate films with identical casting conditions. Annealed mixed-matrix membranes from previous studies (black open circles) entailed a heating process at a temperature above 200 °C.

for the neat polymer to 907 Barrers; the improvement in CO₂ permeability was also apparent, from 165 Barrers to 650 Barrers for the polymer and mixed-matrix membranes, respectively. To benchmark our membranes, we selected a commonly studied and commercially used polymer called Matrimid, since data for stand-alone pure MOF membranes without supports is virtually unavailable. The membranes used in this work display an enhancement in permeability by nearly two orders of magnitude over that with Matrimid, which has a CO₂ permeability of only 10 Barrers.^[26] This performance places UiO-66-(OH)₂/6FDD mixed-matrix membranes beyond the current Robeson upper bounds for CO₂/CH₄, H₂/CH₄ and H₂/N₂ pairs. The membranes also closely approach the CO₂/N₂ Robeson upper bound and show promise for CO₂ capture from flue gas. Overall, the mixed-matrix membranes developed in this work demonstrate a desirably high permeability and selectivity, enabling enhanced molecular sieving of several challenging gas pairs in a highly productive fashion.

To seek insights into the gas transport mechanism in the membranes, we further studied gas diffusivities

and solubilities by using CO₂/CH₄ as the modeling gas pair. Specifically, CO₂ and CH₄ diffusivities were estimated by using the time-lag method,^[3] whereas their solubilities were back-calculated from gas permeabilities and diffusivities based upon the solution-

diffusion model (Figure 4 and Table S7).^[27] Both CO₂ and CH₄ diffusivities increase on incorporation of UiO-66-(OH)₂ in the mixed-matrix membranes, as expected, since MOFs generate additional diffusion channels for gas transport (Figure 4 a). The diffusion selectivity of CO₂ over CH₄ tends to drop with increased UiO-66-(OH)₂ loading, likely owing to the subtly divergent responses of CO₂ and CH₄ diffusivities with MOF loadings. Likewise, the CO₂ solubility increases with UiO-66-(OH)₂ loading (Figure 4 b), since the MOF forms extra sorption sites for CO₂ molecules in the membranes, compared with neat polymers. The CH₄ solubility is generally stable in the span of various UiO-66-(OH)₂ loadings. Interestingly, the CO₂/CH₄ sorption selectivity is greater than the diffusion selectivity at all given MOF loadings in membranes, clearly suggesting the presence of MOFs favors the sorption separation of CO₂ over CH₄. In fact, such a preferential sorption of CO₂ over CH₄ contributes to the increase in sorption selectivity when more MOFs are introduced. At the maximum loading of 50 wt% UiO-66-(OH)₂, the CO₂/CH₄ sorption selectivity reaches 21.1, in reasonable agreement with reported gas adsorption selectivities ($S_{\text{CO}_2}/S_{\text{CH}_4} \sim 18.8$). The fundamental gas transport analyses indicate that the favorable sorption of MOFs for a gas pair such as CO₂/CH₄ helps to govern the gas transport mechanisms in mixed-matrix membranes.

[21]

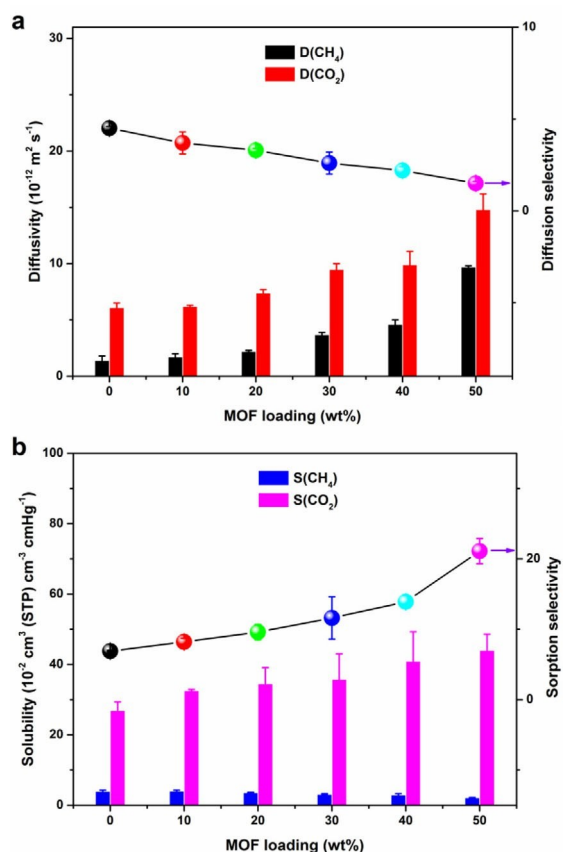
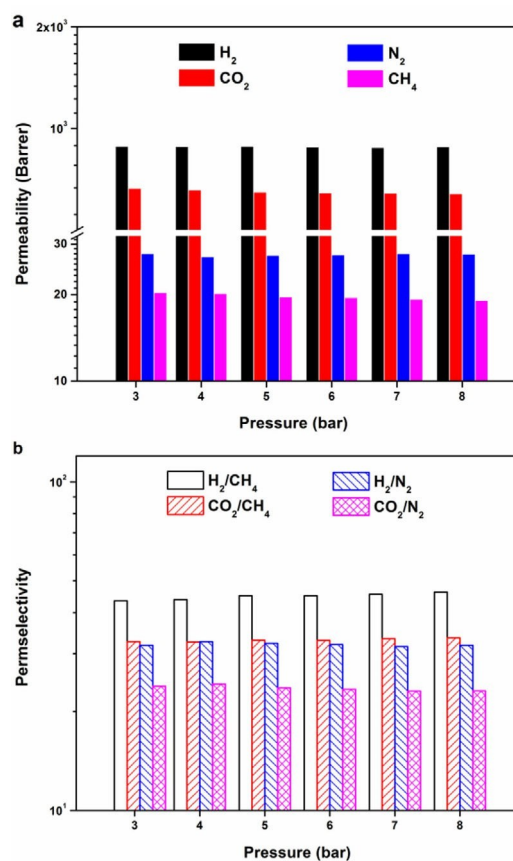


Figure 4. Analyses of gas transport in UiO-66-(OH)₂/6FDD mixed-matrix membranes: a) CO₂ and CH₄ diffusivities and b) CO₂ and CH₄ solubilities of membranes with 0-50 wt% UiO-66-(OH)₂ loadings. Membrane samples were tested at 3 bar and 35 °C. Gas transport parameters were estimated by averaging at least two membrane samples from duplicate films with identical casting conditions.

To assess separation performance under various operating conditions, we subjected the mixed-matrix membranes to elevated feed pressures (Figure 5 and Figures S8-S12). Despite a minor drop in permeability at elevated pressures, gas permeabilities for all gases tested here remain stable at all different feeding pressures. Based on the dual-mode sorption model,^[28] such a negligible decrease in permeability is likely attributed to the saturation of Langmuir sorption sites for gas molecules at increased feed pressure. Moreover, the selectivities of the four gas pairs (CO₂/CH₄, CO₂/N₂, H₂/CH₄ and H₂/N₂) demonstrate negligible change during the measurements, which is indicative of their minimal dependence on the testing pressures. Although an even higher CO₂ feed pressure (e.g., 50 bar) is desirable in the future to study the CO₂ plasticization resistance of membranes, the pressure of 8 bar examined here is significantly higher than the practical feed pressure for several important CO₂ separations, such as biogas upgrading and post-combustion CO₂ capture. The appealing stability of



both permeability and selectivity in this preliminary test demonstrate the robust and well-maintained properties of UiO-66-(OH)₂/6FDD mixed-matrix membranes in the presence of elevated-pressure feeding streams.

Figure 5. Effects of feed pressure on UiO-66-(OH)₂/6FDD mixed-matrix membranes: a) Gas permeabilities and b) selectivities of mixed-matrix membranes with 50 wt% UiO-66-(OH)₂ loading and feeding pressures of 3–8 bar at 35 °C.

Aging, a natural phenomenon essentially occurring in all kinds of membranes, refers to the process of separation productivity diminishing over time, encompassing mainly physical aging and sorption-induced aging. Physical aging corresponds to the time-dependent relaxation of membranes towards a “more equilibrium” or “lower energy” state.^[29] Likewise, sorption-induced aging involves the physisorption/chemisorption of contaminants in membranes, leading to a loss in permeability, owing to increased transport resistance and reduced sorption capacity.

To gain insights into aging, we subjected the membrane samples to ambient air in the presence of moisture, oxygen, and other chemical species and tracked the aging response of membranes for over 2300 h (Figure 6). The rationale of this design was to mimic the practical membrane manufacturing conditions where membranes are often exposed in an open and ambient environment. Foreseeably, the membrane samples undergo a reduction in permeability on aging. However, they display different degrees of aging at different stages. For example, the H₂ permeability drops by about 27 % in the first 340 h of aging (Figure 6 a). Surprisingly, only 8 % loss of H₂ permeability was observed thereafter (i.e., at $t = 340$ h) and the curves tended to level-off after 1500 h aging. Despite this aging trend, the membranes became more selective and continue to perform beyond the Robeson upper bounds (CO₂/CH₄,

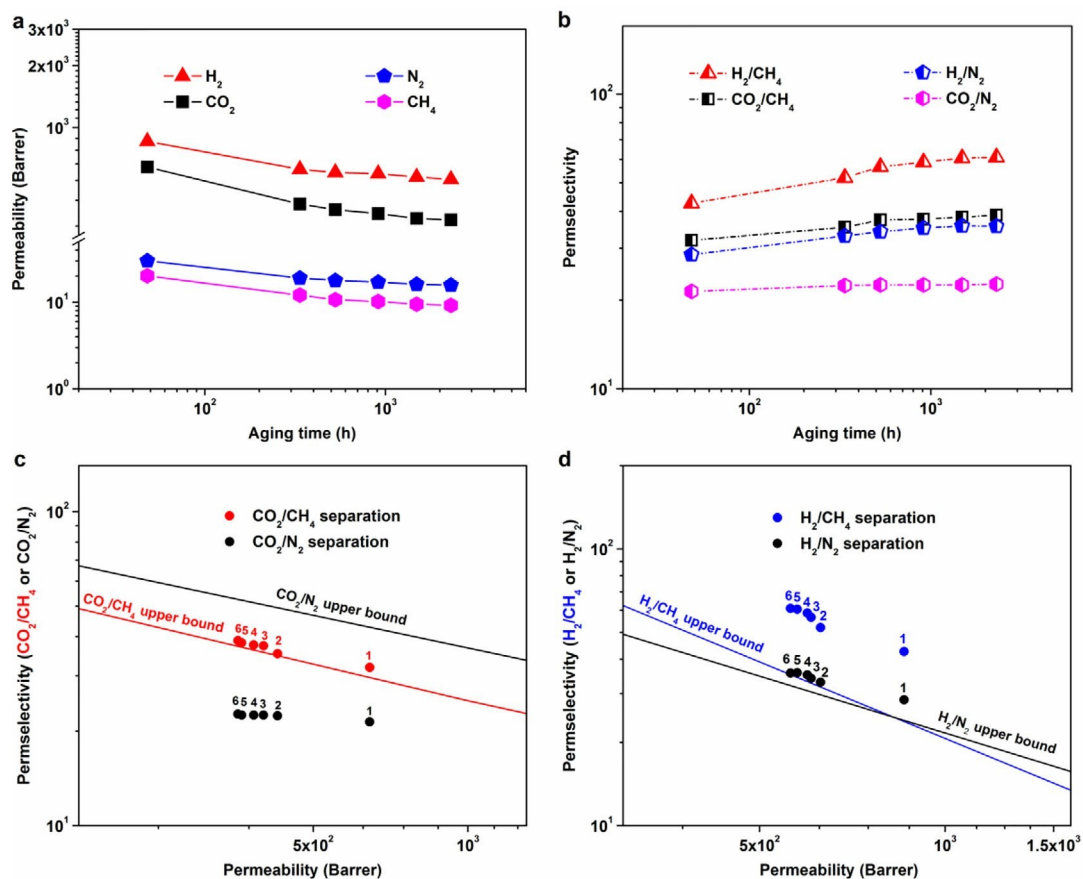


Figure 6. Aging of UiO-66-(OH)₂/6FDD mixed-matrix membranes. Numbers 1, 2, 3, 4, 5 and 6 refer to aging times of 50, 340, 530, 910, 1500, and 2300 h, respectively, for UiO-66-(OH)₂/6FDD mixed-matrix membranes with 50 wt% UiO-66-(OH)₂ loading. Membrane samples were tested at 3 bar and 35 °C.

H₂/CH₄ and H₂/N₂) during the aging study, corroborating their appealing performance and durability for protracted operations of gas separations.

Although prior studies have been scarce, the mechanical properties of dense-film mixed-matrix membranes have been reported and are prone to decline with increasing MOF loading,^[18c] which is expected but should not undermine the key findings of this work. Pragmatically, mixed-matrix membranes that are useful for large-scale gas separations preferably take the form of composite hollow fibers with the highest surface/volume ratio, which consist of a sheath layer with embedded MOFs and a core polymer supporting layer.^[9a,c] The sheath layer has a thickness that is a fraction of the supporting layer (usually less than 10 %) and the mechanical strength of composite hollow fibers primarily relies on the core layer material instead of the sheath layer with MOFs.^[9a,c] This fact clearly means that, despite the reduced mechanical strength of dense-film mixed-matrix membranes in the presence of MOF particles, mixed-matrix membranes with high MOF loadings work both technologically and practically, as the ultimate format of mixed-matrix membranes for gas separations is essentially the composite hollow fiber

mixed-matrix membrane.

Our findings underscore the crucial relevance of molecular structures of polymer and MOFs to design ultra-permeable membrane materials, providing a ready route to fabricating mixed-matrix membranes beyond the Robeson upper bounds

for gas separation. Highlighting the role of mutual interactions of functional units, our study demonstrate a promising process through rational design of materials without aggressive treatments (e.g., annealing). With 50 wt% MOF loadings, the mixed-matrix membranes exhibit a H₂ and CO₂ permeability of 907 and 650 Barrers, respectively, with a H₂/CH₄, H₂/N₂ and CO₂/CH₄ selectivity of 45, 29, and 32, respectively. The exceptional performance with an ideal combination of high permeability, selectivity, and durability is translated into an enhanced recovery of gas products without losing purity, significantly reducing cost by using lower membrane areas and a more energy-efficient process with lower compression cost. The step-change advance could substantially broaden the design principles to other classes of materials. Apart from an enhanced applicability in industrial gas separations, the approach could have potential implication in reducing energy associated with other key chemical separation processes, such as seawater desalination, water treatment, and food, beverage, and pharmaceutical industries.

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Conflict of interest

The authors declare no conflict of interest.

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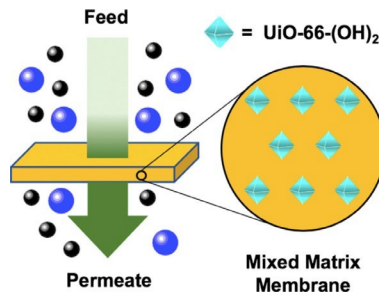
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 Enhanced CO₂ Capture and Hydrogen Purification by Hydroxy Metal-Organic Framework/Polyimide Mixed Matrix Membranes



Out of bounds: Mixed-matrix membranes incorporating the hydroxy-functionalized metal-organic framework UiO-66-(OH)₂ exhibit gas separation performance beyond the 2008 Robeson CO₂/CH₄, H₂/CH₄, and H₂/N₂ upper bounds, owing to intimate hydrogen-bonding interactions between hydroxy groups and carboxylic acid groups in the UiO-66-(OH)₂ and polymer phase, respectively.
