

Amino Acid-Decorated MOF Membranes Toward Facilitated CO₂ Separation Under Varying Humidities

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Although proven to be promising for CO₂ capture from flue gas, maintaining superior separation efficiency of CO₂-philic membranes under widely differing humidities remains highly challenging to date. Targeting high-efficiency and humidity-resistant flue gas separation, in this study, a multi-scale structure optimization protocol is pioneered to fabricate highly (200)-oriented 55 nm-thick MIL-140A membrane. On one hand, employing L-histidine as modulator retards crystallization kinetics and inhibits multilamellar-stacking crystal growth, warranting formation of MIL-140A nanosheets and ultrathin oriented membrane; on the other hand, bulky L-histidine segments coordinates in MIL-140A framework not only induced distorted pore configuration toward precise discrimination of CO₂ from N₂ but also serves as reactive-carriers toward CO₂-facilitated diffusion. Relying on facilitated diffusion mechanism, the CO₂/N₂ selectivity of obtained MIL-140A membrane reached 79.0 under high-humid environments, which is 32.1% higher than that in dry environments; moreover, the membrane exhibited stable CO₂/N₂ separation performance over a wide humidity range due to its intrinsic hydrophobicity, showing great promise in practical flue gas separation.

energy consumption.^[3–5] In contrast to polymeric membranes confronting with inherent permeability-selectivity trade-off, facilitated transport membranes (FTMs) with abundant amine groups as reactive carriers hold great potential in overcoming this obstacle, relying on reversible CO₂ hydration reaction that formed carbamate or bicarbonate anions enabling facilitated CO₂ diffusion through membranes.^[6,7] For instance, PVAm-based FTMs with cross-linked piperazine carriers exhibited excellent CO₂/N₂ selectivity of 277 with CO₂ permeance of 6500 GPU under humidified conditions.^[8] Nevertheless, degraded performance and inferior durability at relative humidity (RH) below 70% caused by unfavorable reaction kinetics and equilibria of CO₂ hydration hindered their practical application.^[9,10] Alternatively, molecular sieve membranes have demonstrated outstanding CO₂/N₂ separation performance.^[11] For instance, SSZ-13 membranes had achieved

superior CO₂/N₂ selectivity of 46 and CO₂ permeance of 1200 GPU.^[12] However, under high humidity environments, their micropores may largely be blocked by water vapors, leading to significant decline in CO₂/N₂ separation performance.^[13]

In recent decades, MOF membranes have shown bright prospects in high-efficiency gas separation through deliberate tailoring of pore micro-environments, e.g., aperture size, shape and functionality.^[14–16] For instance, Eddaoudi et al. introduced asymmetry in parent trefoil-shaped pores of Zr-*fum*-fcu-MOF membrane to disrupt original match for trefoil-shaped CH₄, leading to record-high N₂/CH₄ selectivity of 15.^[17] Aiming at high-efficiency flue gas separation under high humidity environments, however, functional groups in the framework must be tailored synchronistically.^[18] By analogy to FTMs, it is anticipated that introduction of bulky CO₂-reactive carrier groups in the framework will initiate reversible CO₂ hydration, facilitating fast CO₂ permeation under moist conditions; simultaneously, distortion of pores induced by partial substitution of ligands with asymmetric carrier molecules may in turn achieve precious screening of CO₂ from N₂, cooperatively contributing to enhanced CO₂/N₂ selectivity. On the other hand, microstructure (e.g., preferred orientation and thickness) is found to play a vital role in gas permeance.^[19] For instance, our

1. Introduction

Sharply elevated atmospheric level of CO₂ caused by industrial discharge poses serious threats toward climate change.^[1,2] Flue gas, which commonly comprises CO₂, N₂, and H₂O with varying composition depending on combustion source and power plant design, accounts for ≈30% of global CO₂ emissions. Membrane represents a promising option for CO₂ capture from flue gas by virtue of its high separation efficiency and low

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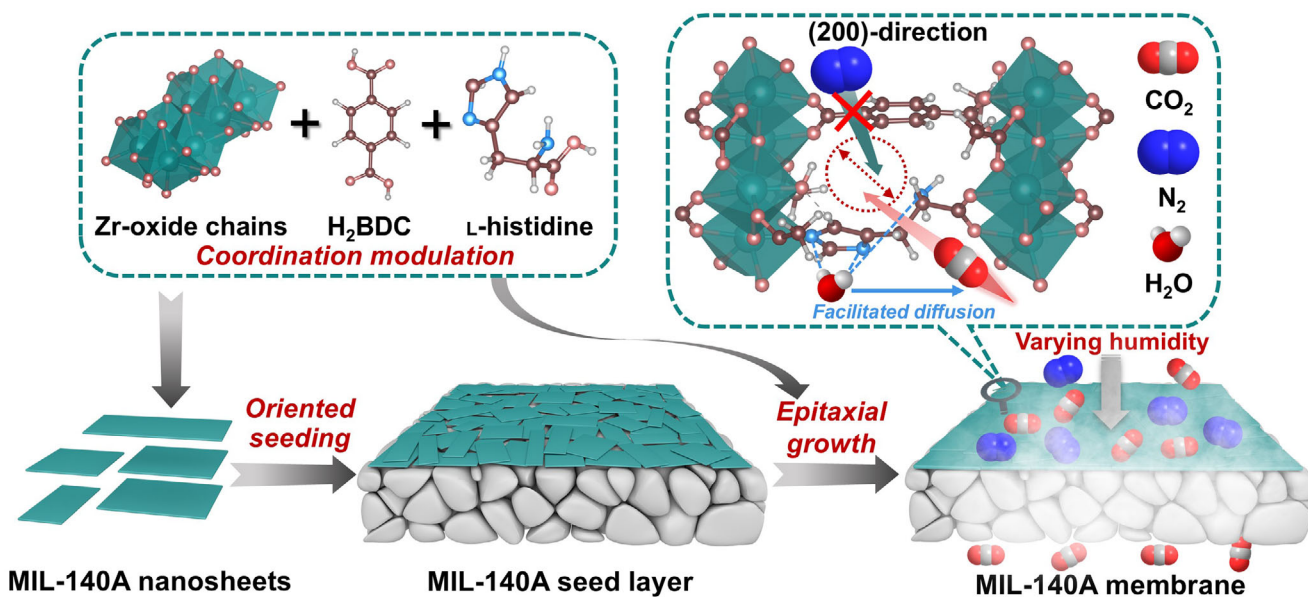


Figure 1. Schematic of the preparation of oriented ultrathin MIL-140A membrane toward high-efficiency flue gas separation.

recent study revealed that CO_2 permeances of highly oriented ultrathin MOF membranes (e.g., MIL-125 and UiO-66) were significantly higher than those of randomly oriented and/or thicker counterparts, owing to minimized transport tortuosity and reduced diffusion path length, respectively.^[16,20–22] Therefore, cooperative tailoring of pore micro-environment and microstructure of MOF membranes was indispensable for transcending the performance upper-bound for CO_2/N_2 under practical operation conditions.

MIL-140A (i.e., $[\text{ZrO}(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2)]$), a structural analogue of UiO-66, features infinite zirconium-oxide chains as inorganic subunit connected to six other chains through terephthalic ligands.^[23] In contrast to UiO-66, MIL-140A possesses exceptional hydrophobicity and smaller micropore size accompanying with higher water/mechanical stability.^[24] Previous studies revealed that the intrinsic CO_2 -philicity endowed MIL-140A with superior CO_2/N_2 adsorption selectivity of 32.9,^[25] rendering it superb membrane candidate for high-efficiency flue gas separation. In this study, a multi-scale structure optimization protocol was proposed to fabricate highly (200)-oriented 55 nm-thick MIL-140A membrane with superior humidity-resistant CO_2/N_2 separation performance (Figure 1). On the one hand, pore micro-environment of MIL-140A membrane was deliberately tailored through coordinating bulky L-histidine, which not only tailored the size and shape of pores toward precise screening CO_2 from N_2 but also provided sufficient amino groups for CO_2 -facilitated transport; on the other hand, employing L-histidine as modulator was found crucial for the formation of MIL-140A nanosheets (NSs) and ultrathin oriented membrane. Through combining with its intrinsic hydrophobicity, the CO_2/N_2 separation performance of obtained membrane under varying humidities far exceeded performance limits of state-of-the-art molecular sieve membranes, holding great promise for practical CO_2 capture from flue gas.

2. Results and Discussion

2.1. Preparation of MIL-140A NSs and Membrane

Our first step involved L-histidine-mediated solvothermal synthesis of MIL-140A NSs. As shown in Figure 2a,b, obtained powders exhibited monodisperse nanosheet morphology with lateral size of 0.5–1.5 μm . All XRD diffraction peaks matched well with those of simulated MIL-140A phase (Figure 2c). It should be noted that addition of L-histidine in precursor solution not only directed the formation of desired crystalline phase, but also reduced reaction temperature to 120 $^\circ\text{C}$, the lowest value ever reported for MIL-140A,^[26] otherwise, uniform octahedral-shaped crystals, belonging to pure UiO-66 phase, would form (Figure S1, Supporting Information). In effect, such modulator-induced phase selection behavior had been observed in synthesis of Cr-BDC (MIL-101/MIL-88B), Fe-BPDC (MIL-88D/MIL-126), and Al-BTC (MIL-100/MIL-96).^[27–29] This could be attributed to the coordinative modulation effect, which effectively retarded the crystallization-driven self-assembly rates through competing with terephthalic ligands toward zirconium ions, ultimately leading to formation of more thermodynamically stable and dense MIL-140A phase.^[30,31]

As confirmed by AFM results (Figure 2d,e), the thickness of MIL-140A NSs reached ≈ 6 nm, which represented the thinnest MIL-140A NSs as reported in the literature. This could be largely attributed to terminal coordination phenomenon of bulky L-histidine, which effectively prevented layer-stacking growth and stabilized ultrathin NSs in the solvent.^[27,32,33] EDXS spectra further confirmed uniform distribution of Zr, C, O, and N (from L-histidine) elements in MIL-140A framework (Figure S2, Supporting Information). The characteristic peaks assignable to vibrations of N–H (3400 and 1217 cm^{-1}), C–H (2925 cm^{-1}) and C–N (1269, 1250, and 1085 cm^{-1}) could be discerned in FT-IR spectrum, demonstrating that L-histidine had been incorporated

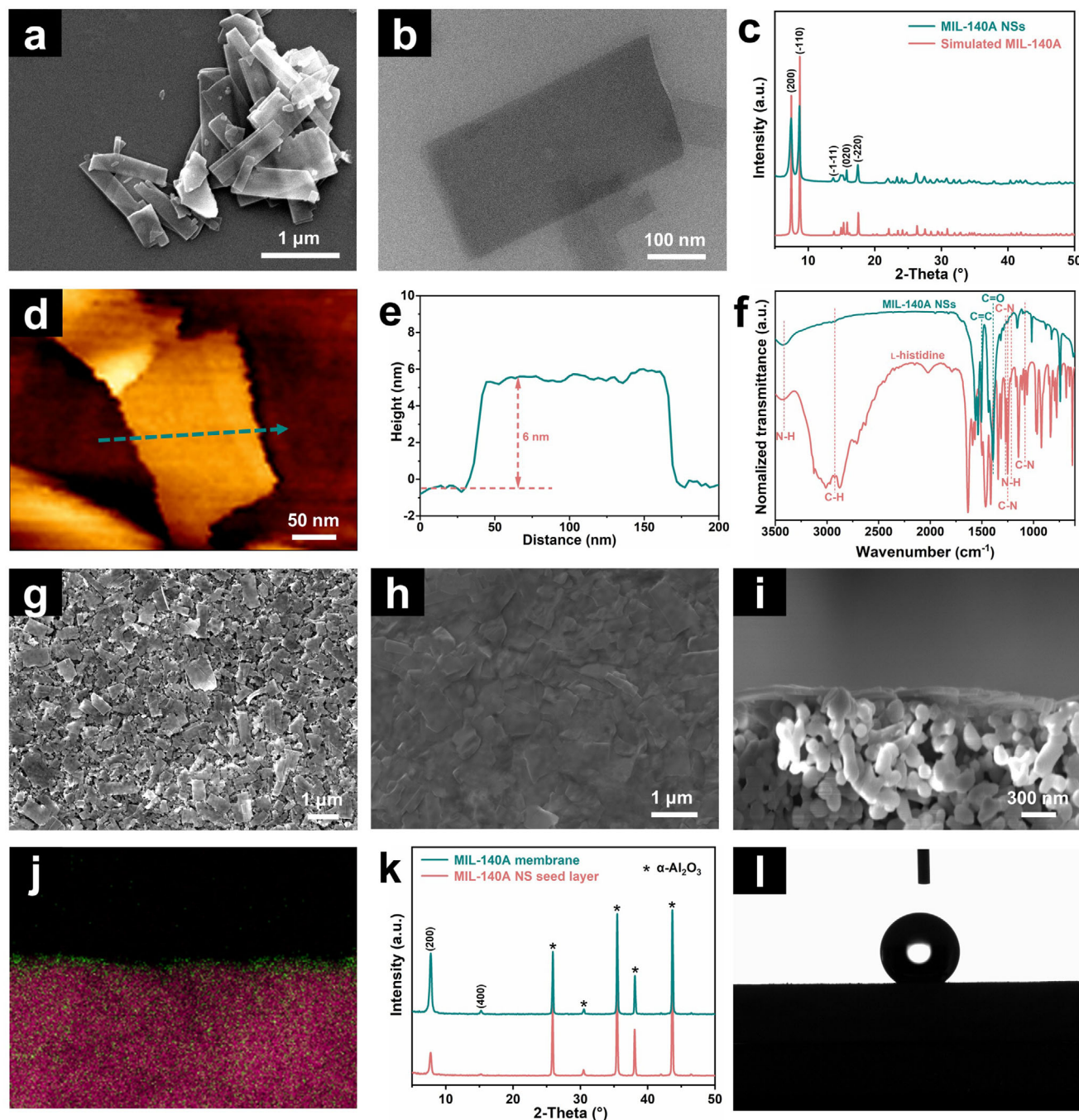


Figure 2. Characterization of MIL-140A NSs and membrane. a) SEM image, b) TEM image, c) XRD pattern, d) AFM surface image, e) relevant line scan, and f) FT-IR spectrum of MIL-140A NSs. SEM images of g) MIL-140A NS seed layer and h,i) MIL-140A membrane. j) Cross-sectional EDXS mapping (Zr elements: green signal; Al elements: pink signal) of MIL-140A membrane. k) Corresponding XRD patterns. l) Wettability characterization of MIL-140A membrane.

in MIL-140A framework (Figure 2f).^[34,35] MIL-140A NSs exhibited high hydrothermal stability either, as evidenced by the maintenance of high-crystallinity even upon long-term dispersion in boiling water (Figure S3, Supporting Information).

Subsequently, dynamic air-liquid-interface-assisted self-assembly method was employed to deposit MIL-140A NSs on porous α - Al_2O_3 substrate in view of the intrinsic hydrophobicity.

As shown in Figure 2g, after deposition, the substrate surface had been uniformly covered with 3–4 layers of monodisperse MIL-140A NSs. Relevant XRD pattern confirmed the dominance of (200)-orientation of the seed layer (Figure 2k). The next step involved oriented epitaxial growth for eliminating intergranular gaps in the seed layer. It has been proven that random attachment of MOF nuclei generated in bulk solution to the seed layer

resulted in undesired twin growth on membrane surface and insufficient intergrowth during epitaxial growth, and therefore, high grain boundary defect density.^[21,36] Herein coordination-mediated epitaxial growth, referring to addition of L-histidine in the precursor solution, was conducted to restrict bulk nucleation whilst trigger sufficient in-plane growth through coordinative modulation.^[16,30,37] Our results revealed that well-intergrown MIL-140A membrane with smooth surface morphology was readily obtained after epitaxial growth under optimized reaction conditions (Figure 2h). Cross-sectional SEM image and EDXS spectrum implied that obtained membrane was only 55 nm-thick with no discernable infiltration into substrate pores (Figure 2i,j); simultaneously, the XRD pattern (Figure 2k) revealed well preservation of (200)-preferred orientation inherited from the seed layer, which could be ascribed to retarded nucleation in bulk solution, and therefore, effective twin suppression as evidenced by the absence of any precipitates after reaction.^[37] To the best of our knowledge, this represented the thinnest oriented 3D MOF membrane ever reported in the literature. It should be noted that obtained MIL-140A membrane retained its morphology and crystallinity even after soaking in water at 60 °C overnight, confirming intrinsic framework robustness (Figure S4, Supporting Information).

For comparison, conventional UiO-66 membrane was prepared with similar procedure except in absence of L-histidine. SEM images revealed that a well-intergrown membrane covered with octahedral-shaped grains on its surface was readily formed (Figure S5, Supporting Information). Contact angle (CA) measurements showed that UiO-66 membrane could be quickly wetted by water droplets with CA of 22.8° (Figure S5, Supporting Information); in contrast, the MIL-140A membrane exhibited strong hydrophobicity with CA as high as 148.7° (Figure 2l), which was promising for direct use in humid flue gas separation with no demand on pre-drying process.

2.2. Textural Properties of MIL-140A Membrane

To better elucidate the interplay between textural properties and separation performance, MIL-140A powders (denoted as P-MIL-140A) synthesized with the same procedure as corresponding membrane except prolonged reaction duration were characterized further. Both XRD pattern and FT-IR spectrum of P-MIL-140A were consistent with MIL-140A NS seeds (Figure S6, Supporting Information). In addition, UiO-66 powders (denoted as P-UiO-66) deposited at bottom of the autoclave during the synthesis of UiO-66 membrane were collected and characterized (Figure S7, Supporting Information). In comparison with P-UiO-66, P-MIL-140A displayed enhanced thermal stability, attributing to higher thermal stability of Zr—O bonds in infinite Zr-oxide chains of MIL-140A than those in isolated $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ clusters of UiO-66 (Figure 3a).^[23]

Structural deficiencies of our samples were further quantified with potentiometric acid–base titration method.^[38] As shown in Figure 3b,c, the first derivatives of titration curves manifested several distinct equivalence points. Upon calculation (detailed procedure was shown in Supporting Information), 24.1% bonding sites on Zr-oxide chains of P-MIL-140A were occupied with L-histidine anions and -OH/-OH₂ pairs derived from trace water;^[39]

while defective sites in $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ clusters of P-UiO-66 accounting for 6.5% of bonding sites were fully capped with OH groups (Figure S8, Table S1, Supporting Information). More defective sites in P-MIL-140A could be attributed to the presence of L-histidine modulator, which competed with terephthalate linkers to bond with Zr-oxide chains;^[31,40] simultaneously, lower temperature and terephthalate/Zr ratio contributed to defective MIL-140A framework.^[38,41]

We further studied coordination modes and chemical states of diverse elements through XPS characterization. Additional characteristic peak for C 1s assignable to C—N bond was observed at 287.9 eV for P-MIL-140A (Figure 3d), which matched well with relevant N 1s XPS spectrum (Figure 3e);^[35] simultaneously, both peaks of Zr 3d_{3/2} and Zr 3d_{5/2} on P-MIL-140A slightly shifted 0.4 eV toward lower binding energy compared with P-UiO-66, attributing to new coordinative bonding between L-histidine modulator and Zr-oxide building subunit (Figure 3f).^[42] To be specific, electron-donating chelated nitrogen groups adjacent to carboxyl groups in L-histidine would increase electron cloud density around Zr atoms, resulting in negative shift of certain Zr atoms.^[43] Therefore, L-histidine modulator indeed served as competitive ligands toward chemical coordination with Zr oxide chains during P-MIL-140A synthesis.

Gas adsorption capacities of above samples were simultaneously investigated. As shown in Figure 3g, BET surface area and micropore volume of P-MIL-140A (425.9 m² g^{−1} and 0.176 cm³ g^{−1}) were lower than those of P-UiO-66 (1116.7 m² g^{−1} and 0.519 cm³ g^{−1}); correspondingly, average micropore size of P-MIL-140A as determined by Horvath–Kawazoe model achieved 0.39 nm (Figure 3h), which was much smaller than P-UiO-66 (0.56 nm). It was observed that adsorption capacities of CO₂, N₂ and CH₄ on P-MIL-140A were lower than those of P-UiO-66, attributing to lower microporosity of P-MIL-140A (Figure 3i). Both *Q_{st}* values of CO₂ were remarkably higher than those of N₂ and CH₄, confirming preferential binding affinity toward CO₂ (Figure 3j; Figure S9, Supporting Information); moreover, P-MIL-140A manifested significantly higher initial *Q_{st}* value of CO₂ (31.1 kJ mol^{−1}) compared with P-UiO-66 (23.8 kJ mol^{−1}), indicating stronger affinity interaction between CO₂ and P-MIL-140A framework. This could be largely attributed to the presence of electronegative imidazole and amino sites in L-histidine, which would interact with CO₂ through extra electrostatic interaction;^[13] moreover, smaller pore size of P-MIL-140A would allow more efficient potential energy overlap between adsorbent-adsorbate surface, providing stronger binding environment for CO₂.^[25] As shown in Figure 3k,l, both CO₂/N₂ and CO₂/CH₄ IAST selectivity on P-MIL-140A (23.3 and 6.2 at 1 bar) was superior to those of P-UiO-66 (16.4 and 4.8 at 1 bar) (Table S2, Supporting Information). We therefore anticipated that CO₂/N₂ separation performance of obtained MIL-140A membrane could be improved by virtue of its multi-scale structure superiority.

2.3. Gas Separation Properties of MIL-140A Membrane

Finally, gas permeation properties through obtained MIL-140A membrane were evaluated under ambient conditions. Single-gas permeation results showed that our membrane exhibited the

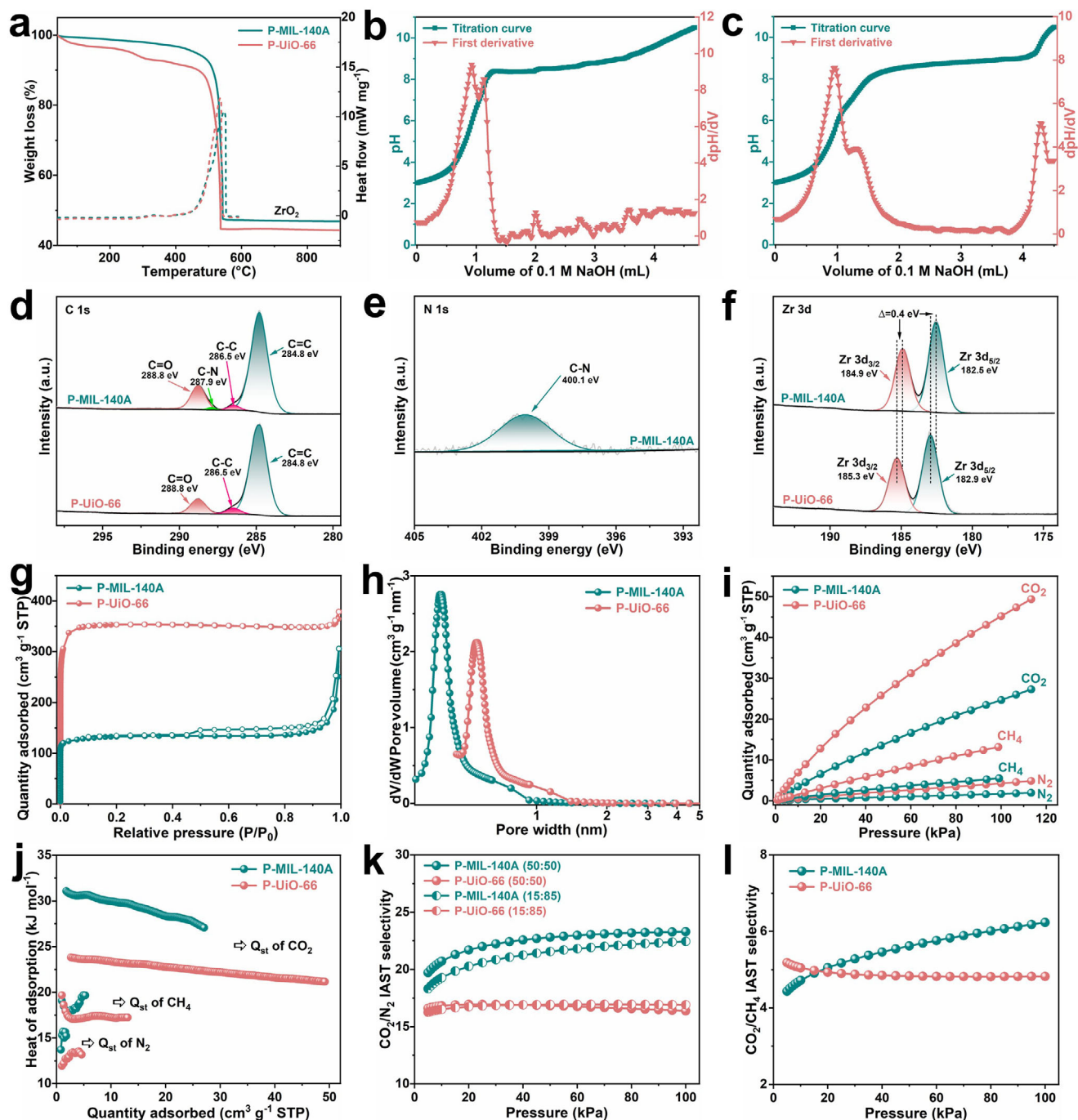


Figure 3. Textural properties of P-MIL-140A and P-UiO-66. a) TG-DSC curves. Acid–base titration and corresponding first-derivative curves of b) P-MIL-140A and c) P-UiO-66. XPS spectra of d) C 1s, e) N 1s, and f) Zr 3d. g) Isotherms of N₂ adsorption–desorption at 77 K, h) micropore size distributions, i) isotherms of CO₂, N₂, and CH₄ adsorption at 298 K, j) isosteric adsorption heats for CO₂, N₂, and CH₄, and k, l) IAST selectivity for CO₂/N₂ and CO₂/CH₄ of P-MIL-140A and P-UiO-66.

highest average CO₂ permeance of $9.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (2755.1 GPU) compared with H₂, N₂, and CH₄, attributing to preferential CO₂ adsorption (Figure 4a), while slightly higher CH₄ permeance relative to N₂ could be ascribed to higher CH₄ adsorption capability ($5.5 \text{ cm}^3 \text{ g}^{-1} \text{ STP}$ at 1 bar) and Q_{st} value (19.1 kJ mol^{-1}) than those of N₂ ($1.7 \text{ cm}^3 \text{ g}^{-1} \text{ STP}$ and 13.7 kJ

mol^{-1}). Correspondingly, average ideal selectivity for CO₂/N₂, CO₂/CH₄, H₂/N₂ and H₂/CH₄ gas pairs attained 60.6, 41.5, 24.8, and 17, respectively (Figure 4b). In terms of equimolar CO₂/N₂ mixture, the MIL-140A membrane manifested average CO₂/N₂ separation factor (SF) of 59.8 accompanying with CO₂ permeance of 2571.9 GPU (Tables S3–S5, Supporting Information). It

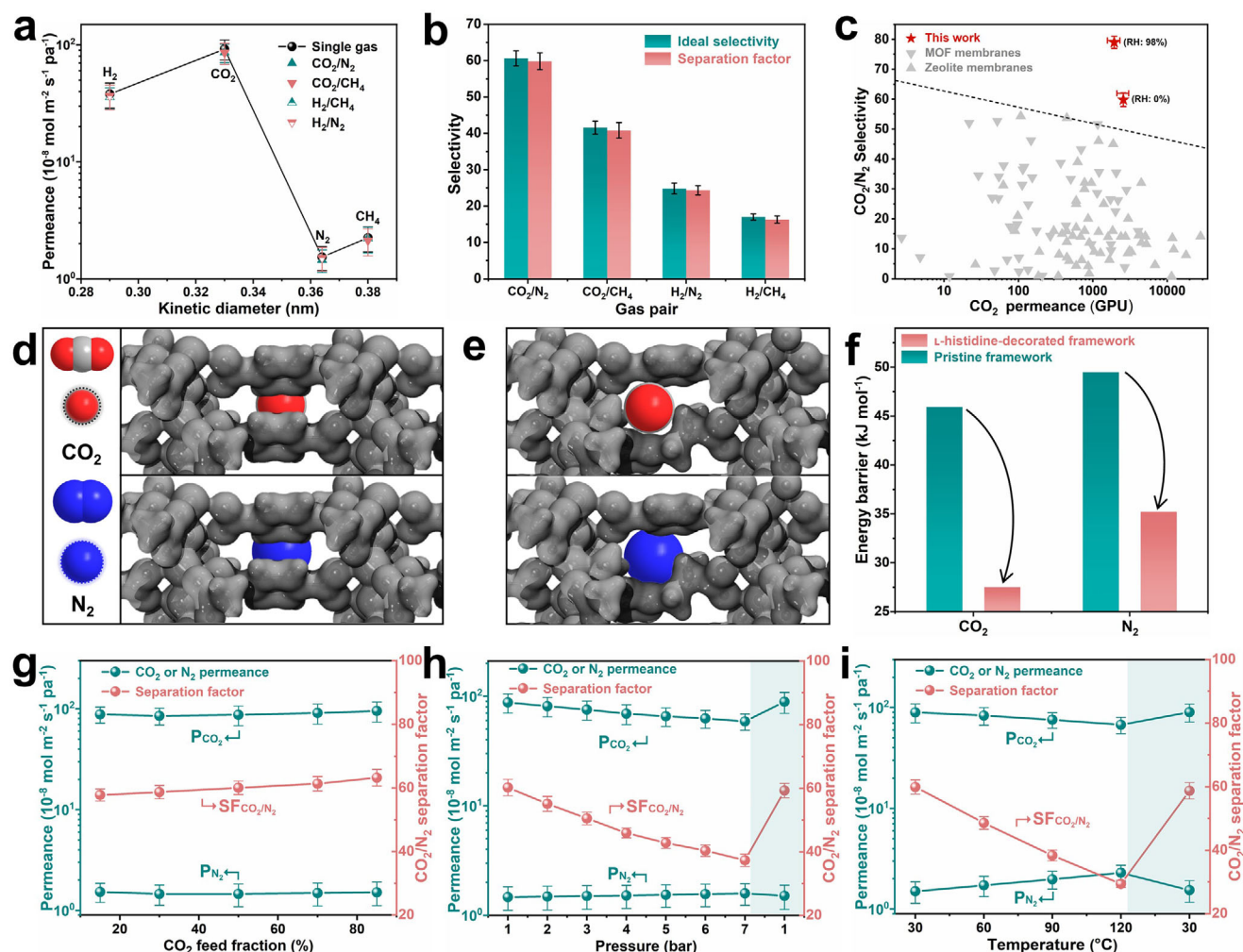


Figure 4. Gas separation properties and diffusion mechanism. a) Permeation results of single-gases and binary-gas mixtures on MIL-140A membrane at 30 $^{\circ}\text{C}$ and 1 bar. b) Corresponding ideal selectivity and SF toward different gas pairs. c) Comparison of CO_2/N_2 separation performance on MIL-140A membrane with reported state-of-the-art polycrystalline MOF and zeolite membranes. Schematic illustrations of diffusions of linear CO_2 and N_2 with circular side-view profile through d) slit-shaped pore-aperture of pristine framework and e) square-shaped pore-aperture of L-histidine-decorated framework in (200)-plane. f) Comparison of simulated energy barriers for the diffusion of CO_2 and N_2 molecules throughout the (200)-plane of corresponding frameworks. The effect of g) feed compositions, h) feed pressures, and i) operating temperatures on CO_2/N_2 SF and CO_2 permeance of MIL-140A membrane.

was worth mentioning that the CO_2/N_2 separation performance of our membrane easily exceeded the upper bound of state-of-the-art molecular sieve membranes measured under comparable conditions, thereby confirming the validity of multi-scale structural optimization in breaking the performance upper-bound (Figure 4c; Tables S6 and S7, Supporting Information).

To gain deeper insights into the effect of pore micro-environment on gas diffusion kinetics in MIL-140A membrane, DFT calculations were carried out with Vienna Ab initio Simulation Package (VASP). Geometry-optimized model of L-histidine-decorated MIL-140A framework was rationally constructed for reaching the lowest energy configuration.^[17] Pristine MIL-140A framework presented narrow slit-shaped pores with the size of 0.253 nm on the (200) plane (Figure 4d); in contrast, L-histidine-decorated MIL-140A framework exhibited enlarged pore size of 0.367 nm with square-shape on the (200) plane, allowing slender

CO_2 to diffuse through while simultaneously impeding diffusion of larger-sized N_2 (Figure 4e). In comparison with pristine MIL-140A framework, the diffusion energy barrier for permeation of CO_2 and N_2 through the (200) plane of L-histidine-decorated MIL-140A framework decreased by 40.13% and 28.85%, respectively, leading to enhanced CO_2/N_2 selectivity (Figure 4f). In addition, stronger affinity interaction between CO_2 and electronegative imidazole and amino sites contributed to high diffusion energy barrier difference between CO_2 and N_2 to some extent.

We further evaluated the effect of operation condition on the CO_2/N_2 separation performance. Experimental results indicated that average CO_2 permeance and CO_2/N_2 SF only slightly fluctuated in CO_2 feed range of 15–85% (Figure 4g); simultaneously, MIL-140A membrane exhibited a certain degree of reduction in average CO_2 permeance (32.9%) and CO_2/N_2 SF (38%) upon elevating feed pressure up to 7 bar (Figure 4h), which could be

interpreted by more intense competition in adsorption sites caused by excessive entry of N_2 in the framework under high pressure as well as high pressure-induced concentration polarization.^[12,44] It was found that average CO_2 permeance gradually decreased upon elevating operation temperature from 30 to 120 °C, whereas N_2 permeance increased steadily, leading to progressive decline in CO_2/N_2 SF (Figure 4i). Fitting temperature-dependent permeation behavior to Arrhenius equation revealed that higher temperature not only weakened CO_2 preferential adsorption but also facilitated diffusion of N_2 in MIL-140A framework, resulting in the opposite trend in CO_2 and N_2 permeances (Figure S10, Supporting Information). Even so, our membrane retained decent performance with average CO_2 permeance of 2491.5 GPU and CO_2/N_2 SF of 48.6 at typical flue gas discharge temperature of 60 °C.

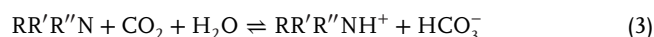
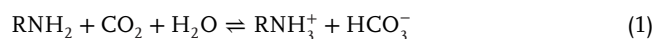
2.4. Performance Comparison with UiO-66 Membrane

As comparative experiment, obtained UiO-66 membrane was subjected to gas permeation test either, displaying average CO_2 permeance of 3.2×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (946 GPU) with ideal CO_2/N_2 selectivity of 9.3 (Figure S11, Supporting Information). Such significant reduction in CO_2 permeance compared with MIL-140A membrane was mainly attributed to thicker membrane thickness (5.5 μm). To elucidate the mechanism of higher CO_2/N_2 selectivity of MIL-140A membrane, gas diffusivity and solubility were further calculated based on solution-diffusion model (Tables S8 and S9, Supporting Information).^[22,44] Negligible discrepancies in CO_2 and N_2 diffusion coefficients on UiO-66 membrane demonstrated that the observed CO_2/N_2 selectivity was dominated by preferential CO_2 adsorption rather than diffusion-controlled separation,^[15] while more pronounced difference in CO_2 and N_2 diffusion coefficients in MIL-140A membrane resulted in significant increase of CO_2/N_2 diffusion selectivity from 0.9 to 4.1 (Figure S12, Supporting Information). Higher CO_2/N_2 solution selectivity of MIL-140A membrane (14.6) in comparison with UiO-66 membrane (10.6) could be attributed to the presence of stronger affinity interaction between CO_2 and L-histidine-decorated MIL-140A framework. Therefore, synergistic enhancement in solution selectivity and diffusion selectivity concurrently contributed to higher CO_2/N_2 selectivity of MIL-140A membrane.

2.5. Influence of the Presence of Water Vapor on CO_2/N_2 Separation Performance

Aiming at practical flue gas separation under varying humidity conditions, the CO_2/N_2 separation performance of MIL-140A membrane was investigated in presence of saturated water vapor (30–98% RH). It was observed that average CO_2 permeance of MIL-140A membrane slightly decreased with increasing RH, attributing to competitive adsorption between H_2O and CO_2 toward Zr–oxygen bridges and amino sites in the framework.^[18,45] Unexpectedly, average CO_2/N_2 SF ($v/v = 50:50$) of our membrane steadily increased with increasing RH from 30% to 98%, reaching maximum value of 79.0 that represented 32.1% increase in comparison with that in drying environments, accompanying with average CO_2 permeance of 1939.5 GPU at 98% RH

(Figure 5a). In contrast, UiO-66 membrane lost 93.7% of CO_2 permeance and 73% of CO_2/N_2 SF at such high humidity level (Figure S11, Supporting Information). This could be attributed to stronger water adsorption in hydrophilic UiO-66 framework (CA: 22.8°), which substantially blocked CO_2 diffusion pathways.^[13,18] In effect, incorporation of amino acid salts (e.g., sarcosine and histidine) as CO_2 -carriers in FTMs had been demonstrated to substantially enhance their CO_2/N_2 separation performance in humid environments, owing to higher CO_2 loading capacity and faster CO_2 hydration kinetics.^[10,46–48] CO_2 -facilitated transport mechanism of FTMs in presence of amino acid salts had been systematically investigated in previous literatures.^[47,49] By analogy to FTMs, significantly enhanced CO_2/N_2 SF of MIL-140A membrane in the presence of water vapors could be attributed to CO_2 -facilitated transport mechanism, in which multiple amino groups in L-histidine (i.e., one primary, one secondary, and one tertiary amino group per molecule) with high spatial mobility and CO_2 loading capacity served as reactive carriers to undergo reversible nucleophilic addition reactions with CO_2 and H_2O , enabling migration of CO_2 across the membrane in form of bicarbonate, as typically depicted in Figure 5b and Equations (1–3).^[6,7,10]



Total CO_2 flux (N_{CO_2}) of our membrane could therefore be illustrated as the sum of conventional molecular-diffusion of unreacted CO_2 and carrier-mediated reaction-diffusion of bicarbonate, which could be expressed as Equation (4).^[6,8,50]

$$N_{CO_2} = \frac{D_{CO_2} (C_{CO_2|up} - C_{CO_2|down})}{L} + \frac{D_{HCO_3^-} (C_{HCO_3^-|up} - C_{HCO_3^-|down})}{L} \quad (4)$$

where D_{CO_2} ($D_{HCO_3^-}$), C_{CO_2} ($C_{HCO_3^-}$), and L represented relevant diffusion coefficient, sorbed concentration in membrane on upstream/downstream side, and membrane thickness, respectively. Attributing to $D_{HCO_3^-}$ being two orders of magnitude higher than D_{CO_2} , transmembrane transport rate of CO_2 was significantly improved;^[9] while chemically inert N_2 was only permitted to permeate following conventional non-reactivity diffusion, resulting in higher CO_2/N_2 SF under humid environments.^[49] Simultaneously, higher hydrophobicity of MIL-140A membrane (CA: 148.7°) warranted weaker binding of H_2O to adsorption sites and more facile replacement of H_2O with CO_2 , rendering diffusion of slender CO_2 through membranes faster than larger-sized N_2 with stronger hindering effect, ultimately contributing to superior CO_2/N_2 SF.^[13,45] To the best of our knowledge, such remarkable elevation of CO_2/N_2 SF in presence of water vapor has been rarely reported in terms of molecular sieve membranes.

We further measured CO_2/N_2 separation performance of MIL-140A membrane with representative flue gas composition (15% CO_2) in moisture (98% RH). Fortunately, our membrane retained exceptional average CO_2/N_2 SF of 79.0 and CO_2 permeance of 1935.7 GPU (Figure 5a); moreover, once switching back to initial drying-condition, CO_2/N_2 separation performance

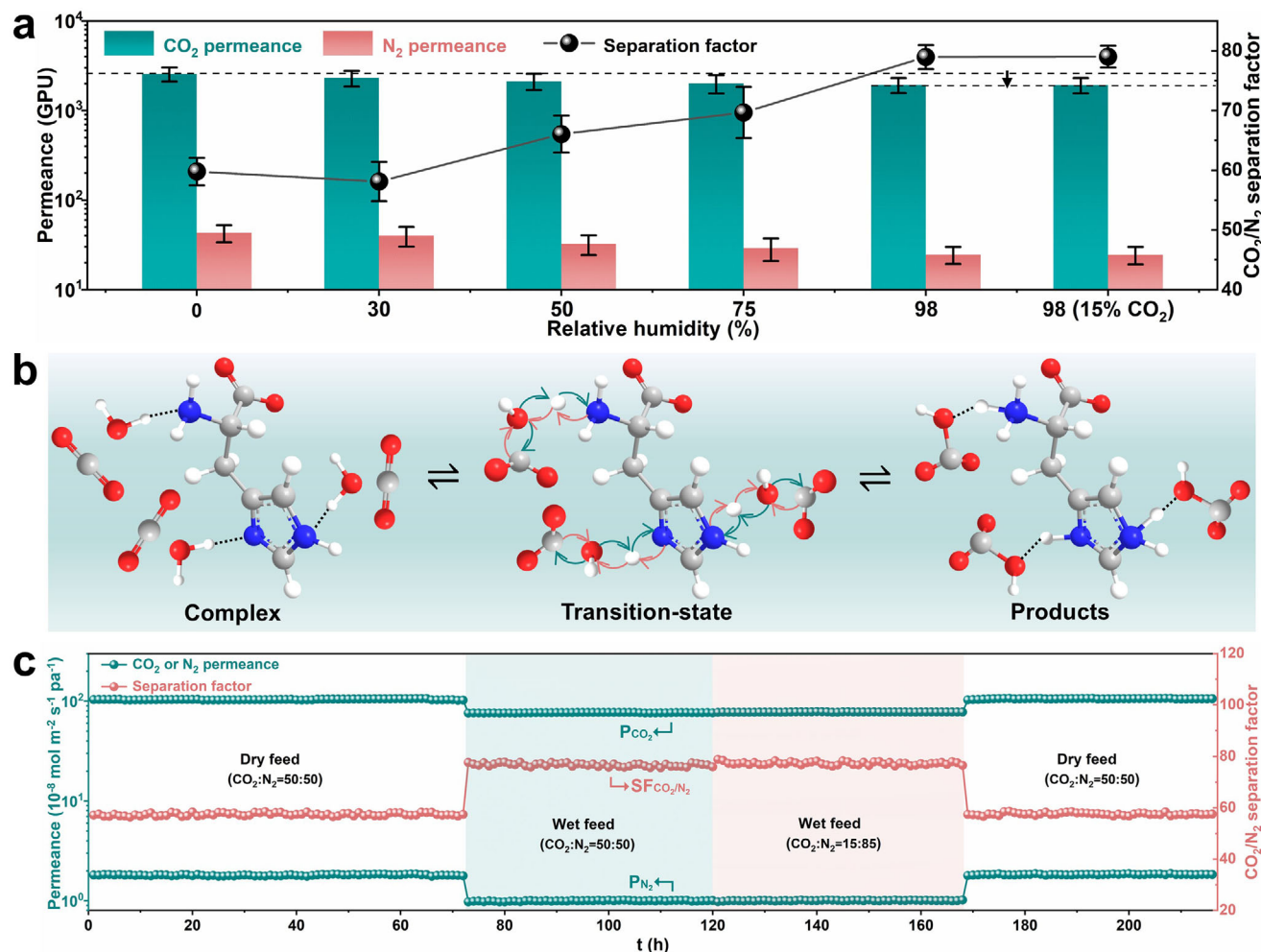


Figure 5. CO₂/N₂ separation performance under humid environments and CO₂-facilitated transport mechanism. a) Comparison of CO₂/N₂ SF and permeance of MIL-140A membrane at different relative humidity. b) Schematic illustration of the pathway for reversible CO₂ hydration reaction initiated by multiple amino carriers in L-histidine. Green (orange) arrows represented atomic trajectories following the forward (reverse) reaction direction. Black dashed lines represented hydrogen bonds. Color codes: C-gray; H-white; O-red; N-blue. c) Long-term operation stability for continuous CO₂/N₂ separation under dry and/or moist (98% RH) conditions.

could completely revert to initial benchmark values through on-stream activation procedure, indicating excellent performance reversibility (Figure 5c). It should be noted that our membrane manifested outstanding operation stability during continuous permeation under dry or humid environments over 216 h (Figure 5c), satisfying requirements for long-term flue gas separation.

3. Conclusion

Targeting high-efficiency and humidity-resistant flue gas separation, herein we reported rational design and fabrication of highly (200)-oriented 55-nm-thick MIL-140A membrane exhibiting superior and stable CO₂/N₂ separation performance under widely differing humidities. Most importantly, incorporation of L-histidine in MIL-140A framework not only finely regulated the membrane microstructure through coordinative modulation effect, but also endowed the membrane with desired pore-

size and configuration for precise screening of CO₂ from N₂ as well as multiple amino groups as carriers toward CO₂-facilitated transport. Obtained membrane exhibited unprecedented average CO₂/N₂ SF (59.8) with high CO₂ permeance (2571.9 GPU), far exceeding the upper bound of state-of-the-art molecular sieve membranes. Most notably, under humid environments (98% RH), its CO₂/N₂ SF was further increased to 79.0 with negligible decay in CO₂ permeance. Our research provides insights into molecular-level design and production of high-performance molecular sieve membranes toward practical CO₂ capture from flue gas.

4. Experimental Section

Preparation of MIL-140A NS Seeds: 0.47 g of ZrCl₄, 0.33 g of H₂BDC and 0.07 g of L-histidine were dissolved in a binary solvent containing 50 mL of DMF and 6 mL of HAc. Above mixed solution was then refluxed in an oil bath at 120 °C for 24 h under stirring. After reaction, above solution

was sequentially cooled down to room temperature (RT), centrifuged, and washed with DMF and ethanol. Finally, white precipitates were suspended in ethanol overnight and dried at 60 °C for 24 h under vacuum.

Deposition of Oriented MIL-140A Seed Layer: The seed suspension was obtained through dispersing 0.02 g of MIL-140A NS seeds in 6 mL of ethanol, followed by sequential stirring of 72 h and ultrasonication of 3 h. Prior to seed layer deposition, porous α -Al₂O₃ disk was horizontally placed in a glass tank filled with distilled-water. Two sides of the glass tank were connected with a circulating water pump to form a turbulent air–liquid interface. Subsequently, obtained seed suspension was slowly injected at the interface with a speed of 2 μ L min^{−1}. The suspension slowly spread on water surface upon contacting with water until the formation of a continuous layer. Finally, the seed layer was transferred onto porous α -Al₂O₃ disk through elevating it to the interface.

Epitaxial Growth of MIL-140A Membrane: The precursor solution was prepared following the same procedure as MIL-140A NS seeds, followed by addition in a 50 mL Teflon-lined autoclave where the seeded substrate was placed vertically. Subsequently, the autoclave was sealed and reaction was carried out at 120 °C in a convective oven for 6 h. After cooling, the membrane was taken out, washed with ethanol, and vacuum dried at RT for 3 days. In addition, MIL-140A powders synthesized with identical recipe and processing conditions as the MIL-140A membrane but prolonged reaction duration (36 h) was sequentially centrifuged, washed with DMF and ethanol, and finally dried at 60 °C under vacuum for 24 h.

Preparation of Octahedral-Shaped UiO-66 Seeds: 0.47 g of ZrCl₄ and 0.33 g of H₂BDC were dissolved in binary solvent containing 50 mL of DMF and 6 mL of HAc. The mixed solution was then sealed in Teflon-lined autoclave and heated at 120 °C in a convective oven for 12 h. After reaction, the above solution was sequentially cooled down to RT, centrifuged, and washed with DMF and ethanol. Finally, white precipitates were suspended in ethanol overnight and dried under vacuum at 60 °C for 24 h.

Deposition of Randomly Oriented UiO-66 Seed Layer: The seed suspension was obtained through dispersing 0.012 g of octahedral-shaped UiO-66 seeds in 5 mL of ethanol, followed by vigorous stirring for 72 h and ultrasonication for 3 h. Randomly oriented UiO-66 seed layer was obtained through spin-coating of 0.15 mL of seed suspension on the substrate surface at 3000 rpm for 60 s, followed by drying under vacuum at 70 °C for 2 days.

Epitaxial Growth of Randomly Oriented UiO-66 Membrane: The precursor solution was synthesized with the same procedure as octahedral-shaped UiO-66 seeds, followed by addition in a 50 mL Teflon-lined autoclave in which the seeded substrate was placed vertically. Subsequently, the autoclave was sealed and heated at 120 °C in a convective oven for 80 h. After cooling, the membrane was taken out, washed with ethanol, and vacuum dried at RT for 3 days. In addition, white precipitates deposited at the bottom of the autoclave were sequentially centrifuged, washed with DMF and ethanol, and finally dried at 60 °C for 24 h under vacuum.

Statistical Analysis: The error bars in Figures 4a–c, g–i, and 5a correspond to the standard deviations, and are obtained from three measurements, where independent sample is tested for each measurement.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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facilitated transport, humidity-resistant separation, L-histidine functionalization, MOF membrane, multi-scale structure

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