Enhancing the Gas Separation Selectivity of Mixed-Matrix Membranes Using a Dual-Interfacial Engineering Approach

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ABSTRACT: We report a dual-interfacial engineering approach that uses a sub-20 nm polycrystalline MOF-74 shell as a transition phase to engineer the MOF–polymer interface. The application of a shell MOF layer divides the original single interface problem into two interfaces: MOF–MOF and MOF–polymer, which can be individually addressed. The greater external surface area created by the uneven MOF-74 shell containing high-density open metal sites allows the MOF to interact with 300% polymer at the interface compared to traditional MOF, thereby ensuring good interfacial compatibility. When applied on UiO-66-NH₂, its respective mixed-matrix membranes exhibit a simultaneous increase of CO₂/CH₄ separation selectivity and CO₂ permeability with increasing MOF loading, implying a defect-free interface. When applied on MOF-801, the mixed-matrix membranes exhibit an ethylene/ethane separation selectivity up to 5.91, a drastic 76% increase compared to that of the neat polymer owing to a “gas focusing” mechanism promoted by the preferred pore orientation in the MOF-74 layer. This represents one of the most selective ethylene/ethane separation membranes reported to date.

INTRODUCTION

Separation is a fundamental industrial process that accounts for a significant portion of the world energy consumption.1 However, many existing separation processes are highly inefficient in terms of energy utilization. For instance, ethylene/ethane separation, an essential step during ethylene production, is accomplished by cryogenic distillation columns over 100-tray.2 This process alone consumes 0.3% of total world energy production.3,4 Membrane separation has been widely considered as a promising alternative to achieve energy efficient gas separation owing to its heat-free separation mechanism.5,6 One key to realizing this technological revolution lies in the development of new membrane materials exhibiting higher permeability and selectivity. This is especially important for ethylene/ethane separation where no current membrane materials have met the industrial demands.7

One feasible approach to advance the membrane separation performance beyond the so-called “upper bound”8−10 for current polymeric membranes is to introduce porous filler particles containing periodically aligned micropores because the well-defined pore structure can not only provide additional free volume for faster diffusion but also induce additional entropic leverage for size selective discrimination of gas pairs, thus leading to a drastic increase of separation selectivity and permeability.11 These composite membranes are best known as mixed-matrix membranes (MMMs).12−23 One class of filler materials that has attracted the most attention is metal–organic framework (MOF) because its pore size, pore geometry, and pore chemistry can be fine-tuned with sub-angstrom precision.24−32 It is now widely accepted that, for MOF-based MMMs to fully exert their separation potential, having a compatible filler–matrix interface is a prerequisite.33−39 Despite the presence of organic constituents within MOFs, their interfacial interaction with polymer matrices, however, is far from ideal. This is likely due to two limiting factors: (1) weak interfacial interaction and (2) small interfacial area.

Over the past decade, numerous efforts have been focused on improving the interfacial interaction in MOF-based MMM through either MOF surface modification with small molecules, metal ions, or cross-linked polymers.40−47 These methods addressed the first factor but failed to address the second. Filler miniaturization is another alternative which addresses the second factor. However, it is synthetically challenging to obtain ultrasmall MOF nanoparticles without agglomeration.34,48−50 Recently, our group pioneered an interfacial engineering strategy that uses covalently grafted polyimide brushes to mediate the MMM interface.50 This approach turns a flat MOF surface into a linear macromolecule.

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Scheme 1. Synthetic Procedures of MOF-801@Ni-MOF-74 MMMs with a Dual-Interfacial Engineering Approach

MOF-801 was selected as the first core MOF of interest due to its high structural robustness and small aperture size suitable for molecular sieving separation (∼4.6 Å). Monodispersed MOF-801 particles with an average size of 147 ± 4 nm were synthesized according to a previously reported method with slight modification (Figure S1a).53 To overcome the difficulty of constructing topologically distinct core–shell MOFs, our previous study revealed the key to achieving a uniform MOF shell was to boost the nucleation kinetics of the MOF and reduce its critical nuclei size.53−55 Microwave-assisted syntheses (MAS) have been widely used for the synthesis of miniaturized MOF nanoparticles as well as MOF on heterostructures.55−57 Here, we adopted this technique for the rapid synthesis of core–shell MOFs containing polycrystalline MOF-801 shells. The TEM images show that, after an MAS step, a layer of polycrystalline Ni-MOF-74 was evenly deposited on the MOF-801 surface to give a core–shell MOF particle (Figure 1a and Figure S1b). The average thickness of the Ni-MOF-74 shell was estimated to be ∼20 nm. Energy dispersive X-ray spectroscopy (EDS) elemental mapping results and line scan results unambiguously show that the Ni signal is distributed on the outer surface of the particle (Figure 1b). The powder X-ray diffraction (PXRD) pattern of 801@Ni74 shows an integration of characteristic peaks from Ni-MOF-74 and MOF-801, suggesting good crystallinity for both layers (Figure 1c). Nevertheless, peak broadening is apparent in the case of Ni-MOF-74 due to the extremely small crystallite size. Using the Scherrer equation (eq S(8)), the average crystallite size of Ni-MOF-74 was estimated to be ∼12 nm. The N2 adsorption isotherm of 801@Ni74 falls in between that of MOF-801 and Ni-MOF-74, affirming that the crystallinity and porosity of both MOFs are well preserved in the core–shell form (Figure 1d). Interestingly, the pore size distribution analysis of 801@Ni74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either MOF-801 or Ni-MOF-74 (Figure 1e). This likely originates from the surface roughness, defects, and interpore gaps in the Ni-MOF-74 layer. This unique structural feature and its impact on the interfacial interaction and transport properties will be discussed in detail in the latter part of the work (vide infra).

Taking a closer look at the Ni-MOF-74 crystallites, we surprisingly found that, on multiple occasions, Ni-MOF-74 grew on MOF-801 surfaces with a preferential orientation. Figure 2a and Figure S4 show that the 1-D pores within several MOF-74 crystallites are perpendicularly to the MOF-801 surface which happens to be its (111) crystal facets. By careful examination of all of the Ni-MOF-74 crystallites with visible pore orientation on a single MOF-801 particle, it is clear that, although Ni-MOF-74 crystals with horizontal pore alignment do exist in the shell layer, the vertical pore alignment is the preferred orientation. The (111) crystal facet of MOF-801 exhibits a hexagonal 2-D lattice with a lattice constant of 12.61 Å. Interestingly, the (001) crystal facet of Ni-MOF-74 also exhibits a hexagonal lattice with a lattice constant of 25.88 Å, doubling that of MOF-801. The high degree of matching in lattice symmetry as well as lattice parameters between the two MOFs enable the anisotropic growth of Ni-MOF-74 from MOF-801 surfaces (Figure 2b). A similar phenomenon has also been observed and documented by other groups.56−58

To demonstrate the generalizability of this MAS method for constructing core–shell MOFs, a series of core–shell structures, UiO-66-NH2@Ni-MOF-74, MIL-101(Cr)@Ni-MOF-801, and MIL-101(Cr)@Co-MOF-74 (Figure 3a) were synthesized by using the MAS method as well. The powder X-ray diffraction (PXRD) pattern of UiO-66-NH2@Ni-MOF-74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either UiO-66-NH2 or Ni-MOF-74 (Figure 3b). The powder X-ray diffraction (PXRD) pattern of MIL-101(Cr)@Ni-MOF-74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either MIL-101(Cr) or Ni-MOF-74 (Figure 3c). The powder X-ray diffraction (PXRD) pattern of MIL-101(Cr)@Co-MOF-74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either MIL-101(Cr) or Co-MOF-74 (Figure 3d). The powder X-ray diffraction (PXRD) pattern of MIL-101(Cr)@Co-MOF-74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either MIL-101(Cr) or Co-MOF-74 (Figure 3e). The powder X-ray diffraction (PXRD) pattern of MIL-101(Cr)@Co-MOF-74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either MIL-101(Cr) or Co-MOF-74 (Figure 3f). The powder X-ray diffraction (PXRD) pattern of MIL-101(Cr)@Co-MOF-74 shows an appearance of mesoporosity in the range from 2 to 10 nm which is not present in either MIL-101(Cr) or Co-MOF-74 (Figure 3g).
MOF-74, UiO-66@Ni-MOF-74, and UiO-66@Co-MOF-74 were synthesized (Figure 1f). Furthermore, examples of core−shell MOFs between topologically distinct Zr, Fe, and Ti MOFs (e.g., UiO-66@MOF-801, UiO-66@MIL-125(Ti), UiO-66@MIL-100(Fe), and MOF-801@UiO-66) can also be easily constructed via this approach (Figure S2). The PXRD analysis of these core−shell structures can be found in the Supporting Information (Figure S3).

Next, MMMs containing different amounts of MOF-801, UiO-66-NH₂, or 801@Ni were prepared through a classic solution casting technique. A high-performance polyimide (PI), 6FDA-durene (6FDA = 4,4’-(hexafluoroisopropylidene) diprophalic anhydride; durene = 2,3,5,6-tetramethyl-1,4-phenylenediamine; the synthesis of 6FDA-durene can be found in the Supporting Information), was selected as the matrix polymer. The MOF loading in the MMMs was carefully quantified by thermogravimetric analysis (TGA) (Figure S5 and Table S1). For simplification, these MMMs are denoted as 801(9)durene, 801(22)durene, UiO-66-NH₂(7)durene, 801@Ni74(10)durene, 801@Ni74(16)durene, and 801@Ni74(26)durene, respectively. The numbers in parentheses represent the weight percentages of the MOFs.

The dispersibility of the MOF particles in the PI matrix was characterized by imaging the cross-section of the MMMs using scanning electron microscopy (SEM). No apparent agglomeration or precipitation was observed in 801(9)durene, 801(22)durene, 801@Ni74(10)durene, 801@Ni74(16)durene, and 801@Ni74(26)durene (Figure S6). To evaluate the interfacial compatibility between the MOF particles and the polymer matrix, 801(9)durene, UiO-66-NH₂(7)durene, and 801@Ni74(10)durene were cut into ∼70 nm ultrathin slices using an ultra-microtome for transmission electron microscopy (TEM) imaging (Figure S7a). Both 801(9)durene and 801@Ni74(10)durene exhibit significantly less mechanical tearing at the MOF−polymer interface along the knife cutting direction compared to that of UiO-66-NH₂(7)durene under the same preparation conditions (Figure S7a and Figure S7b). This result suggests that both MOF-801 and 801@Ni74 surfaces can interact favorably with the PI matrix. The interaction between UiO-66-NH₂ and PI is, however, comparably inferior.

To further investigate how MOF-801 and 801@Ni74 interact with PI, we performed a surface polymer adsorption experiment. Specifically, MOF-801 and 801@Ni74 were
dispersed in chloroform along with an excess of 6FDA-durene to allow PI to adsorb to the MOF surface. After incubation, centrifugation, and successive chloroform washing, TEM images were taken (Figure 3b(i) and (iii)). It is apparent that a thin layer (<5 nm) of PI was evenly coated on the surface of MOF-801 with good uniformity, suggesting excellent wettability of 6FDA-durene on the MOF-801 surface (Figure 3b(i)). After dissolving MOF-801 using HF, the remaining PI manifests a capsule-like shape, retaining the full morphology of MOF-801 particles (Figure 3b(ii)). 801@Ni74, on the other hand, exhibits a much smoother surface after PI adsorption, implying that the PI fills the mesoscopic gaps between the MOF-74 crystallites (Figure 3b(iii)). This became more revealing after selectively removing the Ni-MOF-74 layer with nitric acid, as the surface PI layer shows greater thickness and more interior wrinkling compared to that on MOF-801 (Figure 3b(iv)). Quantification of the surface adsorbed PI using TGA reveals that the 801@Ni74 surface can retain 13.4 wt % PI, whereas MOF-801, despite its smaller particle size, can only retain 4.1 wt % (Figure 3c and Figure S8). This tripling of surface polymer adsorption can be attributed to the extra external surface area and mesoscopic gaps contributed by the roughened MOF-74 shell layer. Figure 3c also shows that subsequent washing using chloroform has little to no effect on removing the surface adsorbed polymer, suggesting relatively strong adhesion at the MOF-PI interfaces.

Next, we sought to investigate the molecular interaction at the interface using molecular dynamic (MD) simulation. Since the exact surface chemistry of Ni-MOF-74 is unknown, we constructed two structural models for the (100) facet of MOF-74. The first model is a partially activated sample in which the surface Ni atoms are coordinated with one water molecule and two hydroxyl groups, leaving one OMS available for coordination. The second model is a fully activated sample in which the coordinated water was removed, leaving two OMSs per atom. Although uncoordinated ligand molecules may also be present on the surface, it interacts with PI mainly through hydrogen bonding identical to that of water. Therefore, the surface dangling ligand was not considered in the structural model. After a 10 ns MD simulation of the Ni-MOF-74/6FDA-durene composite system, we found that the interfacial interaction is dominated by a HO···O hydrogen bond, a Ni−O coordination bond, and a Ni−F coordination bond (Figure 3e). Through comparison between the partial activation and full activation models, it is apparent that the removal of the coordinated water molecule led to an increased contribution of Ni−O and Ni−F coordination and decreased contribution of hydrogen bonding. Figure 3d shows an example of a segment of the 6FDA-durene chain with six repeating units that has established four Ni−O coordination bonds and one HO···H hydrogen bond with the MOF surface. Encouraged by the structural characterizations, we sought to investigate the pure gas transport properties of the MMMs. Recalling from our previous study,36 direct mixing of neat UiO-66-NH2 and ODPA-DAM (ODPA = 4,4′-oxiphthalic anhydride, DAM = 2,4,6-trimethyl-1,3-phenylenediamine) resulted in a weak and defective interface. As shown in Figure 4a and Table S2, incorporating neat UiO-66-NH2 into ODPA-DAM led to a stepwise increase of CO2 permeability from 61 to 83 for neat ODPA-DAM to 148 Barrer for UiO-66-NH2(24)-44a andTable S2, incorporating neat UiO-66-NH2 into ODPA-DAM with increasing MOF loading. Meanwhile, the CO2/CH4 selectivity decreased from 28 to 24. Such behavior is consistent with our previous report and therefore indicative of the presence of nonselective voids at the MOF–polymer interface.38 In contrast, with the increase of 66-NH2@Ni74 loading in ODPA-DAM, CO2 permeability increased continuously from 61 to 75 and 90 Barrer for ODPA-DAM, 66-NH2@Ni74(10)ODPA, and 66-NH2@Ni74(22)ODPA, respectively. Meanwhile, the CO2/CH4 selectivity also increased from 28 to 32 to 44, respectively. This trend is reminiscent of our previous study where covalently grafted polyimide brushes were used to improve interfacial compatibility in MMMs.39

Next, MOF-801 and 801@Ni-74 were also used as fillers to fabricate MMMs. Due to the small aperture size of MOF-801,
we are keen to evaluate their transport properties for C$_2$H$_4$/C$_2$H$_6$ separation. As shown in Figure 4b, incorporating neat MOF-801 into 6FDA-durene resulted in a stepwise increase of C$_2$H$_4$ permeability from 36 to 40 to 48 Barrer for 6FDA-durene, 801(9)durene, and 801(22)durene, respectively. C$_2$H$_4$/C$_2$H$_6$ selectivity increased from 3.36 for 6FDA-durene...
to 3.47 and 3.77 for 801(9)durene and 801(22)durene, positioning 801(22)durene slightly above the 2013 upper bound for C2H4/C2H6 separation. This permselectivity trend suggests that MOF-801 has a favorable interaction with the PI matrix, thus leading to a series of defect-free MMMs. The permeability and selectivity values of 801(x)durene membranes satisfactorily followed the Maxwell model with the C2H4/C2H6 ideal selectivity and C2H4 permeability of neat MOF-801 membrane estimated to be 13 and 526 Barrer, respectively (eq S(7) and Figure S14). In contrast, the C2H4/C2H6 selectivity of 801@Ni74(x)durene membranes increased sharply from 3.36 for neat 6FDA-durene to 4.23, 5.44, and 5.91 for 801@Ni74(10)durene, 801@Ni74(16)durene, and 801@Ni74(26)durene, respectively. Meanwhile, the C2H4 permeability only decreased slightly from 36 to 26 with increasing MOF loading. The C2H4/C2H6 separation performance of 801@Ni74(16)durene and 801@Ni74(26)durene well surpassed the 2013 upper bound, positioning them as one of the highest performing C2H4/C2H6 separation membranes reported to date (Figure 4b and Table S12). Interestingly, when 801@Ni74 was replaced by larger pore analogues, 66-NH2@Ni74 and 66@Ni74, their respective MMMs, 66@Ni74(9) and 66@Ni74(12)durene, did not show an appreciable increase of C2H4/C2H6 selectivity even with the
presence of Ni-MOF-74 interphase (Figure S13). Furthermore, the MMMs of 6FDA-durene containing 2.4 and 18 wt % neat Ni-MOF-74 exhibit a slightly lower \( C_2H_4/C_2H_6 \) ideal selectivity compared to that of the neat 6FDA-durene, implying that Ni-MOF-74 alone does not contribute to the increase of \( C_2H_4/C_2H_6 \) selectivity (Figure 4b). Therefore, it is reasonable to conclude that the increase of selectivity can be attributed to the size selectivity of MOF-801. When 6FDA-durene was replaced by another high-performance PI matrix, 6FDA-DAM (6FDA = 4,4′-(hexafluoroisopropylidene) diphthalic anhydride; DAM = 2,4,6-trimethyl-1,3-phénylenediamine), the \( C_2H_4/C_2H_6 \) ideal selectivity also drastically increased from 3.39 for 6FDA-DAM to 4.49, 4.60, and 5.34 for 801@Ni74(8)DAM, 801@Ni74(10)DAM, and 801@Ni74(18)DAM, respectively, which is similar to that of 801@Ni74(x) durene membranes. \( C_2H_6 \) permeability, on the other hand, increased slightly from 20 to 33 with increasing MOF loading.

To gain more insights on the gas transport mechanisms, the \( C_2H_4 \) and \( C_2H_6 \) permeability (\( P \)) in neat 6FDA-durene, 801(22)durene, and 801@Ni74(18)durene was deconvolved to the product of the sorption coefficient (solubility, \( S \)) and the diffusion coefficient (diffusivity, \( D \)) based on the solution-diffusion model.\(^{22} \) Solubility was obtained from the high-pressure adsorption isotherms of the membrane samples (Figure S20b). Diffusivity was then calculated accordingly using \( P \) and \( S \) (Figure 4c and Table S3). The addition of MOF-801 and 801@Ni74 into 6FDA-durene simultaneously increased the solubility of \( C_2H_4 \) and \( C_2H_6 \) in the membranes due to preferential adsorption in MOFs. However, the sorption selectivity remains at \( \sim 1 \) even after MOF incorporation, suggesting C2 selectivity does not originate from preferential adsorption in either MOF or polymer (Figure 4d). On the other hand, 801(22)durene exhibits a slightly higher \( C_2H_4 \) diffusivity and lower \( C_2H_6 \) diffusivity than those in neat 6FDA-durene, resulting in a noticeable increase of diffusion selectivity from 3.09 to 3.61. In contrast to 801(22)durene, the diffusivity of both \( C_2H_4 \) and \( C_2H_6 \) was decreased in 801@Ni74(16) compared to neat polymer (Figure 4d). This is likely due to the presence of grain boundaries in the MOF-74 layer. However, this drop of permeability was more conspicuous for \( C_2H_6 \) than \( C_2H_4 \). Consequently, the diffusivity selectivity of 801@Ni74(16) was drastically improved. Overall, the enhancement of \( C_2H_4/C_2H_6 \) selectivity can be attributed to the diffusion selectivity of the MOF-801 core and the presence of the Ni-MOF-74 shell layer amplified this effect. To further unveil the role of OMS on the transport behaviors, two membrane samples, 801@Ni74(x)durene (\( x = 10 \) and 16), were exposed to a humid environment (60–100% R.H.) for a prolonged period of time to have all of the OMSs blocked by water molecules. The membranes were then activated at 80 °C in a membrane cell to remove water in the MOF pores without eliminating coordinated water molecules.\(^{63} \) The transport data shows that these membranes exhibit lower selectivity and permeability compared to their parent membrane, suggesting that the blockage of OMSs in Ni-MOF-74 is detrimental to the interfacial integrity and transport properties of the membranes (Figure S13). Since Ni-MOF-74 only accounts for a small fraction of the membranes (2.9 and 4.6 wt %), we reason that the loss of membrane selectivity is a result of coordination bond dissociation at the interface.

\( C_2H_4 \) and \( C_2H_6 \) adsorption kinetics was studied by a pressure decay method (Figure S15). Using the constant surface concentration model (a.k.a. Fickian diffusion model\(^{64}) \) (eq S(1)), \( C_2H_4 \) and \( C_2H_6 \) kinetic uptake curves were fitted and \( D_j/r^2 \) (where \( D_j \) is the diffusion coefficient and \( r \) is the diffusion length; \( D_j/r^2 \) represents the gas adsorption rate) values were calculated. Due to the presence of artificial effects (for the pressure decay method, the initial data points after closing the valve were found to be the influenced response of the pressure transducer as well as rapid expansion to dead volume expansion\(^{65,66}) \) when measuring sorption kinetics of fast diffusing gases (i.e., \( CO_2 \), \( CH_4 \), \( C_2H_6 \), and \( C_2H_2 \)), large Ni-MOF-801 (\( \sim 5 \mu m \)) and Ni-MOF-74 (\( \sim 1.2 \mu m \)) crystals were synthesized and used to minimize this effect (Figure S16). As shown in Figure 4e and Table S4, the \( D_j/r^2 \) value of \( C_2H_4 \) in MOF-801 is 6.84 \( \times 10^{-3} \) s\(^{-1} \) (308 K, \( P/P_0 = 0.003 \)), doubling that of \( C_2H_6 \) (3.27 \( \times 10^{-3} \) s\(^{-1} \)). The diffusion coefficient (\( D_j \)) calculated from molecular dynamic (MD) simulation shows that \( C_2H_4 \) diffuses 9 times faster than \( C_2H_6 \) in MOF-801 at 0.01 bar, which is comparable to the ideal selectivity calculated through the Maxwell model (Figure S14, Figure S19, and Table S11). On the contrary, the \( D_j/r^2 \) value of \( C_2H_4 \) in Ni-MOF-74 is 5.55 \( \times 10^{-3} \) s\(^{-1} \), which is less than half of that of \( C_2H_6 \) (Figure S17 and Table S4). Static gas adsorption experiments show that the \( C_2H_2 \) isotherm of MOF-801 is slightly higher than that of \( C_2H_6 \) whereas the \( C_2H_4 \) isotherm of Ni-MOF-74 is appreciably higher than \( C_2H_6 \) (Figure S20a). However, compared to the kinetic factor, the difference in solubility is relatively inconsiderable. This suggests that the increase of \( C_2H_4/C_2H_6 \) ideal selectivity in MMMs is a result of kinetic separation in the MOF-801 core.

Interestingly, despite that MOF-801 interacts favorably with PI, the drastic increase of \( C_2H_4/C_2H_6 \) selectivity was only observed when the MOF-74 interphase was present. A plausible explanation is that the oriented growth of the polycrystalline MOF-74 shell encourages vertical transport of gas molecules through the 1-D channels perpendicular to the MOF-801 surface, while it hinders the horizontal diffusion of gases due to the impermeable pore walls and the presence of grain boundaries. Consequently, this action directs gas molecules into the MOF-801 core, resulting in an increase of the partition of gas flux through the selective MOF-801 phase and subsequently the increase of C2 selectivity. We name this transport mechanism as “gas focusing”. On the other hand, without the MOF-74 interphase, gas molecules preferably travel through the highly permeable polymer matrix, thereby lowering the partition of gas flux in the MOF-801 core (Figure 4f).

**CONCLUSION**

In conclusion, we demonstrated a dual-interfacial engineering approach as a generalizable strategy to improve the interfacial compatibility in MMMs. The sub-20 nm MOF-74 shell synthesized by a microwave-assisted method exhibits an uneven, mesopore-containing surface texture leading to a drastic increase of interfacial area. This factor along with the exposed OMS and hydrogen bond forming groups from the MOF-74 surface contribute to a strong interaction with the polymer matrix at the interface. In addition, the anisotropic growth of Ni-MOF-74 crystallites in the shell layer inhibited the horizontal transport of gas molecules, thus leading to an increase of \( C_2H_4/C_2H_6 \) selectivity through a “gas focusing” mechanism. We believe this dual-interfacial designing approach offers a generalizable solution for enhancing MMM interfaces.
and will shed light on the rational design of high-performance MMMs with more complex architectures for gas separation.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c07378.

Materials, synthesis, characterization, supplemental figures and tables, and references (PDF)

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Notes
The authors declare no competing financial interest.

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