INTRODUCTION

The fossil-fuel-based economy is recognized as the main cause for the greenhouse gas emission worldwide with more than 2 billion tons of exhaust carbon dioxide each year.1 A sustainable economy is able to the drastically reduce the quantity of carbon dioxide (CO2) released in the atmosphere, with the aim of arriving at zero carbon by 2050.1 Nevertheless, the continuous population and economy growth is expected to increase the CO2 emissions that need to be captured and stored or used at a feasible cost. The existing (current conventional) technology is energy intensive and costly and thus not ideal for the needed scale to mitigate the colossal amounts of yearly emitted CO2, nearly 40 Gt/year. Logically, an energy-efficient CO2 capture process is identified to represent the dominant factor for the prospective cost reduction in the whole CO2 capture and storage system. Accordingly, energy-efficient CO2 capture process is highly desirable.2−5 Membrane-based separation offers substantial advantages over conventional processes, including lower power consumption, smaller footprint, and notable economic benefits over other competing separation technologies.6−9

The unique structural features of nanoporous metal−organic frameworks (MOFs), in contrast to other nanoporous materials, including the ease to rationally functionalize and fine-tune their pore system,10 paved the way for incorporating MOFs into various fields of applications pertaining to sensing, gas separation, and storage.11 Certainly, MOFs have shown great potential in CO2 separation predominantly from gases containing CH4, N2, and H2 using principally kinetics and equilibrium-based adsorption technologies.10−12 As bulk microcrystalline powders MOFs have been explored and tested for various practical purposes, like adsorption based-separation and gas storage, sensing catalysis, and drug release, conferred by their large pore volumes that can accommodate a large amount of guest molecules and regulated small pore-apertures that can selectively control and/or discriminate between guest molecules.13

The tunability of nanoporous MOFs offers great potential for their deployment as gas separating agents, especially the membrane-based approach is emerging and has gained notable consideration in the last years.14 The deployment of MOFs as membranes for gas separation and purification remains challenging and mostly relies on the ability to construct continuous/defect-free MOF thin-films.14,15 Despite the intensive research concerned with the fabrication of MOF
membranes, it is still in its early stages and a more constructive and cooperative efforts are needed to overcome the persisting challenges, like growing defect-free thin films that exhibit very good bonding/adhesion to the support. In fact, only a few studies are found in the literature on pure MOF grown as membrane for gas thin films.\textsuperscript{14} Because of the more convenient and reliable preparation methods of bulk MOF materials, there is growing interest in the application of MOF nanocrystals as fillers in mixed-matrix membranes (MMM), which potentially would lead to improved gas permeabilities and selectivities in comparison to the pure polymer-based membranes.\textsuperscript{8,9} The fundamental understanding of pure MOF membrane properties (intrinsic/inherent permeation and selectivity) and performances is vital to building the knowledge necessary for the construction of the looked-for MMM.

Despite the importance of pre- and postcombustion capture and upgrading of natural gas (NG) applications, a limited number of reports were published on the separation of CO$_2$/H$_2$ and CO$_2$/CH$_4$ gas systems based on pure MOF membranes. A highly efficient membrane for carbon capture from gases, mainly containing CH$_4$ and H$_2$, has to express a high permeance for CO$_2$ in contrast to other tested gases, promoting highly valuable supplies such as H$_2$ and CH$_4$. It is to be noted that reports pertaining to the separation perme-selectivity in favor of CO$_2$ are scarce with pure MOF-based membranes and are limited; to the best of our knowledge, only bio-MOF-1, a single-crystal membrane of [Cu$_2$(bza)$_2$(puz)],\textsuperscript{16} and our sod-ZMOF membrane have been reported.\textsuperscript{17}

Recently, our group reported CO$_2$ sorption studies on isoreticular nanoporous MOFs with periodically arranged hexafluorosilicate (SIFSIX) pillars, namely SIFSIX-2-Cu-I and SIFSIX-3-M, where M = Zn, Cu, and Ni.\textsuperscript{18–20} The resultant nanoporous MOFs offer a tunable pore-aperture size (rather than high surface area) and the required pore system chemistry, affording unique adsorbent materials with homogeneously aligned strong CO$_2$ adsorption sites in a confined one-dimensional pore system and offering fast and highly selective CO$_2$ behavior over CH$_4$ and H$_2$.\textsuperscript{18} Markedly, the contracted pores in the isoreticular analogues, namely SIFSIX-3-M, expressed a relatively steeper CO$_2$ sorption isotherms in contrast to SIFSIX-2—Cu-I. In addition, we demonstrated that slightly reducing the pore-aperture size of these materials by cation replacement/substitution of Zn with Cu from 0.384 to 0.350 nm resulted in unprecedented CO$_2$ uptake and selectivity in the perspective of direct air capture (DAC) and trace CO$_2$ removal. The replacement of Zn with Ni led to successful synthesis (using both solvolothermal and solvent-free approaches) of new isostructural CO$_2$ selective analogue (SIFSIX-3-Ni) with a pore-aperture size of 0.369 nm, a high selectivity for CO$_2$ (similar to Zn analogue), and a notable stability/high tolerance to H$_2$.\textsuperscript{20}

In light of the unique properties of this class of materials, we found it compelling to explore their deployment as a continuous MOF membrane for CO$_2$ capture, paving the way to shift the use of this platform from solid adsorbent to a membrane-based separation. To begin with, our countless attempts to fabricate a defect-free thin film of the SIFSIX-3-Zn on the porous alumina substrate were not successful. Therefore, we concentrated our efforts on the fabrication of Cu and Ni analogues on the porous alumina substrate. Initially, the used conventional solvolothermal method led to the construction of noncontinuous thin films, composed of small crystals of SIFSIX-3-Cu of about 500 nm in size (Figures S1 and S2), whereas in the case of SIFSIX-3-Ni, the thin films were composed of crystal agglomerates ~2 μm in size (Figures S3 and S4).\textsuperscript{19,20} The fast precipitation, occurring immediately upon mixing the reagents, prohibited the crystal intergrowth and prompted us to explore other alternative approaches. Accordingly, we embarked in an exploratory study aiming to fabricate the first nanoporous SIFSIX-3-M membrane using the liquid-phase epitaxy (LPE) growth approach (see Scheme 1),\textsuperscript{21–31} which was successfully used to grow defect-free thin films on porous alumina support as demonstrated earlier in the case of ZIF-8 membrane.\textsuperscript{22} The LPE process has the merit to slow down and control the crystal growth rate and enhance the quality of the thin films.\textsuperscript{24} The LPE technique has many other advantages compared to the other growth approaches in terms of mild fabrication conditions and ability to control thickness, postfunctionalization, and crystal orientation.\textsuperscript{24–26} The LPE synthesis approach for the SIFSIX-3-M membrane is presented in Scheme 1. To the best of our knowledge, none of these SIFSIX-3-M MOFs have ever been synthesized nor grown as a thin film attached to a surface using the LPE approach and subsequently explored as a membrane for gas separation.

**RESULTS AND DISCUSSION**

The fabrication of defect-free and continuous thin films of SIFSIX-3-M (M = Zn, Cu, Ni) on the porous alumina substrate (diameter = 21 mm) was not an easy task. We explored initially the use of conventional solvolothermal method and a seeding approach to fabricate a thin film membrane. However, all obtained membranes were not defect-free thin films and not of a good quality for the targeted application as inferred/suggested from scanning electron microscope (SEM) and gas permeation studies. As a result, we focused our attention on the LPE method because of the many advantages it has over the other methods in terms of mild fabrication conditions and the ability to control thickness and crystal orientation in the film.\textsuperscript{24} To the best of our knowledge, this is the first example of SIFSIX-3-M MOF materials to be synthesized and grown using the LPE approach as a thin film.

![Scheme 1. (a) Scheme of the Liquid-Phase Epitaxy (LPE) Method Applied for the Growth of SIFSIX-3-M Thin Film, (b) View of SIFSIX-3-M Assessable Accessible Channel, (c) Scheme of SIFSIX-3-M Membrane Grown on Al$_2$O$_3$ Substrate](https://dx.doi.org/10.1021/acsanm.0c00909)
Our countless attempts to fabricate a defect-free thin film of the SIFSIX-3-Zn analogue with the LPE method were not successful. As a result, we directed our efforts for the fabrication of Cu and Ni thin film analogues. Delightfully, after many attempts, we were successful in isolating the optimized condition to fabricate a continuous SIFSIX-3-Cu membrane. A new activated alumina substrate was dipped in the 0.13 M methanolic solution of CuSiF6 for 10 min at 65 °C. The sample was then rinsed with methanol and dipped for 10 min at 65 °C in the 0.5 M pyrazine methanolic solution, and afterward removed and solvent over washed, completing the first cycle. The thickness of the thin film based on the LPE approach, as commonly acknowledged from earlier studies, is governed by the quantity of growth cycles, governing the overall thickness of the fabricated SIFSIX-3-M membrane.23,24 The structural features were confirmed by X-ray diffraction (XRD) and morphological features by SEM. The structure of the fabricated SIFSIX-3-Cu thin film was established by XRD patterns as depicted in Figure S5 for the Cu analogue. The XRD patterns of the grown thin films agree perfectly with the calculated pattern. SEM images (Figure S6) attest that using the LPE approach led to the fabrication of a homogeneous and defect-free thin film of SIFSIX-3-Cu. Particularly, further examination of the resultant thin-film revealed the formation of densely packed microsized and very well intergrown SIFSIX-3-Cu crystallites on the surface of the support with no visible defects like cracks or pinholes (Figure S6).19

To evaluate the gas transport property of the resulting membrane, we performed pure-gas permeation tests. The resulting SIFSIX-3-Cu thin-film membrane was fixed in a permeation cell and tightly sealed from both sides for gas permeation measurements.17 Unfortunately, our tests showed that the preliminary evacuation of the cell containing the membrane, with vacuum upstream and downstream, resulted in the formation of cracks. Consequently, we were not able to collect single permeation with steady-volume/variable-pressure permeation tests shown in Scheme S1. To prevent the cracks during the permeation tests, we opted to use in the case of SIFSIX-3-Cu the mixed-gas permeation associated with a gas analysis system, which is shown in Scheme S2,14 where 1−2 bar of flowing helium is used as an activation gas instead of a vacuum. We were successful in evaluating the CO2 selectivity against H2 and CH4 for the SIFSIX-3-Cu membrane. Notably, CO2/H2: 30/70 and CO2/CH4: 50/50 mixed-gas permeation experiments at 308 K and 2 bar showed a favorable selectivity for CO2 of ca. 27 and 14.6 over H2 and CH4, respectively (Figure 1).

In light of these promising results, we extended our studies to the Ni membrane analogue. The suitable conditions affording the continuous growth of SIFSIX-3-Ni thin film on the alumina support were isolated. In particular, a similar procedure used for the Cu analogue was implemented for the Ni analogue with the exception of the concentration of the pyrazine methanolic solution, which was reduced to 0.26 M. The XRD pattern of the resultant SIFSIX-3-Ni-grown thin film is presented in Figure 2, reflecting a perfect match with the simulated XRD pattern in terms of the positions of the peaks and attesting to the formation of a pure phase SIFSIX-3-Ni. However, the relative peak intensity is considerably dissimilar. In fact, the peak at 2θ of 12.4°, corresponding to the (100) planes within the lattice of the SIFSIX-3-Ni crystal, is relatively more intense in contrast to other peaks, attesting to the preferential orientation growth of the film along the direction orthogonal to the (100) plane.14 As a result, the one-dimensional channels of SIFSIX-3-Ni are readily exposed for the passage of gases. Distinctly, this appropriate preferential
orientation offers the advantage of directly exposing the desired channels within SIFSIX-3-Ni, regarded as the sole accessible path for the gas to enter the associated pore system.19

SEM images (Figure 3a) affirm the successful fabrication of a homogeneous and defect-free SIFSIX-3-Ni membrane. The thin film is mainly composed of the desired densely packed, well-inter-grown nanoporous microsized crystallites of SIFSIX-3-Ni on the surface of the alumina support only, with no indication of defects like pinholes or macro-sized cracks.20,32

The cross-section SEM image attests to no crystals growth within the pores of the substrate, and corroborates the high quality of the grown membrane of SIFSIX-3-Ni with nearly a 5 μm thickness resulting from 25 cycles (Figure 3b), attesting to the appropriateness of the LPE method in producing continuous and densely packed ultrathin films.32

Figure 3. SEM images of SIFSIX-3-Ni thin films fabricated on alumina support, (a) top view, (inset) optical image of the as synthesized membrane. (b) Cross-section.

Figure 4. (a) Time-lag measurement for CO2. (b) SIFSIX-3-Ni membrane single gas permeability at 308 K vs the Lennard–Jones diameter of He, H2, CO2, O2, N2, and CH4. (c, d) Estimated diffusion coefficient and adsorption coefficient from the permeation data for tested gases.
permeation tests, which resulted in limiting the active area of the membrane to be of 1.4 cm².32

The single gas permeation measurements of injected gases He, H₂, CO₂, O₂, N₂, and CH₄ (with a purity of >99.99%) were done for the SIFSIX-3-Ni membrane using the constant-volume/variable-pressure (CV/VP) permeation technique.20,24 To eliminate any possible residual guest molecules (mostly methanol), an additional step of activation was carried out in situ by applying vacuum to both upstream and downstream sides of the cell at 308 K. In contrast to the Cu analogue, preliminary tests showed that the SIFSIX-3-Ni membrane is much robust when it is exposed to vacuum conditions.

The full evacuation of the resultant membrane was assumed when the rise in the downstream pressure during the test was smaller than 1%. In the case of pure single gas, the permeation tests were done using 2 bar upstream pressure. Consecutively, we monitored the rise in the downstream pressure for each run in the single-gas permeation of He, H₂, CO₂, O₂, N₂, and CH₄ using a 10 Torr scale transducer. When no notable change was detected in the pressure rise after the time lag was started, i.e., 7–10 times, the steady state in gas permeation was considered to be reached. Notably, the permeability of the material for gas can be derived from the steady-state region.32 Figure 4a shows the pressure response for the CO₂ permeation measurement through the SIFSIX-3-Ni membrane at 308 K. The observation of pressure-rise curves in the case of the single gases (Figure 4a) revealed the gas-transport diffusional resistance, typical for high-quality films with negligible contribution from intercrystalline defects or gaps. Remarkably, this time-lag phenomena was mostly noted for tested gases, except He (Figure 4b), confirming the nonappearance of defects in the film. The relatively high O₂/N₂ selectivity of 1.5 is an additional evidence to the nonappearance of defects in the film. The single-gas permeation tests displayed a distinct maximum in the permeability of CO₂ in contrast to other evaluated gases except H₂ (Figure 4b). Therefore, as shown in Figure 4b, the SIFSIX-3-Ni membrane unveiled higher ideal selectivity for CO₂ over N₂, O₂, and CH₄. The achieved ideal separation factors for CO₂ in contrast to other gases were (CO₂/N₂) = 4 (CO₂/O₂) = 3.6 and (CO₂/CH₄) = 2. Interestingly and in contrast to all other single gas permeations, SIFSIX-3-Ni shows slightly favorable ideal selectivity for H₂ vs CO₂.

The obtained single-gas permeation data were additionally evaluated by applying the solution-diffusion model that is appropriate to structures possessing nominal pore diameter smaller than 10 Å.33–35 The gas permeability through a dense or microporous framework is simply calculated as the multiplication of diffusion and solubility coefficients. In this model, diffusion is described by means of a diffusion coefficient, D, that reflects the kinetics of gas transported through a membrane, which can be associated well with the value of the molecular size of gas.

It is to be noted that D is calculated experimentally from permeation time-lags and the solubility (S), defined as the sorption coefficient taking into account the interactions of gases with the framework and gas condensability, is calculated indirectly using the solution-diffusion model with a preknowledge of values of P and D, herein, S = P/D.32–35

Figure 4c reveals that all tested gas molecules faced resistance to diffusion through the SIFSIX-3-Ni membrane, leading to an overall drop in diffusion coefficients with increasing the diameter size of probe molecules (here expressed as Lennard–Jones diameters). When the gas diameter size approach 3.8 Å (which is the pore-aperture size calculated from crystal data), the gas diffusion comes to be more constrained. Almost a 20-fold decrease in D values occurred going from H₂ (2.8 Å) to CO₂ (≈3.8 Å). In contrast, the S values for CO₂ vs all the other studied gases as shown in Figure 4d is in an excellent agreement with adsorption measurements performed on the bulk material.15–17 From single gas permeation data, the essential observation is that despite the diffusion restriction of CO₂ and the completely inversely interplay between CO₂ diffusion and solubility, the remarkable affinity of SIFSIX-3-Ni to CO₂ promotes CO₂ to be favorably driven by adsorption vs all other gases except for H₂.

Furthermore, to assess the real separation behavior of CO₂ against different gases for the SIFSIX-3-Ni membrane, CO₂/ H₂: 30/70 and CO₂/CH₄: 50/50 permeation tests were done by means of a mixed-gas permeation associated with continuous-gas analysis system.15–17 Interestingly, binary mixtures (mixed-gas) testing through the SIFSIX-3-Ni membrane unveiled a selectivity of 20.4 and 9.9 toward CO₂ vs H₂ (CO₂/H₂:30/70 mixture) and (CH₄ CO₂/CH₄:50/50 mixture, respectively. In spite of the highly favorable diffusivity of

Figure 5. Mixture mixed-gas permeation tests for the of SIFSIX-3-Ni membrane tested using VP-continuous permeate composition analysis system, using an upstream feed pressure of 2 bar at 308 K. (a) CO₂/H₂: 30/70, (b) CO₂/CH₄: 50/50. The real selectivity is calculated directly from the partial pressure in the permeation side of each gas.
single H₂ through the membrane (acquired from pure-gas permeation testing at 2 bar as depicted in Figure 5a), suggesting a high ideal selectivity in favor of H₂, the permeation in case of CO₂/H₂ mixture is highly favorable to CO₂ (even higher than CO₂/CH₄ in gas mixtures case Figure 5b) due mainly to the high CO₂ adsorption selectivity vs H₂. This is really evident from the analysis of different value of Sᵢₚ (ideal permeation selectivity), Sᵢₚ (ideal diffusivity selectivity), Sᵢₛ (ideal solubility selectivity), and Sᵢᵦₚ (real permeation selectivity) (Table 1), where it is clearly shown that the trend in Sᵢₚ follow the trend of Sᵢₛ in case of CO₂/H₂ and CO₂/CH₄ mixture.

| selectivity | CO₂/H₂ | CO₂/CH₄ |
|-------------|--------|---------|
| Sᵢₚ         | 0.89   | 1.96    |
| Sᵢᵦₚ        | 20.40  | 10.00   |
| Sᵢₛ         | 0.05   | 0.27    |
| Sᵢᵦₛ       | 4.42   | 7.29    |

*Sᵢₚ: ideal permeation selectivity; Sᵢᵦₚ: ideal diffusivity selectivity; Sᵢₛ: ideal solubility selectivity; Sᵢᵦₛ: real permeation selectivity.

Table 1. Comparison of Single and Mixed-Gas Permeation Selectivities for SIFSIX-3-Ni Membrane in Case of CO₂/H₂ and CO₂/CH₄.46

It is to be stated that the noted high diffusivity of H₂ in the single gas H₂ permeation tests is drastically reduced in the presence of CO₂ as in the case of the CO₂/H₂ mixture. Decidedly, this unique reversed selectivity behavior is mainly due to the opposite thermodynamic effect in favor of CO₂ in accordance with the high adsorption equilibrium selectivity studies on SIFSIX-3-M bulk materials. The shift in CO₂ capture/separation from adsorbent to membrane led to a CO₂ selective membrane, albeit with much lower permeation selectivity than best polymer materials in case of CO₂/CH₄ system.34 To the best of our knowledge, the obtained mixed-gas CO₂/H₂ selectivities for the Cu and Ni analogue of SIFSIX-3-M membranes are the highest ever reported for pure MOF membranes. Although (conservatively) the CO₂/H₂ selectively is relatively high as compared to polymers, it is to be stated that the experimental mixed-gas permeation system used tend to underestimate the selectivity toward CO₂. In fact, at the steady state a high driving force is occurring upstream the cell, particularly for H₂ and CH₄ promoting diffusion (favorably more than CO₂) through the membrane when a combination of high selective CO₂ membrane is used with the total pressure of 1500 Torr and less than 10 Torr upstream and downstream, respectively. The nonpenetrant nature of the diffusion of gases in case of a MOF with permanent porosity as compared to nonporous polymers, i.e., the notable high affinity of the MOF adsorbent to CO₂ provoked the blocking of the MOF pore system for other gases in the case of mixtures containing CO₂. This could be another reason that promotes the diffusion/passing of the molecules with less affinity to the SIFSIX-3-M framework (H₂, CH₄) as compared to CO₂.

Thus, for critical assessment, the separation performance of all CO₂ selective (over H₂) MOF membranes reported in the open literature has been included in the plot shown in Figure 6. This analysis permitted us to position our pure MOF membrane as one of the best performing membranes when directly compared with corresponding data for selected zeolites and other benchmark polymer composite/MMM materials-based membranes, operating at room temperature (Table S1).

Figure 6. Robeson trade off plot (red line, calculated from Freeman fundamental study;23 pale red line, empirical Robeson plot; dashed, 1991;22 solid, 20084) for comparison of separation performances for representative CO₂-selective membranes in the case of CO₂/H₂ separation. These data points represent the results from mixed-gas studies (blue stars, MOFs; black squares, zeolites; black circles, polymer composites/MMM).

In conclusion, we have demonstrated that the key for further improvement of the membrane-based separation is to choose materials that have the right parameters for the targeted separation application (i.e., pore-aperture size and pore system with suitable surface chemistry). Therefore, we opted to select the nanoporous SIFSIX-3-M MOF platform (M = Ni, Cu), that fulfill these requirements. The prospective shift and deployment of pure SIFSIX-3-M (M = Ni, Cu) membranes, offering the potential to translate the exceptional sorption properties of these unique adsorbents into a membrane-based process, was recognized and unveiled due to our ability to successfully grow a defect-free SIFSIX-3-M (M = Ni, Cu) thin
film membranes using the LPE method. The excellent SIFSIX-3-Ni membrane quality in terms of continuity was affirmed via the noted time-lag occurrence for all tested gases, in addition to the expressed competitive permeation in favor of O\textsubscript{2} vs N\textsubscript{2}. The Ni and Cu analogues of SIFSIX-3-M membrane showed CO\textsubscript{2}/H\textsubscript{2} reversed selectivity of 20.6 and 27 and elevated selectivity for CO\textsubscript{2}/CH\textsubscript{4} of 9.9 and 15 toward CO\textsubscript{2} in case of the mixtures of CO\textsubscript{2}/H\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} respectively. The CO\textsubscript{2} favorable gas mixture permeation-selectivity is a clear indication of adsorption governed/dominance in permeation selectivity toward CO\textsubscript{2} in mixtures for all tested gases. This highly adsorption dominant permeation behavior in favor of CO\textsubscript{2} for this type of MOF membranes, well corroborated with analysis of ideal diffusivity and solubility selectivities, contributes to better understanding and advancing, by few steps toward, the ongoing quest for the development of CO\textsubscript{2} selective membranes.

The acquired knowledge in this study can potentially benefit our ongoing research activities pertaining to the deployment of SIFSIX-3-M nanoscale particles as suitable fillers in mixed-matrix membranes.

The study pinpoints the uniqueness of the reverse selectivity in MOFs and paves the way for researchers to look into MOFs for this specific industrially relevant application. It is to be stated that a more comprehensive method for the fabrication of a pure MOF membrane, under harsh conditions such as high temperature, remains extremely challenging for now, and thus in this study we opted to perform our testing under very mild condition as a start and a proof of concept. The SIFSIX-3-M class of materials, although not the most stable among fluorinated MOFs (compare to its analogues based on NbOF\textsubscript{5} \textsuperscript{36} AlF\textsubscript{5} \textsuperscript{37} instead of SiF\textsubscript{6}), because of the existence of 2D to 3D transition, allowed us to construct the first fluorinated MOF membrane of this kind with well-defined one-dimensional channel-like pore structure. It is to be noted, that the observed low permeability might be avoided with the deployment of three-dimensional interconnected pores, and work is in progress to explore this research avenue.

**EXPERIMENTAL SECTION**

**Materials.** All starting materials for synthesis were purchased commercially and were used without further purification.

**Support.** The alumina substrates (purchased from Cobra Technologies BV) were rinsed with water and later on dried at 140 °C.

**X-ray Diffraction (XRD).** PANalyticalX'Pert PRO diffractometer was used to measure the samples at ambient temperature using 45 kV, 40 mA for CuK\textsubscript{α} (\(λ = 1.5418\) Å) as operating conditions. The patterns were collected using 1.0° min\textsuperscript{-1} as a scan speed of and 0.01° as a step size of in 2θ range of 4°–40°.

**Scanning Electron Microscope (SEM).** Quanta 600 was used to acquire top and cross-section SEM images of MOF-on-MOF films.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnanm.0c00909.

Gas permeation measurements, SEM images, XRD patterns, and time-lag measurement (PDF)

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**Notes**

The authors declare no competing financial interest.

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