Computational Screening of Metal–Organic Frameworks for Membrane-Based CO$_2$/N$_2$/H$_2$O Separations: Best Materials for Flue Gas Separation

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ABSTRACT: It has become a significant challenge to select the best metal–organic frameworks (MOFs) for membrane-based gas separations because the number of synthesized MOFs is growing exceptionally fast. In this work, we used high-throughput computational screening to identify the top MOF membranes for flue gas separation. Grand canonical Monte Carlo and molecular dynamics simulations were performed to assess adsorption and diffusion properties of CO$_2$ and N$_2$ in 3806 different MOFs. Using these data, selectivities and permeabilities of MOF membranes were predicted and compared with those of conventional membranes, polymers, and zeolites. The best performing MOF membranes offering CO$_2$/N$_2$ selectivity $>350$ and CO$_2$ permeability $>10^6$ Barrer were identified. Ternary CO$_2$/N$_2$/H$_2$O mixture simulations were then performed for the top MOFs to unlock their potential under industrial operating conditions, and results showed that the presence of water decreases CO$_2$/N$_2$ selectivity and CO$_2$ permeability of some MOF membranes. As a result of this stepwise screening procedure, the number of promising MOF membranes to be investigated for flue gas separation in future experimental studies was narrowed down from thousands to tens. We finally examined the structure–performance relations of MOFs to understand which properties lead to the greatest promise for flue gas separation and concluded that lanthanide-based MOFs with narrow pore openings (<4.5 Å), low porosities (<0.75), and low surface areas (<1000 m$^2$/g) are the best materials for membrane-based CO$_2$/N$_2$ separations.

1. INTRODUCTION

Considering the increasing energy demand of our world, it is not possible to entirely stop the use of fossil fuels and the resulting anthropological CO$_2$ emission. As a result of burning of fuels, 41 billion tons of CO$_2$ has been released to the atmosphere. On the other hand, it is possible to reduce greenhouse gas emissions by CO$_2$ capture. There is a tremendous incentive to achieve CO$_2$ separation from power plant flue gas, which mostly consists of N$_2$, with high efficiency. Commercial technologies for CO$_2$/N$_2$ separation include absorption, adsorption, cryogenic distillation, and membrane-based separations. Among these technologies, membrane-based gas separation processes provide great advantages such as energy efficiency and easy scale-up, in addition to being environmentally safe. Polymer membranes have been commonly used in flue gas separations because of the ease of processability and large-scale production. However, these membranes are limited because of the trade-off between their selectivities and gas permeabilities. Therefore, there is an ongoing search for the new membrane materials offering high selectivity and high permeability for flue gas separations.

Metal–organic frameworks (MOFs) are porous structures combining metals with organic linkers. The utmost advantage of MOFs over traditional porous materials is that a very large variety of MOFs having different pore shapes/sizes and chemical functionalities can be synthesized by changing the combination of metal clusters and organic ligands. MOFs have received significant interest for many different processes, including gas storage, separation, drug storage and delivery, and catalysis, thanks to their interesting physical and chemical properties such as very large surface areas, high porosities, and a wide range of pore sizes. Gas separation, specifically CO$_2$ separation, using MOFs as adsorbents has been very widely investigated. Studies on gas separation with MOF membranes are still limited compared to adsorption-based separations with MOFs because of the difficulties in fabricating defect-free, thin-film membranes. Although several thousands of different MOFs have been deposited to the database, only a very small number of these materials have been fabricated and used as gas-separating membranes. Some of the well-known MOFs such as IRMOF-1 (MOF-5), CuBTC (HKUST-1), ZIF-8 (zeolite imidazolate framework), and ZIF-90 were tested as membranes for gas separations. These MOF membranes offered high selectivities, suggesting that they can replace traditional membrane materials for CO$_2$ separation processes in the future.

Recently, there have been significant efforts on the development of MOF membranes with high stability, high selectivity, and high gas permeability to achieve efficient CO$_2$ separations. Examining MOFs as membranes using purely...
experimental methods is not straightforward because fabrication and performance tests of a new membrane material for a target gas separation require a long time. Computational studies, especially molecular simulations, provide very useful information for the adsorption, diffusion, and separation of gases in MOFs. Results of molecular simulations can be used to quickly investigate a large number of MOFs to classify a handful of promising materials for a desired separation process. In this way, experiments can be directed to the more promising materials for accelerating the development of MOF membranes.

Several computational studies have been reported that use high-throughput grand canonical Monte Carlo (GCMC) simulations to screen hundreds of different MOF structures to identify the best materials for adsorption-based separation of CO\(_2\) from N\(_2\). Membrane-based CH\(_4\)/N\(_2\) separation performances of MOFs were examined by molecular simulations. Our group recently explored membrane-based H\(_2\)/CH\(_4\) separation performances of MOFs using molecular simulations. However, there is no large-scale molecular simulation study in the literature that screens the entire MOF database for membrane-based CO\(_2\)/N\(_2\) separation. One reason for this is that predicting membrane-based gas separation performances of MOFs requires diffusivities of gas molecules through the membrane material, which are obtained from computationally expensive molecular dynamics (MD) simulations of gas mixtures. Adsorption data obtained from GCMC simulations should be combined with the diffusion data obtained from MD simulations to estimate the permeability and selectivity of MOF membranes. GCMC and MD simulations of the CO\(_2\)/N\(_2\) mixture are computationally challenging because they require calculation of the electrostatic interactions between adsorbate–adsorbate (CO\(_2\)–CO\(_2\), CO\(_2\)–N\(_2\), N\(_2\)–N\(_2\)) and adsorbate–MOF (CO\(_2\)–MOF, N\(_2\)–MOF). Both CO\(_2\) and N\(_2\) molecules form polar, multi-atom, linear molecules compared to the nonpolar, single-atom, spherical representation of H\(_2\) and CH\(_4\). Because of the computational expense and long time requirement of modeling CO\(_2\) and N\(_2\) molecules, molecular simulations of the entire MOF database have not been performed for CO\(_2\)/N\(_2\) separation. Molecular simulations generally examined a single type of MOF membrane such as IRMOF-1, CuBTC, MgMOF-74, ZnMOF-74, MOF-177, ZIF-8, and BioMOF-111 for CO\(_2\)/N\(_2\) separation. Sumer and Keskin predicted CO\(_2\) selectivity and permeability of five different MOFs for CO\(_2\)/N\(_2\): 15/85 mixtures, and Yilmaz and Keskin predicted CO\(_2\)/N\(_2\) separation performances of 15 different MOFs using molecular simulations. The only study that examines a large number of MOFs for membrane-based CO\(_2\)/N\(_2\) separation was performed by Watanabe and Sholl, who computed selectivity and permeability of 179 MOF membranes at infinite dilution using GCMC and MD simulations. They reported CO\(_2\)/N\(_2\) selectivity and CO\(_2\) permeability of MOFs as 2–2.6 × 10\(^{4}\) and 1–10\(^{8}\) Barrers, respectively.

Given the availability of a very large number of synthesized MOFs, it is very likely that numerous MOFs, which have not yet been studied as membranes, may offer good CO\(_2\)/N\(_2\) separation potential. In this work, we screened the most complete and recent MOF database maintained by the Cambridge Structural Database to find out the best membrane materials for CO\(_2\)/N\(_2\) separation. This recent MOF database has not been investigated for any membrane-based CO\(_2\) separation application to date. We used a high-throughput computational screening approach of increasing complexity and computational cost: we first performed GCMC and MD simulations to acquire adsorption and diffusion data of CO\(_2\) and N\(_2\) in all MOFs under infinite dilution conditions. Using these adsorption and diffusion data, MOF membranes' selectivity and gas permeability were estimated. We also repeated both GCMC and MD simulations by switching off gas–MOF electrostatic interactions to reveal the influence of these interactions on the predicted performance of MOF membranes. Predicted CO\(_2\)/N\(_2\) selectivities and CO\(_2\) permeabilities of 3806 MOFs were compared with those of widely studied polymers and zeolites. Promising MOF membranes that can exceed the upper bound defined for polymer membranes were identified. GCMC and MD simulations of CO\(_2\)/N\(_2\): 15/85 mixtures were then carried out for the most promising 15 MOFs to evaluate their flue gas separation performances under practical conditions, 1 bar and 298 K.

Finally, molecular simulations were performed for ternary CO\(_2\)/N\(_2\)/H\(_2\)O: 10/87/3 mixtures to investigate the effect of the presence of water in the flue gas streams on the selectivity and permeability of the top MOF membranes. By applying this stepwise screening procedure, the number of promising MOF membranes for flue gas separation was narrowed down from thousands to tens. Structural properties of MOFs were examined to gain molecular-level insights into the influence of physical and chemical belongings of materials on the membranes’ performances. The quantitative structure–performance relationships we provided in this study will guide the design of new MOF membranes having extraordinarily good performances for flue gas separation.

### 2. DETAILS OF CALCULATIONS

Our high-throughput computational screening approach was designed to have increasing complexity and computational cost. We used the most recent collection of MOFs, which consists of 54,808 nondisordered structures. Solvent molecules were removed from the MOFs using a Python script. The Zeo++ software was used to calculate geometrical descriptors of MOFs, such as pore limiting diameter (PLD), the largest cavity diameter (LCD), accessible gravimetric surface area (SA), and porosity (\(\phi\)). More details on the calculation of these properties are available in our earlier reports. We considered only the MOFs with nonzero accessible surface areas. Diffusion coefficients of gases should be assessable within the MOFs’ pores to calculate gas permeabilities of the membranes. We therefore refined this large database to include only the MOFs with PLDs > 3.75 Å so that both CO\(_2\) (3.3 Å) and N\(_2\) (3.64 Å) molecules can pass through the membranes’ pores and considered the MOFs in which gas diffusivities were computed to be >10\(^{-8}\) cm\(^2\)/s, the limit to characterize molecular diffusion using MD simulations. At the end of these refinements, 3806 MOFs having a large variety of chemical and structural properties were studied in this work.

In the first level of screening, we performed molecular simulations for single-component CO\(_2\) and N\(_2\) gases in 3806 MOFs. MC and MD simulations were used to compute Henry’s constants (\(K_H\)) and self-diffusion coefficients (\(D^G\)) of CO\(_2\) and N\(_2\) at infinite dilution, respectively, as implemented in the RASPA simulation code. \(K_H\) values of gas molecules were calculated using the Widom particle insertion method, with 10\(^4\) moves at 298 K. In MD simulations, we switched off the adsorbate–adsorbate interactions and inserted 30 adsorbate molecules into every single MOF to mimic the infinite dilution
consistent with the literature. Ideal selectivities of the MOF
uncertainties resulting from the time scale limitation of MD
several MOF membranes, as we will show below. This restriction eliminates the MOFs for which
interactions between guest molecules and MOFs to investigate
their effects on the performance predictions of our molecular
simulations. The results of simulations (with and without charges) were compared to elaborate on the necessity of calculating framework charges, which is a computationally time-consuming process in large-scale MOF screening studies. The validity of the force field and charge assignment method used in our molecular simulations was shown by the good agreement between simulation results and experimentally measured CO2 and N2 adsorptions of many MOFs in our earlier studies.42,50,51 Results of our simulations were additionally compared with the experimental reports of both single-component and mixture permeabilities of CO2 and N2 through several MOF membranes, as we will show below.

$K^0$ and $D^0$ values of gases were employed to compute permeabilities of MOFs using $P_i^0 = K_i^0 \times D_i^0$. We considered only the MOFs in which both CO2 and N2 self-diffusivities were calculated to be $>10^{-8}$ cm$^2$/s, the limit for which the diffusion of gases can be readily described using MD simulations. This restriction eliminates the MOFs for which diffusion selectivity could be very high because of the slow-diffusing gas component, but this is necessary to eliminate uncertainties resulting from the time scale limitation of MD simulations. We reported gas permeabilities in Barrer to be consistent with the literature. Ideal selectivities of the MOF membranes were computed using the ratio of permeabilities of gas species, $S_{\text{mem,CO2/N2}}^0 = P_{\text{CO2}}^0 / P_{\text{N2}}^0$. Adsorption selectivities ($S_{\text{ads,CO2/N2}}^0 = K_{\text{CO2}}^0 / K_{\text{N2}}^0$) and diffusion selectivities ($S_{\text{diff,CO2/N2}}^0 = D_{\text{CO2}}^0 / D_{\text{N2}}^0$) of MOFs were calculated and discussed in detail. Both adsorption and diffusion selectivities were computed for CO2 over N2 to be consistent with the definition of membrane selectivity. The top 15 MOFs having high membrane selectivities, $S_{\text{mem,CO2/N2}}^0 > 350$, and high CO2 permeabilities, $P_{\text{CO2}}^0 > 10^6$ Barrer, were chosen.

In the second level of calculations, GCMC simulations were done for the top 15 MOF membranes considering binary CO2/N2: 15/85 mixtures at 1 bar and 298 K to represent industrial operating conditions for the flue gas separation. Both adsorbate–adsorbate and adsorbate–MOF interactions were considered in these simulations. A cut-off distance of 13 Å was used to truncate the intermolecular interactions, and the simulation cell lengths were increased to minimum 26 Å along each dimension. Molecular simulations were performed for 10 000 cycles, the first 5000 for initialization and the last 5000 for getting the ensemble averages. The initial states of the mixture MD simulations were taken from the binary GCMC simulations that were carried out for CO2/N2: 15/85 at 1 bar and 298 K, and 106 cycles were used in the NVT ensemble with a time step of 1 fs. A minimum of three trajectories were collected from these simulations to calculate the self-diffusivities of gas molecules. Details about using MD simulations are available in the literature.30,47 Results of GCMC and MD simulations were used to compute mixture permeabilities ($P_{\text{mix}}^0 = c_{\text{mix}} \times D_{\text{mix}}^0 / f_i$), where $c_0$, $D_0$, and $f_i$ represent the adsorbed loading of the gas component in the MOF, self-diffusion coefficient of the gas in the mixture, and partial pressure of the gas at the feed side of the membrane, respectively. Permeate pressure of the membrane was assumed to be vacuum as validated before.27 Selectivities of the MOF membranes for gas mixtures were calculated as the ratio of permeabilities of gas species ($S_{\text{mix}} = P_{\text{mix}}^0 / P_{\text{N2}}^0$) in their corresponding mixtures and referred to as “mixture selectivity” throughout the article.

In the final level of calculations, we ran the molecular simulations for the best MOF membranes identified from the second level of screening for a ternary gas mixture of CO2/N2/H2O: 10/87/3, which mimics flue gas streams that are usually saturated with water in the industrial post-combustion processes. The partial pressure of water was fixed at 0.0328 bar (3280 Pa) to maintain the relative humidity at 80%, whereas the partial pressures of CO2 and N2 were set as 0.09672 and 0.87048 bar, respectively, to represent the post-combustion process.48 We followed the literature and used the TIP4P model to represent H2O. However, it must be noted that H2O is a difficult molecule to simulate, and results can be sensitive to the force field selection. The effect of water on the CO2/N2 selectivity of MOF membranes was evaluated, and the potential of MOF membranes for flue gas separations was assessed under realistic operating conditions.

3. RESULTS AND DISCUSSION

3.1. Screening of MOF Membranes. Figure 1 compares predictions of our molecular simulations with available experimental data for CO2 and N2 permeabilities of different MOF membranes. Conditions of the molecular simulations were same as those the experiments. Details of these conditions together with the experimental references are available in Table S1. Figure 1 shows that there is a remarkably good agreement between our molecular simulations and experimental measurements for single-component CO2 and N2 permeabilities of IRMOF-1, MIL-53 (Al), Ni-MOF-74, ZIF-90, and ZIF-95 membranes in addition to the CO2/N2 mixture permeabilities reported for the ZIF-69 membrane. Molecular simulations generally overestimate gas permeabilities compared to the experiments because of the perfect, defect-free membrane assumption, which may not be true in experiments. Selecting the appropriate force field for molecular simulations of MOFs is critical to make reliable predictions about the materials’ membrane performances. We recently examined the impact of the force field on high-throughput computational screening of MOFs for CO2 separations by

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performing molecular simulations for MOFs using UFF and Dreiding force fields. Our results showed that rankings of the top MOF materials are generally similar, indicating that both generic force fields can be used in high-throughput molecular simulations of MOFs to identify the useful materials. The good agreement shown in Figure 1 demonstrated the validity of our computational method. Motivated from this, we used the same method to study 3806 MOFs for membrane-based CO2/N2 separation with the aim of identifying the best membrane candidates.

Adsorption, diffusion, and membrane selectivities of MOFs computed at infinite dilution are shown in Figure 2 to assess the impact of adsorption and diffusion of gases on the membrane performance. All selectivities were calculated using the equations described in Section 2. Adsorption selectivities of all MOFs favor CO2 over N2 because CO2 is more strongly adsorbed than N2 and selectivities are between 1.72 and 8.8 × 10^4. To be consistent with the adsorption selectivity, both diffusion and membrane selectivities are given for CO2 over N2 in Figure 2. Diffusion selectivities for CO2/N2 range from 3.94 × 10^{-4} to 4.31. In a very large number of MOFs (3664), shown by red and blue points, diffusion selectivities are less than 1 because CO2 diffuses slower than N2. In 65 MOFs, N2 diffusion is significantly faster than that of CO2, resulting in diffusion selectivities between 3.9 × 10^{-4} and 0.01, as shown by blue points. In 142 MOFs, CO2 diffuses faster than N2 and diffusion selectivities become larger than 1, represented by orange points in Figure 2. In fact, those points correspond to the MOF membranes in which both adsorption and diffusion favor CO2 over N2. Membrane selectivities of MOFs computed at infinite dilution \( \kappa_{\text{mem,CO}_2/N_2}^0 \) were between 0.76 and 2288. Almost all of the MOFs (3795) were identified to be CO2 selective membranes for flue gas separation. Only 11 MOFs have membrane selectivities less than 1 (0.76–1), indicating that they are very weakly N2 selective. MOFs combining high adsorption selectivity toward CO2 with low diffusion selectivity toward N2 become the top promising membranes, and stars in Figure 2 represent the best membrane candidates, as we will discuss in detail below.

Figure 3 shows our predictions for CO2/N2 selectivities and CO2 permeabilities of 3806 MOF membranes at infinite dilution at 298 K. Red stars represent the best membrane candidates.

Figure 1. Comparison of our simulated gas permeabilities with the experimental data for various MOF membranes. Measurement conditions and related experimental references are given in Table S1.

Figure 2. Adsorption, diffusion, and membrane selectivities of 3806 MOFs for CO2/N2 separation computed at infinite dilution at 298 K. Stars represent the top 15 MOF membranes.

Figure 3. Predicted CO2/N2 selectivity and CO2 permeability of 3806 MOF membranes at infinite dilution at 298 K. Red stars represent the best membrane candidates.
energy landscape of the guest molecules inside the zeolites. They developed an efficient algorithm that can accurately characterize both adsorption and diffusion properties of structures to find the optimal materials from a large database of zeolites in a reasonable time. They showed that zeolite membranes have a positive correlation between CO$_2$/N$_2$ selectivity and CO$_2$ permeability, in contrast to polymer membranes. Our results in Figure 3 show that a similar conclusion is valid for MOFs. These results indicate that nanoporous membranes such as MOFs and zeolites have a different permeability–selectivity behavior than the polymers.

As we discussed in the beginning, one challenge of studying adsorption and diffusion of CO$_2$ and N$_2$ molecules in MOFs is calculating the electrostatic interactions between gases and framework atoms, which requires computation of partial point charges for MOF atoms. This is a time-consuming process considering the facts that some MOFs have very large structures with several thousands of atoms and there are already thousands of MOFs that we aim to study. To understand the effects of electrostatic interactions between the adsorbate molecules and frameworks on the membranes’ performances, we repeated all molecular simulations by switching off the gas–MOF electrostatic interactions. Our aim at that point was to examine whether MOF membranes for the separation of two polar molecules (CO$_2$/N$_2$) can be screened by skipping the tedious charge assignment procedure to save significant computational time. Figure 4 compares CO$_2$/N$_2$ selectivities and CO$_2$ permeabilties of MOF membranes computed with and without framework charges at infinite dilution at 298 K. Red and black stars represent the best membrane candidates computed with and without charges, respectively.

Figure 4. Comparison of CO$_2$/N$_2$ selectivity and CO$_2$ permeability of MOF membranes computed with and without framework charges at infinite dilution at 298 K. Red and black stars represent the best membrane candidates computed with and without charges, respectively.

CO$_2$/N$_2$ selectivities and CO$_2$ permeabilities of MOF membranes calculated from molecular simulations considering electrostatic interactions (referred to as “with charges”) with the ones computed by neglecting these interactions (referred to as “without charges”). The range of calculated CO$_2$ permeabilities decreased from 296–6.72 × 10$^8$ to 81–4.18 × 10$^8$ Barrer when the framework charges were neglected. Similarly, the range of predicted CO$_2$/N$_2$ selectivities changed from 0.76–2288 to 0.37–1405. As can be seen from Figure 4, the top 15 MOFs that we identified would have been missed if the electrostatic interactions between gas molecules and MOFs were neglected. In fact, most of the promising MOF membranes were located under the upper bound when framework charges were absent. To understand this result, effects of the electrostatic interactions on the gas adsorption and diffusion in MOFs were studied in detail.

Figure 5a represents the Henry’s constants ($K^0$) of CO$_2$ and N$_2$ in MOFs computed with and without charges. $K^0$ values of CO$_2$ are larger than those of N$_2$, supporting the fact that MOFs are CO$_2$ selective in adsorption. Comparison of $K^0$ values calculated with and without charges showed that neglecting charges significantly underestimates the $K^0_{CO_2}$ in many MOFs, whereas the effects of charges are less pronounced for $K^0_{N_2}$ because of the smaller quadrupole moment of N$_2$ (4.7 cm$^2$) compared to CO$_2$ (13.4 cm$^2$). Figure 5a shows adsorption selectivities of MOFs calculated at infinite dilution as the ratio of Henry’s coefficients of gases, and neglecting charges resulted in lower CO$_2$/N$_2$ adsorption selectivities because $K^0_{CO_2}$ was underpredicted. There are many MOFs for which adsorption selectivity significantly decreased from thousands to tens in the absence of framework charges. The effect of framework charges on the self-diffusion coefficients ($D^0$) of gases is shown in Figures 5b. $D^0_{CO_2}$ ($D^0_{N_2}$) values vary between 1.21 × 10$^{-8}$ and 6.19 × 10$^{-9}$ (3.95 × 10$^{-8}$ to 1.61 × 10$^{-8}$) cm$^2$/s. Simulations without MOF charges overpredicted CO$_2$ diffusivities because CO$_2$ molecules are less strongly adsorbed in MOFs in the absence of electrostatic interactions, and therefore, they diffuse faster. The effects of charges on N$_2$ diffusivities were insignificant. As a result of this, CO$_2$/N$_2$ diffusion selectivities were overpredicted when the electrostatic interactions were switched off, as shown in Figure S1b. Neglecting MOF charges decreased the adsorption of CO$_2$ but increased the diffusion of CO$_2$. The decrease in CO$_2$ permeability in the absence of charges shown in Figure 5c indicates that adsorption is the dominant factor in determining the CO$_2$ permeability of MOF membranes. Overall, switching off the electrostatic interactions between gas–MOF underestimates both CO$_2$ permeabilities and CO$_2$ selectivities, whereas N$_2$ permeabilities are almost unchanged. There are significant differences between the CO$_2$ permeability predictions of simulations considering MOFs’ charges and the ones neglecting charges, as shown in Figure 4. On the other hand, the correlation between the rankings of MOFs in terms of CO$_2$ separation performances obtained from those two sets of simulations is good. We computed the Spearman’s ranking correlation coefficient (−1 ≤ SRCC ≤ 1) for the MOF ranking obtained from simulations with and without charges. The SRCC for the rankings of MOFs in terms of CO$_2$ permeability (CO$_2$/N$_2$ selectivity) obtained from simulations with and without charges was calculated as 0.85 (0.77). These results indicate that neglecting the gas–MOF electrostatic interactions may be a reasonable approximation in quickly ranking MOF membranes in terms of CO$_2$ permeabilities and selectivities. This would save a tremendous amount of time because assigning partial charges to thousands of MOFs is computationally costly even if approximate methods are used. On the other hand, caution should be warranted because neglecting charges does not accurately identify the most promising MOF membranes, as shown in Figure 4.

3.2. Binary and Ternary Mixture Separations. All the membrane properties of MOFs discussed above were calculated using single-component adsorption and diffusion data of gases at infinite dilution. It is discussed that multicomponent mixture effects could impact membrane selectivities.55,56 However, performing computationally de-
manding MD simulations for several thousands of MOF membranes is not trivial. Considering the fact that MOF membranes with low ideal membrane selectivities are unlikely to exhibit high mixture selectivity under practical operating conditions, we performed GCMC and MD simulations for binary CO$_2$/N$_2$: 15/85 mixtures only for the top 15 MOF membranes, which were identified in the first level of screening based on the criteria $S_{\text{mem,CO}_2/N_2} > 350$ and $P_{CO_2} > 10^6$ Barrer. Mixture simulations were done at 1 bar and 298 K to represent post-combustion CO$_2$ capture conditions. Table 1 summarizes separation performances of the top 15 MOF membranes for the binary CO$_2$/N$_2$ mixture. Mixture selectivities of MOF membranes were estimated to be high, 16.4–820. Nine of the top 15 MOFs have CO$_2$/N$_2$ selectivities > 100. CO$_2$ permeabilities of these MOFs were also calculated to be high, 1.19 $\times$ 10$^5$ to 1.95 $\times$ 10$^6$ Barrer. One common feature of top MOFs is that they all have high adsorption selectivities, generally >100.

According to Table 1, VIHHIE is the most promising membrane candidate with the highest selectivity, 820. This high membrane selectivity can be explained by the very high adsorption selectivity of this MOF for CO$_2$ over N$_2$, 2251. Table 1 illustrates that top MOFs, including VIHHIE, generally have narrow pores. PLDs and LCDs of the top

### Table 1. Predicted CO$_2$/N$_2$ Mixture Separation Performances of the Top 15 MOFs

| MOF       | PLD, LCD (Å) | $D_{CO_2}^{\text{mix}}$ (cm$^2$/s) | $D_{N_2}^{\text{mix}}$ (cm$^2$/s) | $P_{CO_2}^{\text{mix}}$ (Barrer) | $P_{N_2}^{\text{mix}}$ (Barrer) | $S_{\text{ads,CO}_2/N_2}^{\text{mix}}$ | $S_{\text{diff,CO}_2/N_2}^{\text{mix}}$ | $S_{\text{mem,CO}_2/N_2}^{\text{mix}}$ |
|-----------|--------------|----------------------------------|----------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| VIHHIE    | 4.55, 6.17   | 8.48 $\times$ 10$^{-6}$          | 2.33 $\times$ 10$^{-3}$          | 1.87 $\times$ 10$^6$           | 2.28 $\times$ 10$^3$          | 2251.99                        | 0.36                            | 819.86                         |
| LUPQES    | 4.03, 4.70   | 8.18 $\times$ 10$^{-7}$          | 2.69 $\times$ 10$^{-6}$          | 1.19 $\times$ 10$^5$           | 1.75 $\times$ 10$^2$          | 2343.37                        | 0.30                            | 680.99                         |
| AEEJEA    | 3.77, 4.56   | 3.64 $\times$ 10$^{-6}$          | 4.60 $\times$ 10$^{-6}$          | 2.72 $\times$ 10$^5$           | 6.06 $\times$ 10$^2$          | 567.36                         | 0.79                            | 449.33                         |
| NURVAZ    | 6.00, 6.58   | 5.80 $\times$ 10$^{-6}$          | 2.33 $\times$ 10$^{-3}$          | 9.35 $\times$ 10$^5$           | 3.04 $\times$ 10$^3$          | 1238.62                        | 0.25                            | 307.77                         |
| PEXSAO    | 4.26, 5.95   | 5.41 $\times$ 10$^{-6}$          | 2.03 $\times$ 10$^{-6}$          | 3.56 $\times$ 10$^5$           | 1.23 $\times$ 10$^3$          | 108.25                         | 2.66                            | 288.45                         |
| SAJFEO    | 6.00, 6.63   | 5.67 $\times$ 10$^{-6}$          | 2.51 $\times$ 10$^{-3}$          | 9.16 $\times$ 10$^5$           | 3.26 $\times$ 10$^3$          | 1245.93                        | 0.23                            | 280.89                         |
| PEXROB    | 4.29, 5.91   | 5.95 $\times$ 10$^{-6}$          | 2.92 $\times$ 10$^{-6}$          | 3.94 $\times$ 10$^5$           | 1.65 $\times$ 10$^3$          | 117.46                         | 2.04                            | 239.15                         |
| LIFWON    | 3.91, 5.03   | 1.97 $\times$ 10$^{-5}$          | 5.41 $\times$ 10$^{-5}$          | 1.95 $\times$ 10$^6$           | 1.07 $\times$ 10$^4$          | 499.68                         | 0.36                            | 182.30                         |
| PEXSES    | 4.25, 5.93   | 2.03 $\times$ 10$^{-6}$          | 2.45 $\times$ 10$^{-6}$          | 1.81 $\times$ 10$^5$           | 1.09 $\times$ 10$^3$          | 200.67                         | 0.83                            | 165.80                         |
| ICORAV    | 4.39, 4.98   | 2.04 $\times$ 10$^{-6}$          | 2.69 $\times$ 10$^{-3}$          | 2.07 $\times$ 10$^5$           | 4.76 $\times$ 10$^3$          | 574.94                         | 0.08                            | 43.57                          |
| KIPJUQ    | 6.98, 7.29   | 2.49 $\times$ 10$^{-6}$          | 5.71 $\times$ 10$^{-3}$          | 1.82 $\times$ 10$^6$           | 6.24 $\times$ 10$^3$          | 670.43                         | 0.04                            | 29.21                          |
| OGAZLOZ   | 3.80, 6.36   | 8.24 $\times$ 10$^{-6}$          | 4.22 $\times$ 10$^{-5}$          | 4.93 $\times$ 10$^5$           | 2.31 $\times$ 10$^4$          | 109.01                         | 0.20                            | 21.28                          |
| OGAHOV    | 3.83, 6.27   | 8.85 $\times$ 10$^{-6}$          | 4.05 $\times$ 10$^{-3}$          | 5.01 $\times$ 10$^5$           | 2.50 $\times$ 10$^4$          | 91.97                          | 0.22                            | 20.08                          |
| OGAAMOA   | 3.80, 6.37   | 9.36 $\times$ 10$^{-6}$          | 5.11 $\times$ 10$^{-3}$          | 5.36 $\times$ 10$^5$           | 2.99 $\times$ 10$^4$          | 98.73                          | 0.18                            | 17.91                          |
| OGAALT    | 3.84, 6.37   | 7.67 $\times$ 10$^{-6}$          | 4.78 $\times$ 10$^{-3}$          | 4.40 $\times$ 10$^5$           | 2.69 $\times$ 10$^4$          | 102.27                         | 0.16                            | 16.38                          |

*MOFs are ranked based on their membrane selectivities.*
MOFs are between 3.77−6.98 and 4.51−7.29 Å, respectively. MOFs possessing small pores offer high CO2/N2 adsorption selectivity because of the strong confinement of the adsorbate molecules, as demonstrated in Figure S2a. Strongly adsorbed CO2 molecules diffuse slower than the weakly adsorbed N2 in the narrow pores, and diffusion selectivity favors N2 in all top MOFs except two, also supported by Figure S2b. As a result, high adsorption selectivity toward CO2 dominates the diffusion selectivity toward N2 in these narrow-pored materials, leading to high membrane selectivities, as shown in Figure S2c. Figure S2a also shows that MOFs with large pore sizes (>15 Å) and high porosities generally have low adsorption selectivities. Both gas molecules diffuse in similar rates in large pores and CO2/N2 diffusion selectivities become unity in these MOFs, as shown in Figure S2b. As a result, the membrane-based separation potential of the large-pored MOFs becomes low, as shown in Figure S2c, and therefore, these MOFs are not present in the top materials list.

We also compared selectivities and permeabilities of the top MOF membranes with zeolite membranes. Kusakabe et al.55 reported the CO2/N2 selectivity of the NaY zeolite membrane as 20, and its CO2 permeance was measured as 1.6 × 10−7 mol/(m2 s Pa) (corresponding to 9.5 × 103 Barrer) at 303 K for a CO2/N2: 50/50 mixture. The selectivity of the ZSM-5 membrane was reported to be 68 for an equimolar CO2/N2 mixture at room temperature.56 Li and Fan57 used SAPO-34 membranes and reported CO2/N2 selectivity in the range of 21−32 and CO2 permeance as 1.5 × 10−6 mol/(m2 s Pa) (corresponding to 2.2 × 104 Barrer) for an equimolar mixture. Molecular simulations of Krishna and van Baten29 for the CO2/N2: 15/85 mixture at 10 bar and 300 K showed that several zeolites such as FAU, MFI, DDR, and CHA exceed the upper bound with CO2/N2 selectivities of 7, 10, 20, and 40, respectively. This comparison showed that top MOF membranes given in Table 1 have higher selectivities and permeabilities than zeolite membranes under similar conditions. Our results for MOFs were also compared with the previous simulation works on MOF membranes. CO2/N2 selectivities of Mg-MOF-74, Zn-MOF-74, and MOF-177 were computed as 18, 6, and 2, respectively, considering the CO2/N2: 15/85 mixture at 1 bar and 300 K.58 Our computed CO2/N2 selectivities for these MOFs, 12, 5, and 1, agreed well with the literature. We calculated CO2/N2 selectivity of ZIF-8 as 5.2, which is in good agreement with the previously computed value of 5.7 at infinite dilution.30 Li et al.59 computed CO2/N2 selectivity of the bio-MOF-11 membrane as 22 for the CO2/N2: 15/85 mixture at 1 bar and 298 K. This value is close to the selectivity computed in this work, 18. Watanabe and Sholl34 considered 179 MOFs with very narrow pores, 2.2 < PLD < 3.6 Å, to study the molecular sieve effects of MOF membranes and predicted CO2/N2 selectivities in the range of 2−2.6 × 104 at infinite dilution. The lowest pore size in our MOF database was 3.75 Å to let both gas molecules to diffuse through the pores. Consequently, the selectivity of the MOFs we studied in this work is lower than theirs.

We finally examined the influence of humidity on the flue gas separation performances of the top MOF membranes using molecular simulations. A ternary gas mixture of CO2/N2/H2O: 10/87/3 was considered to mimic flue gas streams for the industrial post-combustion processes. It is important to note that ternary MD simulations were performed only for 10 of the top MOFs because of the difficulty of equilibration of highly
polar $\text{H}_2\text{O}$ molecules in the MOFs during GCMC and MD simulations. GCMC simulations showed that $\text{H}_2\text{O}$ molecules adsorb in MOFs and compete with the strongly adsorbed $\text{CO}_2$ molecules rather than the weakly adsorbed $\text{N}_2$ molecules. The amount of adsorbed $\text{CO}_2$ decreases in the presence of $\text{H}_2\text{O}$, which is in agreement with the literature,\cite{25,58,59} whereas $\text{N}_2$ adsorption is not significantly affected. Therefore, $\text{CO}_2/\text{N}_2$ adsorption selectivities computed for ternary mixtures were found to be less than those calculated for binary mixtures in Figure 6a. Diffusivities of gases do not significantly differ in the binary and ternary mixtures. Consequently, permeabilities and membrane selectivities of MOFs computed mimicking the presence of humidity were found to be generally less than those computed for the binary mixture, as shown in Figure 6b. There are significant decreases in the gas permeabilities of three MOFs when a ternary gas mixture was considered. A detailed analysis of these materials showed that these three MOFs have the narrowest pore sizes among the top MOFs. Therefore, the reduction in their $\text{CO}_2/\text{N}_2$ adsorption selectivities was more distinct than the others, resulting in more observable decreases in their gas permeabilities. Figure 6c compares the selectivities and permeabilities of the top MOF membranes computed from different levels of our screening approach, using single-component gas data, binary mixture data, and ternary mixture data. The top MOF membranes identified at the first level of screening (infinite dilution) remain above the upper bound at the higher levels of the screening procedure when binary and ternary mixture simulations were performed. These results indicate that screening MOFs in terms of membrane selectivity and permeability considering single-component gases ($\text{CO}_2$ and $\text{N}_2$) or binary flue gas mixture ($\text{CO}_2/\text{N}_2$) works well for accurately identifying the best performing MOF membranes for the separation of the humid flue gas mixture ($\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$). Finally, we would like to note that our molecular simulations did not give any data about the stability of MOF membranes under water vapor. Some MOFs are known to lose their crystal structures under humid atmospheric conditions.\cite{60}

**Figure 7.** Effects of structural properties on the $\text{CO}_2/\text{N}_2$ separation performances of MOFs. Black columns represent all 3806 MOFs, red columns represent the top 15 MOFs that have $S_{\text{mem,CO}_2/\text{N}_2} > 350$ and high $\text{CO}_2$ permeabilities, $P_{\text{CO}_2} > 10^6$ Barrer.
This type of membranes may not be useful, although they possess very high CO₂ selectivities. This issue is more likely to be examined by further experimental studies on the top materials.

3.3. Structure—Performance Relations. One of the advantages of studying a large material database is to get an insight into the structure—performance relationships. If clear relationships can be established between structural descriptors of MOFs (size of the pore openings, pore volume, SA, etc.) and their membrane performance such as selectivity, one can easily estimate the flux gas separation performance of a newly synthesized MOF by just examining its structural properties. If these relations also include direct structural information such as the metal type and lattice type of the MOFs, it can facilitate experimental studies to make MOFs with the appropriate structural properties that can lead to materials having high separation performance. With this motivation, we investigated the distribution of PLD, LCD, ϕ, SA, ρ, metal type, and Bravais lattice on all MOFs and on the top 15 MOFs. Figure 7 shows that 35 (54)% of all MOFs and 73 (53)% of the top 15 membranes have PLDs < 4.5 Å (6 < LCD < 12 Å). None of the top MOF membranes have pore sizes >12 Å, and 80% of the top MOFs have porosities between 0.5 and 0.75. Half of the MOFs we considered and 80% of the top membranes were found to have SA < 1000 m²/g. MOFs with a large SA > 2000 m²/g are not in the top membrane list. An interesting feature of Figure 7 is that although only a small fraction of the MOFs (190) have lanthanides among the 3806 MOFs we considered, a significant number of the top 15 materials (11 MOFs) have lanthanides. Previous work on the adsorption-based separation of CO₂/N₂ also demonstrated that MOFs with lanthanides outperform other MOFs because of the combination of high CO₂ selectivity and capacity. We also examined the effect of the difference between the heat of adsorption of CO₂ and N₂ computed at infinite dilution, ΔQₙₑₐₜ, on the membrane performances of MOFs. In fact, ΔQₑₐₜ is not a direct structural property, but it is a good representative of the affinity of the framework for adsorbate molecules. Figure 7 shows that although a quarter of the MOF database was found to have ΔQₑₐₜ < 20 kJ/mol, none of these MOFs is in the top membrane list. A small portion of the MOFs, 18%, has high ΔQₑₐₜ > 30 kJ/mol, and these MOFs become 67% of the top membranes. This knowledge may be useful to rapidly screen MOFs after gas adsorption measurements to identify the potential membrane candidates. Overall, Figure 7 concluded that MOFs with 3.75 < PLD < 4.5 Å, 6 < LCD < 12 Å, 0.5 < ϕ < 0.75, SA < 1000 m²/g, 1.0 < ρ < 1.5 g/cm³ and the ones having lanthanides and monoclinic lattice types are the most promising MOF membranes. The similarities of the top MOF membranes can be listed as narrow pore openings, low surface areas, and lanthanide-type materials, which lead to high CO₂ selectivities and high CO₂ permeabilities for CO₂/N₂ separation.

Finally, we will discuss the assumptions used throughout our computational screening. We used a rigid MOF assumption in all molecular simulations. This assumption saves tremendous computational time, and it is necessary for large-scale screening studies, which consider thousands of MOF structures. On the other hand, the rigid framework assumption can overpredict the diffusion selectivity toward the small gas molecule (CO₂) by underestimating the diffusion of the large gas molecule (N₂). We previously presented that MOF flexibility has an insignificant effect on the selectivity and permeability of MOF membranes having large pores, whereas it affected the permeability without varying the selectivity for materials having narrow pores. In this study, we specifically considered MOFs having pore openings greater than the kinetic diameters of the adsorbates; hence, we expect that MOF flexibility has a negligible effect on our results. Another point is that we used the QEq method to assign partial charges to MOFs because this approximate was readily implemented within RASPA. A good agreement between experiments and our molecular simulations for CO₂ and N₂ permeabilities of several MOF membranes, as shown in Figure 1, indicates that the QEq method can accurately estimate properties of MOF membranes. Furthermore, we recently showed that adsorption selectivities do not significantly change depending on the method by comparing the results of simulations using the QEq and density-derived electrostatic and chemical charge methods.

4. CONCLUSIONS

We used high-throughput molecular simulations to screen the MOF database for membrane-based CO₂/N₂ separations. Single-component gas adsorption and diffusion calculations performed at infinite dilution were used to assess CO₂ permeabilities and CO₂/N₂ selectivities of MOF membranes. The adsorption and diffusion of binary CO₂/N₂ mixtures in MOFs were then computed for the top MOFs identified from the first level of screening under post-combustion CO₂ separation conditions. The top 15 MOF membranes were found to exhibit CO₂ selectivities of 15–820 and CO₂ permeabilities of 1.19 × 10⁻⁴ − 1.95 × 10⁻³ Barrers for the separation of the CO₂/N₂: 15/85 mixture at 1 bar and 298 K. High membrane selectivities of MOFs were attributed to the strong adsorption affinity toward CO₂, which dominated the diffusion selectivity toward N₂. We finally examined ternary CO₂/N₂/H₂O mixtures to better assess separation performances of the selected top membranes. Our results show that selectivities and permeabilities calculated from the ternary mixture simulations are generally lower than the values computed using binary mixture simulations, indicating that humidity can negatively affect performances of some MOF membranes. The structure—performance analysis demonstrated that MOFs with narrow pores (3.75 < PLD < 4.5 Å), low surface areas (<1000 m²/g), and monoclinic and lanthanide-containing structures are the best candidates for CO₂/N₂ membrane-based gas separation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b05416. Permeability measurement conditions of MOF membranes; comparison of adsorption and diffusion selectivities of all MOFs computed with and without charge; and selectivities of MOFs computed at infinite dilution as a function of PLD and porosity (PDF).

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