Effects of electrostatic interactions on gas adsorption and permeability of MOF membranes

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We examined the effects of electrostatic interactions on gas adsorption and permeability of metal organic framework (MOF) membranes and MOF-filled mixed matrix membranes (MMMs) for CO2/CH4, CO2/N2 and H2/CO2 separations using molecular simulations. Adsorption isotherms and diffusion rates of CO2, CH4, N2 and H2 in several MOFs were computed using grand canonical Monte Carlo and equilibrium molecular dynamics simulations, respectively. Gas permeability and selectivity of pure MOF membranes and MOF-filled MMMs were then evaluated using theoretical permeation models. The accuracy of our molecular simulations was validated by comparing theoretical predictions for gas permeability and selectivity of MOF-filled MMMs with the available experimental data. We then used the same modelling approach to predict the performance of new MOF-filled MMMs in CO2/CH4, CO2/N2 and H2/CO2 separations. Promising MOF/polymer combinations which offer high selectivity and permeability relative to pure polymer membranes were identified. Our results showed that including electrostatic interactions between adsorbate molecules and MOF atoms is crucial for modelling pure MOF membranes but has less significance for modelling MOF-filled MMMs whenever the MOF volume fraction, \( f \leq 0.30 \). This result suggests that preliminary screening studies of MOF-filled MMMs can be carried out without assigning partial charges to MOF atoms.

Keywords: adsorption; diffusion; membrane; metal organic framework; polymer

1. Introduction

Metal organic frameworks (MOFs) are a new class of nanoporous materials that show great potential in gas adsorption and separation applications due to their large surface areas, high-pore volumes, wide ranges of pore sizes and tunable topologies.[1,2] Although a small number of MOF membranes have been fabricated and tested for gas separations so far, the number of mixed matrix membranes (MMMs) that have been synthesised by incorporation of MOFs into polymers has been increasing rapidly. MOF-filled MMMs combine easy and low-cost fabrication of polymers together with the high CO2 permeability of MOFs. Recent experimental and computational studies showed that incorporation of MOFs as fillers into polymers can significantly enhance the gas permeability and selectivity of pure polymers and carry the polymers above the Robeson’s upper bound that has been established for gas separations.[3–10]

Yehia et al. [11] synthesised the first MOF-based MMM containing copper(II)biphenyl dicarboxylate triethylenediamine (Cu(II)BPDC-TED) in poly 3-acetoxyethylthiophene and found that CH4 selectivity of Cu(II)BPDC-TED-based MMMs increases, but CO2/CH4 selectivity decreases with the filler loadings of 20 and 30 wt%. Liu et al. [12] reported the first patent by incorporating MOF-5 (IRMOF-1) and HKUST-1 (CuBTC) into Ultem and Matrimid polymers. They observed higher H2, CO2 and CH4 permeabilities in MOF-filled MMMs than pure polymers. The CO2/CH4 selectivity of MOFs did not change, whereas H2/CH4 selectivity slightly decreased because the increase in CH4 permeability was found to be higher than the increase in H2 permeability when 20 wt% MOF-5 was incorporated into Ultem. Perez et al. [13] also studied incorporation of MOF-5 into Matrimid and reported that permeability of H2, O2, CO2, N2 and CH4 increased compared with that of pure polymer membrane. Car et al. [14] used CuBTC and Mn(HCOO)2 as filler particles in poly-dimethylsiloxane (PDMS) and polysulphone (PSF) for CO2/N2 and CO2/CH4 separations. The CO2/N2 and CO2/CH4 selectivity of MMMs slightly increased due to the voids formed at the interface of filler particles and polymers. These voids enhance the gas transport through MMMs at high-MOF loadings. Therefore, the enhancement in selectivity was found to be lower than expected. Hu et al. [15] fabricated a hollow fiber MMM which consists of CuBTC and polyimide (PI) and suggested that CuBTC/PI hollow fiber MMM can be very useful in H2 separation processes due to the high H2 selectivity over CH4, CO2, O2, N2 and high H2 permeance of MMM. In a recent study, Ge et al. [16] have fabricated CuBTC/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymer membrane using ultrasonication treatment to enhance the compatibility of the interface between PPO and CuBTC. They found that CO2, N2, CH4 and N2 permeabilities and CO2/CH4, CO2/N2, H2/N2 and H2/CH4 selectivities of MMMs increased
compared with those of pure PPO due to the improvement in both diffusivity and solubility of gas molecules.

Zeolitic imidazolate frameworks (ZIFs), which are a subclass of MOFs, have also been used as filler particles in MMMs. ZIFs consist of transition metals (zinc, cobalt, copper, etc.) connected by imidazolate ligands. Ordoñez et al. [21] measured the permeability of pure H2, CO2, O2, N2, CH4 and C2H6 through ZIF-8/Matrimid MMMs. They found that MMMs composed of > 40 wt% ZIF-8 exhibit higher gas permeability than pure Matrimid. Ideal selectivity for CO2/CH4 and H2/CH4 pairs also increased due to the size-sieving ability of ZIF-8. Similarly, Díaz et al. [22] reported the enhancement in the permeability of H2, N2, CO2, CH4, C2H6 and C2H2 in ZIF-8/poly(1,4-phenyleneether-ether-sulfone) MMMs without any change in ideal selectivity. The formation of large free volumes in the MMMs by incorporation of ZIF-8 into the polymer matrix increased the diffusion of gas molecules through the MMMs. Song et al. [23] observed permeability enhancements of H2, N2, CO2, CH4 and O2 molecules in ZIF-8/Matrimid MMMs compared with those in unfilled polymer membrane. Dai et al. [24] fabricated asymmetric hollow fiber ZIF-8/Ultem membrane and reported a good contact between the polymer and ZIF-8 particles. Due to this good compatibility, the selectivity of CO2/N2 increased for pure gases and mixed gas pairs. Bae et al. [3] fabricated ZIF-90-filled MMMs using Ultem, Matrimid and 6FDA-DAM polyimide and measured both pure and mixture gas permeation of CO2 and CH4. Among these MMMs, ZIF-90/6FDA-DAM MMM was found to be a good candidate for CO2/CH4 and CO2/N2 separations due to its high CO2 permeability and high CO2 selectivity. ZIF-90-based 6FDA-DAM membranes could exceed the upper bound established for CO2/CH4 separation due to the enhancement in the separation performance of pure polymer with the addition of ZIF-90. Yang et al. [25] synthesised ZIF-7/polybenzimidazole (PBI) MMMs and reported that H2 permeability and H2/CO2 selectivity increased because rigidified chains formed at the PBI and ZIF-7 interface improved the molecular sieve effect.

The main challenge in fabricating MOF-filled MMMs is the correct matching of polymer and MOF to obtain high-performance MMMs. Selecting the appropriate MOF that can enhance both CO2 selectivity and permeability of pure polymer membrane is crucial but challenging due to the large number of available MOFs in the literature. Even if one single polymer is considered, there are hundreds of MOFs that can potentially be used as filler particles. Computational studies have been useful to efficiently screen a large variety of MOFs to identify the most promising MOFs prior to experimental efforts. Keskin and Sholl [26] introduced the first computational method that combines atomic simulations with theoretical permeation models (Maxwell and Bruggeman) to examine MOF-filled MMMs for CO2/CH4 separations. Erucar and Keskin [5,6] tested several theoretical permeation models (Maxwell, modified Maxwell, Bruggeman, Lewis Nielson, Pal, Felske and modified Felske models) by comparing the predictions of these models with the experimental data and examined the performance of 80 (119) new MOF-filled MMMs for CO2/CH4 (H2/CH4) separations. Incorporation of a highly CO2 selective MOF, Zn-Atz, into polymers has been recently examined for H2/CH4 and CO2/CH4 separations using molecular simulations, and results showed that Zn-Atz-filled polymers were located well above the Robeson’s upper bound due to the improvements in gas permeability and selectivity. Thornton et al. [8] used the Bruggeman model to predict the separation performance of ZIF-8/Matrimid MMMs in H2/CO2, H2/N2, CO2/N2, CO2/N2 and O2/N2 separations and ZIF-90-filled MMMs for CO2/N2 and CO2/CH4 separations. Yilmaz and Keskin [7] predicted H2, CO2, CH4 and N2 permeance of ZIF-filled MMMs by predicting gas selectivity and permeability of 360 new MMMs composed of 15 different ZIFs and 24 different polymers. Zhang et al. [28] developed a fully atomistic approach and studied H2/CO2 permeation in ZIF-7/PBI membranes. This has been the first study in the literature that models both the MOF and polymer phases at the atomic level. Their predicted H2/CO2 selectivity for neat PBI was lower than the experimental data and this was attributed to the lower density predictions for PBI membrane, which results in a larger fractional free volume and higher gas permeability. More detailed discussions on computational modelling of MOF-filled MMMs can be found in recent reviews. [29,30]

As the summarised literature survey suggested, most of the MMM studies focused on CO2/CH4 separation, and a limited number of studies examined the potential of MOF-based MMMs in CO2/N2 separations. Effective capture of CO2 from flue gas streams is crucial due to global warming caused by CO2 emissions. MMMs that can exhibit high CO2 selectivity and permeability are required to achieve effective CO2/N2 separations. In this study, we used molecular simulations and theoretical permeation models to predict gas permeability and selectivity of MOF-filled MMMs in CO2/N2 separations. We first validated our approach by comparing theoretical results with the experimental measurements of CO2 and N2 permeability for eight different MOF-filled MMMs. Because both CO2 and N2 have quadrupole moments, partial point charges were assigned to all atoms of each MOF to include electrostatic interactions between adsorbates and MOF atoms (EIAM). Watanabe and Sholl [31] recently carried out a detailed computational study on the effects of adsorbate–MOF electrostatic interactions on adsorption and diffusion coefficients in 359 MOFs for CO2/N2 separations and identified many pure MOFs lying above...
Robeson’s upper bound. In order to examine the effects of EIAM when MOFs were incorporated into MMMs, we carried out MOF-filled MMM calculations both with and without EIAM and compared our findings with experimental data. After showing good agreement between calculations and experiments, performance of new MOF-based MMMs in CO2/N2 separations was examined and predicting MOF/polymer combinations which offer high CO2/N2 selectivity and permeability relative to pure polymer membranes were identified. These calculations were then extended to CO2/CH4 and H2/CO2 separations, which are important in natural gas purification and hydrogen recovery from plants and refineries.

2. Computational details

2.1 MOFs and polymers

We examined 12 different MOFs in this work. MOF-5,[32] CuBTC,[33] ZIF-8 [34] and ZIF-90 [35] were studied because several MMMs in which these MOFs were used as filler particles were fabricated and tested for various gas separations in the literature.[3,12–15,21–24] MOF-5 is one of the most widely studied MOFs which exhibits a cubic structure with pore sizes of 8/15.1 Å.[32] CuBTC is also widely studied for CO2 separations and it has main channels of 9 Å in diameter surrounded by tetrahedral pockets (5 Å) and triangular windows (3.5 Å) that connect the pockets and main channels.[33] ZIF-8 consists of Zn atoms tetrahedrally coordinated by four 2-methylimidazolate linkers and its large cages (11.6 Å) are connected by narrow windows (3.4 Å). [34] ZIF-90 has a sodalite cage-like structure with pore windows having diameters of 3.5 Å and cages having diameters of 11.2 Å. The other eight MOFs (CECYOY, FEVVIM, IDUDOA, IJOMOJ02, KEXFAU, OHETIE, YARYEV and ZUQPOQ) were chosen from the Cambridge Structural Database (CSD) to represent materials having different topologies, metal sites and pore sizes. These MOFs are designated by their reference codes throughout the manuscript and no MMM has been fabricated using these MOFs to date in the literature. The unit cell representation of MOFs is taken from the Mercury 3.1[36] program is given in Figures S1–S8 of the Supplementary Information available via the article webpage. Table S1 lists pore-limiting diameters, largest cavity diameters and total pore volumes of these materials calculated by MOFomics, an automated computational method for characterising the three-dimensional porous networks of MOFs.[37] The atomic positions of each MOF were taken from the CSD, and rigid, solvent-free structures were used in calculations. CECYOY,[38] IJOMOJ02 [39] and ZUQPOQ [40] do not have solvent molecules in their frameworks. The solvents present in FEVVIM [41] and IDUDOA [42] were removed because the synthesis of these MOFs without the solvent was also reported in the literature. Solvent molecules were removed from KEXFAU,[43] OHETIE [44] and YARYEV,[45] but no information is available in the literature about the stability of these structures without the solvent molecules. MOFs are generally synthesised using hydrothermal or solvothermal techniques in which crystals are slowly grown from a hot solution of a metal precursor. The solvents used in the synthesis of MOFs remain in the pores of the framework and an activation procedure, generally heating, is required to remove the solvents from the structure in order to make the pores available for guest molecules. Majority of MOFs retain their crystalline structures after the solvent removal [46]; therefore, we expect these three MOFs to be stable without the solvents.

The polymers that we considered in this study can be divided into three groups: polymers that have been widely used in MOF-filled MMM fabrication in the literature (Matrimid, PSF, PDMS, 6FDA-DAM and PI), polymers that form the Robeson’s upper bound [47] for CO2/CH4, CO2/N2 and H2/CO2 separations such as poly(trimethylgermylpropyne), poly(diphenyl acetylene), liquid-crystalline polyester and polymers that are located below the upper bound such as poly[1-(trimethylsilyl)-1-propyne] (PTMSP), silicon rubber and PPO. Gas permeability and selectivity of polymers that are considered in this work were taken from the literature,[48] and these data are given in Tables S2–S4.

2.2 Details of molecular simulations

We carried out grand canonical Monte Carlo (GCMC) and equilibrium molecular dynamics (EMD) simulations to obtain adsorption data and diffusivity coefficients of gases (CO2, CH4, H2 and N2) in MOFs. We initially carried out GCMC simulations to estimate equilibrium adsorption of gas molecules. To mimic the experimental measurements, the chemical potential, volume and temperature were kept constant and the number of molecules at equilibrium was determined. We used Lennard-Jones (LJ) 12-6 potentials and the Coulomb potential to model repulsion–dispersion forces and electrostatic interactions, respectively. These kinds of force fields, which have been widely used to simulate gas adsorption in MOFs, have been recently reviewed by Getman et al. [49]. The LJ (electrostatic) interactions were truncated at a cut-off radius of 13 Å (25 Å). The Lorentz–Berthelot mixing rules were used to calculate adsorbent–adsorbate and adsorbate–adsorbate LJ cross interaction parameters. Simulations at the lowest fugacity were started from an empty MOF matrix. Each simulation at higher fugacity was started from the final configuration of the previous run. Simulations were carried out for $3 \times 10^7$ trial configurations which consist of 1.5 $\times 10^7$ cycles for the equilibration and 1.5 $\times 10^7$ cycles for the production step. We then used EMD simulations in the canonical ensemble with a Nose–Hoover thermostat.
to calculate corrected diffusivity \( (D_{\alpha,i}) \) which is the collective motion of the gas molecules at the adsorbed loadings:

\[
D_{\alpha,i} = \lim_{t \to \infty} \frac{1}{6Nt} \left\langle \left( \frac{1}{N} \sum_{i=1}^{N} [r_{i\alpha}(t) - r_{i\alpha}(0)] \right)^2 \right\rangle.
\]

In this formula, \( N \) is the number of the molecules, \( r_{i\alpha}(t) \) is the three-dimensional position vector of molecule \( i \) of species \( \alpha \) at time \( t \) and the angular brackets show the ensemble average. Corrected diffusivities of pure gases were calculated by carrying out 20 independent EMD simulations because collecting a large number of independent trajectories is important to accurately compute corrected diffusivities. Periodic boundary conditions were applied in all simulations. The size of the simulation box was set to \( 2 \times 2 \times 2 \) unit cells for all GCMC simulations. For EMD simulations, a minimum of \( 1 \times 2 \times 3 \) and a maximum of \( 13 \times 13 \times 13 \) unit cell simulation boxes were used to contain enough particles during the simulations. More technical details about the GCMC and EMD simulations can be found in our earlier studies.[51,52]

The Buch[53] and TraPPE potentials[54] were used to model \( \text{H}_2 \) and \( \text{CH}_4 \), respectively, whereas \( \text{CO}_2 \) was modelled as a three-site linear molecule with three charged LJ interaction sites located at each atom using the EPM2 potential.[55] We represented \( \text{N}_2 \) as a three-site model with two sites located at two \( \text{N} \) atoms and the third site located at its centre of mass with partial point charges.[56] We used the universal force field (UFF)[57] LJ parameters for the MOF atoms because our previous studies showed that results of molecular simulations using UFF LJ parameters agree well with the experimental measurements of gas permeability through MOF and ZIF-filled MMMs.[5,7,58] Moreover, in another study,[59] we compared the predictions for gas permeability of ZIF membranes obtained from molecular simulations based on the Dreiding force field with the predictions obtained from simulations based on UFF and showed that changing the force field does not change the conclusion about the permeability performance of ZIF materials.

As explained in Section 2.3, net atomic charges were assigned to MOF atoms to describe the electrostatic interactions between adsorbates that have a quadrupole moment (i.e. \( \text{CO}_2 \) and \( \text{N}_2 \)) and MOF atoms (EIAM). Molecular simulations were repeated by switching off the EIAM to examine the effects of electrostatic interactions on the performance of MOF membranes and MOF-filled MMMs.

### 2.3 Charge assignment to MOFs

The partial charges of MOFs which have been used as filler particles in fabricated MMMs, MOF-5, CuBTC and ZIF-8 were taken from the literature.[60–62] The partial charges of ZIF-90 were defined using REPEAT charges of Watanabe et al. [63] which gave an electrostatic potential and \( \text{CO}_2 \) adsorption isotherm close to that obtained using the ab initio density functional theory (DFT) electron density distribution. For this material, the density derived electrostatic and chemical (DDEC) method also produced an electrostatic potential and \( \text{CO}_2 \) adsorption isotherm close to that obtained using the ab initio DFT electron density distribution.[63] Partial charges of eight new MOFs considered in this study were assigned using the DDEC method. Among these new MOFs, only IJOMOJ02 has an experimental \( \text{CO}_2 \) adsorption data in the literature [39] and our molecular simulations which used DDEC charges agreed well with the experimental isotherm data as shown in Figure S9, indicating that the DDEC method is reasonable to define electrostatic interactions between \( \text{CO}_2 \) and MOF atoms. DDEC charges were simultaneously optimised to reproduce the chemical states of atoms in a material and the electrostatic potential surrounding the material.[64,65] Several recent studies compared DDEC charges with other point charge models and the ab initio electrostatic potential for constructing rigid or flexible force fields used in atomic simulations.[31,63–66] These studies show that DDEC charges achieve a good balance between transferability of the charge values (among similar materials and different conformations of the same material) and accuracy of reproducing the electrostatic potential around a material.

The electron density distribution of eight new MOFs was generated holding the geometry fixed at the experimental crystal structure. DFT calculations were carried out in the Vienna ab initio simulation package [67] using the Perdew–Burke–Ernzerhof exchange-correlation functional.[68] Computations were carried out at the Gamma point using a 400-eV plane-wave cut-off and the projector augmented wave (PAW) method. The PAW method is an all-electron frozen core method.[69,70] The spin (i.e. magnetic) state was relaxed during these calculations. IJOMOJ02 converged to a magnetic ground state whereas FEVIM, CECCYO, IDUDOA, KEXFAU, OHETIE, YARYEV and ZUQPOQ converged to nonmagnetic ground states. Atomic spin moments were computed using a previously published method.[71] Net atomic charges were computed from the electron density distribution using the DDEC method.[64,65] DDEC net atomic charges for the eight new MOFs (and atomic spin moments for IJOMOJ02) are listed in Tables S5–S12. The average partial charge for each crystallographically distinct atom type was used in the molecular simulations.

### 2.4 Calculating gas permeability of MOF membranes and MOF-filled MMMs

We used the results of molecular simulations to predict gas permeability in pure MOF membranes and MOF-filled
MMMs. Room-temperature adsorption isotherms of CO$_2$, CH$_4$, H$_2$ and N$_2$ molecules were computed using GCMC simulations. The feed (permeate) pressure was set to 2 bar (10$^{-6}$ bar). EMD simulations were used to calculate corrected diffusivities ($D_c$) of each gas molecule at the mean adsorbate loading assuming shell model.[72] The transport diffusivity ($D_t$) is then calculated by using the corrected diffusivity ($D_c$) and the thermodynamic correction factor,[72] where the latter is a partial derivative relating the adsorbate concentration, $c$, and bulk phase fugacity, $f$. Thermodynamic correction factor was defined using single component adsorption isotherms of each gas molecule by GCMC simulations:

$$D_t(c) = D_o(c) \cdot \frac{\partial \ln f}{\partial \ln c}.$$  \hspace{1cm} (2)

Steady state fluxes ($J$) of each gas species were then calculated using Fick’s law [72]:

$$J = -D_t(c) \cdot \nabla c.$$  \hspace{1cm} (3)

Here, $\nabla c$ is the concentration gradient of the adsorbed species based on the difference between the feed and permeate side pressures of the membrane and membrane thickness [72,73]:

$$\nabla c = \frac{c_{\text{permeate}} - c_{\text{feed}}}{L}.$$  \hspace{1cm} (4)

We then estimated gas permeability of MOF membranes using Equation (5) based on the pressure difference between feed and permeate sides ($\Delta \rho$), and membrane thickness, $L$:

$$P_{\text{MOF}} = \frac{J}{\Delta \rho / L}.$$  \hspace{1cm} (5)

The ideal selectivity of pure MOF membranes was calculated as the ratio of permeabilities of two competing gas pairs ($i/j$):

$$S_{ij} = \frac{P_{\text{MOF}i}}{P_{\text{MOF}j}}.$$  \hspace{1cm} (6)

Gas permeability and selectivity of MOF-filled MMMs were calculated using the molecular simulation results for gas permeability in pure MOFs, experimental data for gas permeability in polymers [47] and theoretical permeation models. One of the most widely used permeation models, the Maxwell model,[74] was used to estimate the gas permeability of MOF-filled MMMs:

$$P_{\text{MMM}} = P_{\text{POLYMER}} \cdot \frac{(2 - \phi) + (1 + 2\phi)\lambda}{(2 + \phi) + (1 - \phi)\lambda}.$$  \hspace{1cm} (7)

In this model, $\lambda$ is the permeability ratio ($P_{\text{MOF}}/P_{\text{POLYMER}}$), $P_{\text{MOF}}$ is the permeability of MOF, $P_{\text{POLYMER}}$ is the permeability of the polymer, $P_{\text{MMM}}$ is the permeability of the MOF/polymer MMM and $\phi$ is the volume fraction of MOF fillers. More discussion about this model can be found in previous works.[5,6]

### 3. Results and discussion

#### 3.1 Comparison of theoretical simulations with experiments

We first compared our theoretical predictions for CO$_2$ and N$_2$ permeabilities of MOF-filled MMMs with the experimental data taken from nine different studies in the literature.[3,12–15,21–24] These experimental results spanned five orders of magnitude in gas permeability. Molecular simulations were carried out in a variety of feed pressures (1, 2, 4, 7 and 10 bar), permeate pressures (0.05, 0.06 and 10$^{-6}$ bar) and temperatures (295, 298 and 323 K) to be consistent with the experimental operating conditions which are listed in Table 1. Simulation results shown in Figure 1 considered all electrostatic interactions (adsorbate–adsorbate and adsorbate–MOF). There is good agreement between our theoretical results and experimental data both for CO$_2$ and N$_2$ permeabilities. Deviations were observed when the volume fraction of MOFs in the MMM increases beyond 0.3 because the accuracy of the Maxwell model decreases at filler volume fractions greater than 0.2. The good agreement between experiments and simulations clearly shows that our computational methodology provides a reasonable description of gas permeation in MOF-filled MMMs.

#### 3.2 Effects of EIAM on gas permeability of MOF-filled MMMs

To assess the relative importance of adsorbate–MOF electrostatic interactions for modelling MOF-based MMMs, we repeated the permeability calculations with EIAM being turned off. Figure 2 compares the computed CO$_2$ and N$_2$ permeabilities of MOF-filled MMMs with EIAM being turned off with those computed with EIAM being turned on. We did not show the results for ZIF-8 in this figure because the CO$_2$ adsorption in ZIF-8 did not change when the EIAM were turned off. The CO$_2$ adsorption isotherms of ZIF-8 with and without EIAM are given in Figure S10. Effects of EIAM on CO$_2$ adsorption in ZIF-8 have been previously studied by Pérez-Pellitero et al. [20] and Watanabe et al. [63] and were found to change the Henry’s constant by approximately 20%.

Results with EIAM being turned off were similar to those with EIAM being turned on. Because gas permeability does not change, the selectivity of the MOF-filled MMMs was not significantly affected from the electrostatic interactions. As shown below, this is a natural result of theoretical permeation models. The gas
permeability of polymers is dominant in determining the gas permeability of MMMs when the volume fraction of filler particles is small (e.g., <0.3). To explain this in more detail, we plotted CO2 permeability of a MOF-filled MMM as a function of CO2 permeability of pure MOF in Figure 3. In the calculations of Figure 3, we used Matrimid as the polymer because it is the most widely used polymer in MMM fabrication. The MOF was hypothetical, and its CO2 permeability was changed from 0.1 to 1013 Barrer. The volume fraction of MOF in MMM was set to 0.2, and the CO2 permeability of MOF/Matrimid MMM was calculated using the Maxwell model. Figure 3 shows that CO2 permeability of MMM does not change once the CO2 permeability of MOF exceeds 103 Barrer and highlights that the permeability of the polymer is much more effective in determining the permeability characteristics of MMM than filler particles.

To understand why this occurs, it is helpful to examine the following limiting cases of the Maxwell model given in Equation (7). First, we notice that the Maxwell model correctly recovers the permeabilities of the pure polymer and MOF for \( f = 0 \) and \( f = 1 \), respectively:

\[
\lim_{f \to 0} P_{\text{MMM}} = P_{\text{POLYMER}} \left[ \frac{2(1 - \phi) + (1 + 2\phi)\lambda}{(2 + \phi) + (1 - \phi)\lambda} \right] = P_{\text{POLYMER}},
\]

\[
\lim_{f \to 1} P_{\text{MMM}} = P_{\text{POLYMER}} \left[ \frac{2(1 - \phi) + (1 + 2\phi)\lambda}{(2 + \phi) + (1 - \phi)\lambda} \right] = P_{\text{MOF}}.
\]

When \( \lambda = 1 \), the polymer and MOF have the same
permeabilities; so, the permeability of the MMM is independent of the filling fraction $f$:

$$\lim_{\lambda \to 1} P_{\text{MMM}} = P_{\text{POLYMER}} = P_{\text{MOF}}.$$  \hfill (10)

For MOF-filled MMMs, the most important limiting condition occurs when $\lambda \gg 1$ (i.e. the MOF has much higher permeability than the polymer) and $f \leq 0.3$. For these conditions,

$$P_{\text{MMM}} \approx P_{\text{POLYMER}} \cdot \left[ \frac{1 + 2f}{1 - f} \right].  \hfill (11)$$

In other words, when the MOF’s permeability is much higher than the polymer’s permeability and the filling fraction is low, the permeability of MMM depends only on the polymer’s permeability and the filling fraction. Under these conditions, the adsorbate–MOF electrostatic interactions have no appreciable effect on the MMM permeability. An analogous limit also occurs when the MOF’s permeability is much lower than the polymer’s permeability (i.e. $\lambda \ll 1$) and the filling fraction is low (e.g. $f \approx 0.3$):

$$P_{\text{MMM}} \approx P_{\text{POLYMER}} \cdot \left[ \frac{2(1 - f)}{2 + f} \right].  \hfill (12)$$

Under these conditions, the permeability of MMM depends only on the polymer’s permeability and the filling fraction; so, the adsorbate–MOF electrostatic interactions have no appreciable effect on the MMM permeability.

The results in Figure 3 ($f = 0.2$) clearly demonstrate these limits. Specifically, as the CO2 permeability of MOF increases from very low values (i.e. $\lambda \ll 1$) to very high values (i.e. $\lambda \gg 1$), the permeability of MMM changes from about 6.5 to 16 with $P_{\text{POLYMER}} = 9$. Substituting $\phi = 0.2$ and $P_{\text{POLYMER}} = 9$ into Equation (11) gives $P_{\text{MMM}} \approx P_{\text{POLYMER}} \cdot (1 + 2\phi)/(1 - \phi) = 15.75$ as $P_{\text{MMM}}$ for the high MOF permeability limit. Substituting these values into Equation (12) gives $P_{\text{MMM}} = P_{\text{POLYMER}} \cdot 2(1 - \phi)/(2 + \phi) = 6.545$ as $P_{\text{MMM}}$ for the low MOF permeability limit. These limits are in excellent agreement with the computational results shown in Figure 3.

The significance of these findings is as follows: to construct an MMM with high-separation performance, it is necessary to start with a polymer that is already close to Robeson’s upper bound. By choosing an MOF that lies above Robeson’s upper bound and has a higher permeability and selectivity than the polymer for the faster gas species, an MMM can be constructed that gives better separation performance than the pure polymer. The filling fraction of this MOF should then be made as large as possible, subject to manufacturing considerations. (If the MOF fraction is too high, the membrane may become brittle or lose mechanical integrity.) For example,

Figure 2. Comparison of molecular simulation results with EIAM on and EIAM off for (a) CO2 and (b) N2 permeability in fabricated MOF-filled MMMs.

Figure 3. Change of MOF-filled MMM’s CO2 permeability as a function of pure MOF’s permeability.
if the filling fraction is \( \phi = 0.4 \), then in the limit \( \lambda \gg 1 \), \( P_{\text{MMM}} = 3P_{\text{POLYMER}} \). Using this strategy, it is possible to construct MMMs that perform much better than the pure polymer.

Although the MOF–polymer combination must be appropriately chosen to maximise MMM performance, \( P_{\text{MMM}} \) becomes insensitive to small changes in \( P_{\text{MOF}} \) for the limiting conditions described in Equations (11) and (12), as demonstrated in Figure 3. Under these conditions, adsorbate–MOF electrostatic interactions having a modest effect on \( P_{\text{MOF}} \) will have negligible impact on \( P_{\text{MMM}} \). For this reason, EIAM are much less important for MMMs than for pure MOF membranes. Accordingly, it is possible to carry out preliminary screening of MOF–polymer combinations for MMMs by neglecting EIAM to accelerate modelling of MOF-filled MMMs. However, to achieve the best accuracy, screening studies of MMMs performed neglecting EIAM should be followed by more detailed calculations including adsorbate–MOF electrostatic interactions. Our molecular simulations showed that EIAM are important for modelling pure MOF membranes as discussed in Section 3.3.

### 3.3 Effects of electrostatic interaction on gas permeability of pure MOF membranes

We observed that EIAM have significant effects on adsorption and diffusion of gas molecules in some MOFs. Table 1 represents the amount of gas adsorption and corrected diffusion coefficients of MOFs that have been used as filler particles in MMM experiments, CuBTC, MOF-5 and ZIF-90. When the EIAM were switched off, CO\(_2\) uptake has significantly decreased for CuBTC and ZIF-90, whereas a small change was observed for MOF-5. On the other hand, there is no important change in \( N_2 \) uptake in all MOFs. This can be attributed to larger quadrupole moment of CO\(_2\) (13.4 e\(\cdot\)m\(^2\)) than that of \( N_2 \) (4.7 e\(\cdot\)m\(^2\)).[75] Because the number of adsorbed CO\(_2\) molecules in ZIF-90 decreases, the diffusivity of CO\(_2\) molecules increases. Table 1 demonstrates that ZIF-90 is the most affected MOF by the electrostatic interactions, which may be attributed to the strong interaction of the carbonyl group of the imidazole linker in ZIF-90 with CO\(_2\) molecules.[3,76]

We then used the same calculation method to investigate the separation performance of new MOFs which have not been fabricated as membranes or MMMs to date. Figure 4 shows predicted CO\(_2\) and \( N_2 \) permeabilities of new MOF membranes. The CO\(_2\) permeability of pure MOFs increased or remained about the same when the EIAM were switched off as can be seen from Figure 4(a). This can be explained by examining the changes in adsorption and diffusion behaviour of CO\(_2\) in MOFs. When the EIAM were neglected, only LJ interactions become active and the adsorbed amount of CO\(_2\) decreases. On the other hand, the diffusion of CO\(_2\) increases in the absence of EIAM because less molecules are present in the pores and steric hindrance becomes less effective. This discussion is valid for all MOFs that we considered, and Table 2 represents adsorption amounts and diffusivities of both gases with and without EIAM. Figure 4(b) shows the \( N_2 \) permeability of pure MOF membranes. In most cases, the \( N_2 \) permeability of MOFs increases when the EIAM were not considered in the simulations due to the enhancement in the transport of gas molecules. However, for OHETIE and ZUQPOQ, the \( N_2 \) permeability slightly decreases when the electrostatic effects were ignored because the decrease in \( N_2 \) adsorption is more pronounced than the increase in \( N_2 \) diffusion. This shows that electrostatic interactions can lead to either an increase or decrease in the gas permeability and the main reason of this is the change in gas adsorption isotherms as we discuss below.

Figure 5 shows how the CO\(_2\) and \( N_2 \) uptakes of MOFs change without EIAM at feed and permeate pressures of the membrane. The MOFs that lie close to the straight line are not affected by EIAM. The CO\(_2\) adsorption in OHETIE decreases dramatically in the absence of electrostatic interactions. This might be due to the presence of \( -\text{NH}_3^+ \) groups in the framework which have strong interaction with CO\(_2\) molecules. Adsorption isotherm of CO\(_2\) in OHETIE is given in Figure S11 and shows that EIAM are important up to 20 bar. As the pressure increases, more
Table 2. Effects of EIAM on gas adsorption and diffusion of new MOFs.

|               | EIAM<sub>on</sub> | EIAM<sub>off</sub> |
|---------------|------------------|---------------------|
|               | \( C_f \) (m./u.c.) | \( C_p \) (m./u.c.) | \( D_o \) (cm²/s) | \( C_f \) (m./u.c.) | \( C_p \) (m./u.c.) | \( D_o \) (cm²/s) |
| CO₂           |                  |                     |                     |                  |                     |                     |
| CECYOY        | 9.55             | 2.28 \times 10^{-4} | 8.38 \times 10^{-5} | 9.88             | 1.12 \times 10^{-4} | 7.27 \times 10^{-4} |
| FEVVIM        | 16.30            | 2.46 \times 10^{-3} | 1.79 \times 10^{-6} | 14.05            | 4.94 \times 10^{-5} | 1.13 \times 10^{-5} |
| IDUDOA        | 16.48            | 1.64 \times 10^{-4} | 8.56 \times 10^{-7} | 15.05            | 5.37 \times 10^{-5} | 1.85 \times 10^{-5} |
| IJOMOJ02      | 2.97             | 3.34 \times 10^{-6} | 3.28 \times 10^{-5} | 2.25             | 1.77 \times 10^{-6} | 5.80 \times 10^{-5} |
| KEXFAU        | 13.77            | 2.97 \times 10^{-4} | 2.81 \times 10^{-5} | 11.09            | 2.83 \times 10^{-5} | 5.75 \times 10^{-5} |
| OHETIE        | 14.49            | 3.29 \times 10^{-4} | 1.36 \times 10^{-5} | 0.61             | 2.63 \times 10^{-7} | 3.15 \times 10^{-4} |
| YARYEV        | 3.93             | 2.75 \times 10^{-6} | 2.15 \times 10^{-5} | 1.11             | 5.42 \times 10^{-7} | 6.99 \times 10^{-5} |
| ZUQPOQ        | 3.99             | 2.63 \times 10^{-4} | 6.70 \times 10^{-5} | 3.35             | 7.76 \times 10^{-6} | 1.16 \times 10^{-4} |
| N₂            |                  |                     |                     |                  |                     |                     |
| CECYOY        | 2.19             | 1.47 \times 10^{-6} | 5.47 \times 10^{-4} | 2.08             | 1.24 \times 10^{-6} | 9.60 \times 10^{-4} |
| FEVVIM        | 4.07             | 3.21 \times 10^{-6} | 4.65 \times 10^{-6} | 3.60             | 2.46 \times 10^{-6} | 5.39 \times 10^{-6} |
| IDUDOA        | 4.30             | 2.85 \times 10^{-6} | 5.60 \times 10^{-7} | 3.95             | 2.91 \times 10^{-6} | 1.26 \times 10^{-6} |
| IJOMOJ02      | 0.41             | 1.92 \times 10^{-7} | 3.37 \times 10^{-5} | 0.37             | 1.94 \times 10^{-7} | 6.12 \times 10^{-5} |
| KEXFAU        | 2.20             | 1.43 \times 10^{-6} | 3.13 \times 10^{-4} | 2.07             | 1.28 \times 10^{-6} | 4.78 \times 10^{-4} |
| OHETIE        | 0.94             | 6.17 \times 10^{-7} | 3.20 \times 10^{-4} | 0.19             | 8.20 \times 10^{-8} | 3.42 \times 10^{-4} |
| YARYEV        | 0.27             | 1.38 \times 10^{-7} | 7.97 \times 10^{-5} | 0.23             | 1.05 \times 10^{-7} | 9.57 \times 10^{-5} |
| ZUQPOQ        | 0.91             | 6.58 \times 10^{-7} | 1.15 \times 10^{-4} | 0.61             | 3.83 \times 10^{-7} | 7.49 \times 10^{-5} |

Note: m./u.c., molecules/unit cell.

Figure 5. Effects of EIAM on CO₂ and N₂ adsorption of MOFs.
adsorbate molecules are present in the pores and adsorbate–adsorbate interactions become dominant compared with adsorbate–MOF interactions. For example, we found that at 2 bar, the difference between CO\textsubscript{2} uptake with EIAM and CO\textsubscript{2} uptake without EIAM is 19.45%, whereas at 10\textsuperscript{-6} bar, this difference increases up to 90.5% for KEXFAU. This result showed that at low pressures, the electrostatic interactions have a more significant effect. Similar results for other MOFs were found by Liu and Zhong [77] and Watanabe et al. [63].

Our results so far suggested that EIAM have a large effect on predicting gas permeability of pure MOF membranes. Figure 6 represents gas permeability and selectivity of pure MOF membranes in CO\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4} and H\textsubscript{2}/CO\textsubscript{2} separations together with commercial polymers. The open (closed) symbols shown in Figure 6 give the permeability and selectivity of pure MOFs when the EIAM were turned off (on). The CO\textsubscript{2} selectivity of MOFs from N\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2} increases when the EIAM were turned off because the CO\textsubscript{2} permeability of MOFs increase as shown in Figure 4. KEXFAU is the only MOF located above the Robeson’s upper bound for all gas separations regardless of the EIAM. KEXFAU has a very high CO\textsubscript{2} permeability, $2.23 \times 10^6$ Barrer and moderate CO\textsubscript{2} selectivity over N\textsubscript{2} (5.61). Figure 6(a) shows that IDUDOA, ZUQPOQ and CECYOY can exceed the upper bound when EIAM were turned off due to the enhancement in CO\textsubscript{2} selectivity from N\textsubscript{2}. This result is expected because the increase in CO\textsubscript{2} permeability is much more pronounced than the increase in N\textsubscript{2} permeability. The increase in CO\textsubscript{2} permeability when the EIAM were not considered results in an increase in CO\textsubscript{2}./
CH$_4$ selectivity and a decrease in H$_2$/CO$_2$ selectivity because the permeability of CH$_4$ and H$_2$ are not affected by EIAM (see Figure 6(b),(c)). These results highlight the importance of the EIAM for the accurate assessment of the separation performance of pure MOFs. It is well known that fabrication of robust and defect-free thin film MOF membranes is challenging and costly. Therefore, we investigated performances of these MOFs as filler particles in selected commercial polymers such as PDMS, PTMSP, 6FDA-DAM and silicon rubber in Section 3.4.

3.4 Separation performances of new MOF-based MMMs
Figure 7 represents predictions of the Maxwell model for separation performance of pure MOFs, pure polymers and MOF-filled MMMs. All the electrostatic interactions including adsorbate–adsorbate and adsorbate–adsorbent were taken into account in these calculations. Because only KEXFAU is above the CO$_2$/N$_2$ upper bound, we considered its performance as a filler in PDMS and PTMSP polymers. PDMS has a moderate CO$_2$ permeability (2520 Barrer) and CO$_2$/N$_2$ selectivity (8.37), whereas PTMSP has a high CO$_2$ permeability (37,000 Barrer) but low CO$_2$/N$_2$ selectivity (5.37). As can be seen from Figure 7(a), CO$_2$ permeability of KEXFAU-filled MMMs increases compared with pure polymer membranes. The inset graph represents how the CO$_2$ permeability of PDMS and PTMSP increases as the volume fraction of MOF increases. Incorporation of KEXFAU at high-volume fractions into PTMSP can even carry this polymer onto the upper bound.

For CO$_2$/CH$_4$ separation, we considered three MOFs: IDUDOA, ZUQPOQ and KEXFAU and three polymers: 6FDA-DAM, silicon rubber and PTMSP. Figure 7(b) demonstrates the importance of polymer/MOF matching on the separation performance of MOF-filled MMMs. Incorporation of IDUDOA into 6FDA-DAM and silicon
rubber enhances both the CO₂/CH₄ selectivity and CO₂ permeability of these polymers, whereas incorporation of IDUDOA into PTMSP increases CO₂/CH₄ selectivity at the expense of decreasing CO₂ permeability. This result is expected because CO₂ permeability of IDUDOA is lower than (5.88 × 10⁵ Barrer) the permeability of pure PTMSP (37 × 10⁵ Barrer). On the other hand, only CO₂ permeability enhancements were obtained for ZUQPOQ/6FDA-DAM and ZUQPOQ/silicone rubber MMMs without any significant change in CO₂ selectivity. Addition of ZUQPOQ into silicon rubber and PTMSP improved both the permeability and selectivity. The CO₂/CH₄ selectivity of PTMSP membrane increases from 2.01 to 2.50 when ZUQPOQ with a volume fraction of 0.3 is incorporated into polymer. Addition of KEXFAU into all polymers increases their CO₂ permeabilities without any significant change in the CO₂ selectivities.

Figure 7(c) shows H₂ permeability and H₂/CO₂ selectivity of MOF-filled MMMs. Incorporation of IDUDOA, YARYEV, FEVVIM, CECYOY and KEXFAU into PDMS and PTMSP improves H₂ permeability of both polymers. Because PTMSP is close to the upper bound, even small volume fractions of MOFs are enough to carry PTMSP above the upper bound. Each MOF has different effects on gas permeability and selectivity of pure polymer. For example, incorporation of FEVVIM into PTMSP increases H₂/CO₂ selectivity but slightly decreases H₂ permeability. On the other hand, addition of KEXFAU into PTMSP increases only H₂ permeability of PTMSP with little change in selectivity. This result highlights the importance of MOF/polymer matching in achieving high-performance MMMs. Because PDMS is away from the upper bound, it is not possible to carry it close to the upper bound by using the MOFs considered in this work.

It is important to note that our theoretical models assumed well dispersion of filler particles in MMMs. However, as the volume fraction of filler increases, agglomeration may occur due to the disruption of polymer chains with the addition of excessive filler loadings.[78] This issue is more likely to be handled by experiments, and the aim of our calculations was to motivate extensive experimental studies for the MMMs identified as highly promising in gas separations.

4. Conclusion
In this article, molecular simulations were combined with the Maxwell permeation model to estimate the performance of different MOF/polymer combinations as MMMs for CO₂/CH₄, CO₂/N₂ and H₂/CO₂ separations. First, the computational methodology was benchmarked to show good agreement with published experimental data. Then, calculations of new MOF/polymer pairs revealed many MMMs that lie above Robeson’s upper bound for gas separation performance. To better understand the role of electrostatic interactions, adsorption isotherms and diffusion coefficients of gases in MOFs were computed with the EIAM being turned on and off. Our results showed that including EIAM is crucial in modelling of pure MOF membranes but has less significance for modelling MOF-filled MMMs. This can be explained in terms of the following limits of the Maxwell model. When the MOF volume fraction, φ ≤ 0.30 and the permeability ratio λ = PMOF/P_POLYMER approaches (1 + 2φ)/(1 − φ) independent of the precise λ value. When λ = PMOF/P_POLYMER = 1, the permeability ratio PMOF/P_POLYMER equals to 1 independent of the φ value. When the MOF volume fraction φ ≤ 0.30 and the permeability ratio λ = PMOF/P_POLYMER ≪ 1, the permeability ratio PMOF/P_POLYMER approaches (1 − φ)/2 + φ independent of the precise λ value. Thus, whenever the MOF volume fraction φ ≤ 0.30, the permeability ratio PMOF/P_POLYMER is only a weak function of λ. Because the EIAM only affect PMOF (and hence the λ value), the EIAM have negligible effect on PMOF whenever φ ≤ 0.3. For high-MOF volume fractions (i.e. φ → 1), the Maxwell model gives PMOF → P_POLYMER. Accordingly, the EIAM are important for high-MOF volume fractions in MMMs and for pure MOF membranes. The results of this study showed that for rapid screening of MOF/polymer MMMs, the EIAM can be neglected as a reasonable approximation if the MOF volume fraction φ ≤ 0.3. For higher MOF volume fractions, the EIAM should be included in the computational model. However, we did encounter one MOF (OHETIE) for which adsorbate–MOF electrostatic interactions changed the adsorption capacity significantly at low pressures (i.e. permeate pressure), which suggests that screening studies of MMMs carried out neglecting EIAM should be followed up by more detailed calculations including adsorbate–MOF electrostatic interactions.

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