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A New Era of Modeling MOF-Based Membranes: Cooperation of Theory and Data Science

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Membrane-based separation can offer significant energy savings over conventional separation methods. Given their highly customizable and porous structures, metal–organic frameworks- (MOFs) are considered as next-generation membrane materials that can bring about high separation performance and energy efficiency in various separation applications. Yet, the enormously large number of possible MOF structures necessitates the development and implementation of efficient modeling approaches to expedite the design, discovery, and selection of optimal MOF-based membranes via directing the experimental efforts, time, and resources to the potentially useful membrane materials. With the recent developments in the field of atomic simulations and artificial intelligence methods, a new era of membrane modeling has started. This review focuses on the recent advances made and key strategies used in the modeling of MOF-based membranes and highlight the huge potential of combining atomistic modeling of MOFs with machine learning to explore very large number of MOF membranes and MOF/polymer composite membranes for gas separation. Opportunities and challenges related to the implementation of data-driven approaches to extract useful structure–property relations of MOF-based membranes and to produce design principles for the high-performing MOF-based membranes are discussed.

1. Background

Metal–organic frameworks (MOFs) are highly tailorable porous structures thanks to the combinations of various metal nodes and organic linkers creating voids of different shapes and sizes.

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Although the history of MOFs goes back to 1950s,[1] the seminal works by Yaghi et al.[2–4] in 1990s brought MOFs under the spotlight as the experimentally proven ultrahigh and permanent porosity of MOFs can offer solutions to the challenging problems in various fields including gas adsorption and separation, catalysis, biomedicine, and sensing.[5–10] The early MOF syntheses mostly relied on methods shaped by trial-and-error approach and experimentalist experience through which synthesis conditions (reaction time, temperature, reactant ratio, etc.) were determined.[11,12] Over the years, it was shown that many different kinds of MOF design involving isoreticular MOFs, MOFs with partitioned pores, open metal sites, functionalized MOFs, and interpenetrated MOFs can be realized.[13,14] With the advancement of rational MOF design techniques, systematic synthesis routes and targeted MOF screenings based on structure–property trends, the number and variety of synthesized MOFs have been significantly expanded in a relatively short period of time.[15] Today, the number of MOFs deposited into the Cambridge Structural Database (CSD)[16,17] has exceeded 100 000 and given the increasing interest in synthesizing many more and diverse MOF structures, a much larger pool of synthesized MOFs can be expected in the near future.[18]

Together with the acceleration of MOF synthesis, there have been significant developments in generating hypothetical (computer-generated) MOFs using different algorithms in the last decade. The pioneering work by Wilmer et al.[19] showcased the hypothetical generation of more than 100 000 MOFs by using a combinatorial technique where combinations of building blocks extracted from the synthesized MOFs were linked together subsequently like tinker toys until a MOF structure is formed.[20] This bottom-up approach sparked much interest among computational researchers as it allowed investigating properties of MOFs at an unprecedented scale. Following the bottom-up approach, as an alternative, top-down approach was utilized to generate hypothetical MOFs where a topology is first selected and combinations of building blocks are placed into the specified network.[21–23] Through the use of hypothetical MOF generation techniques, the diversity and number of hypothetical MOFs have seen an unprecedented expansion.[24–26] Recently, new computational tools have been introduced by which MOFs with defects and/or functional groups can be designed.[27,28] The expansion

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of such computational approaches for the design of novel MOFs with different structural and chemical properties enabled generating thousands of materials quickly. A recent study[28] reported trillions of computer-generated MOFs using automation showing the vast possibilities of MOFs that can be realized. MOFs have been computationally investigated to determine their various properties including ion separation capability,[29] bandgaps,[30] reaction barriers,[31,32] free energy of immersion,[33] which can help identify the promising materials for ion extraction, conductivity, catalysis applications, and evaluate their thermodynamic stability. For instance, MOF-based membranes can be used for many kinds of ion separation applications including heavy metal removal, desalination, and lithium extraction which can remediate various environmental problems.[29,34] The separation of ions is typically performed via affinity differences caused by functional groups, pore size sieving, and/or electrostatic repulsion.[34,35] The use of MOF-based membranes in ion separation applications could lead to high selectivity, sustainable, and facile operation as well as relatively low capital cost.[29] To this end, water-stable MOF-based membranes can be highly beneficial as many types of ion separations are performed in aqueous environments.[29] Recently, it has been demonstrated that a ZIF-based anion exchange membrane can promote the transport of target ion (Cl^-) while hindering that of multivalent anions (PO_4^{3-}, SO_4^{2-}), which enables more efficient ion separation than that achieved through a commercial anion exchange membrane.[35]

Yet, one of the most investigated applications of MOFs has been their membrane-based gas separation performances assessed via molecular simulations, which provide an atomic-level understanding of their separation properties. Membrane-based gas separation is renowned for its operational and economic advantages over traditional methods such as low capital and operation cost, ease of operation, and low footprint.[5] Indeed, it has been envisioned that membrane-based separation can cut down the energy costs by 90% compared to the currently used conventional techniques such as absorption, and cryogenic distillation.[36] Most of the current membranes are typically made up of polymers due to their good mechanical strength, low cost, and ease of processability, but they have a well-known trade-off between membrane selectivity and gas permeability called Robeson's upper bound.[5,37–39] Both high gas permeability and membrane selectivity are desired to achieve an economic and efficient membrane-based gas separation as the former would enable the construction of membranes with small surface areas while the latter would enable obtaining streams with high purity.[40] Membrane separation processes rely on both the adsorption and diffusion properties of the molecules desired to be separated in the porous materials. As too strong or too weak adsorption of the desired specie in the materials may not result in high membrane separation performance due to slow diffusion or low specie concentration, the features of membrane materials should be optimized to provide an optimal medium for both adsorption and diffusion. Thanks to their tailorable and highly porous structures, MOFs can offer many advantages such as high gas permeability and selectivity when used as membranes. Regarding the gas separations, the criteria used to assess membrane materials may change depending on the separation needs (e.g., separations requiring large volumes of streams to be separated and/or high-purity products), yet, for many applications,

one of the first targets is to achieve surpassing the Robeson's upper bounds of conventionally used polymer membranes.[38,39] These bounds have been exceeded by many synthesized and hypothetical MOFs examined using experiments and molecular simulations.[41–46] Given their high potential, the number of studies on MOF-based membranes has exploded in the last decade exceeding 3800 publications as of early 2023 (based on a Web of Science search using the keywords of metal–organic framework and membrane in article topics), implying that further improvement in membrane-based gas separations with MOFs is very likely.[5,47] While it may take time to see the use of MOF-based membranes in the industry, some of the MOFs already showed much success at the laboratory scale.[48,49] Thin film MOF membranes were initially generated in the lab, but difficulties regarding their scalable and defect-free fabrication prompted the synthesis of alternative MOF-based membranes.[50] One of the most advantageous types of membranes in terms of affordable cost, facile processability, and high performance is mixed-matrix membranes (MMMs), where MOFs are dispersed as fillers in the polymer matrix.[50] Thanks to their broad physical and chemical properties, MOF-based membranes hold the promise to offer unprecedented opportunities for various gas separation applications. Yet, experimental investigation of all viable MOF-based membranes would be a never-ending task due to the sheer number of MOF building block combinations. To accelerate the discovery of high-performing MOF-based membranes, the coupling of various modeling and simulation tools and data science techniques is highly warranted through which information can be supplied to experimentalists. Taking MOF-based membranes from the lab to practical use will take effort and time, however, this process can only be carried out efficiently through the combined use of experimental, theoretical knowledge, and big-data science.

Figure 1 shows an overview of the different methodological approaches for the investigation of MOF-based membranes. While studies on MOFs were intensified after 1990s following the synthesis of MOFs with large surface areas,[4] the syntheses of MOF membranes have been reported in 2000s, for example, Mn formate MOF membrane in 2006,[51] HKUST-1 (CuBTC) membrane in 2007.[52] Since then, the total number of MOF membranes synthesized and tested for different gas separations has expanded considerably. Yet, most of the experimental studies still typically focus on the synthesis, characterization, and testing of a single or a few MOF membranes due to the large time, effort, and resource requirements of making robust membranes from new crystalline materials.[7] Examining the computational side, one of the first MOF membrane modeling studies appeared in 2007 where CO_2/CH_4 separation performance of a MOF-5 membrane was investigated by combining theoretical models and earlier GCMC and MD simulation results.[53,54] Ever since, high-throughput computational screening (HTCS) studies investigating gas separation performances of hundreds (or more) of different types of MOF membranes have become more common as discussed below. Currently, molecular simulation studies of MOF membranes mostly employ generic force fields that were not specifically derived for MOFs, and with the development and use of specialized force fields such as the first principles-based force fields, it is possible to obtain more accurate computational predictions for MOF membranes. For instance, it was shown that
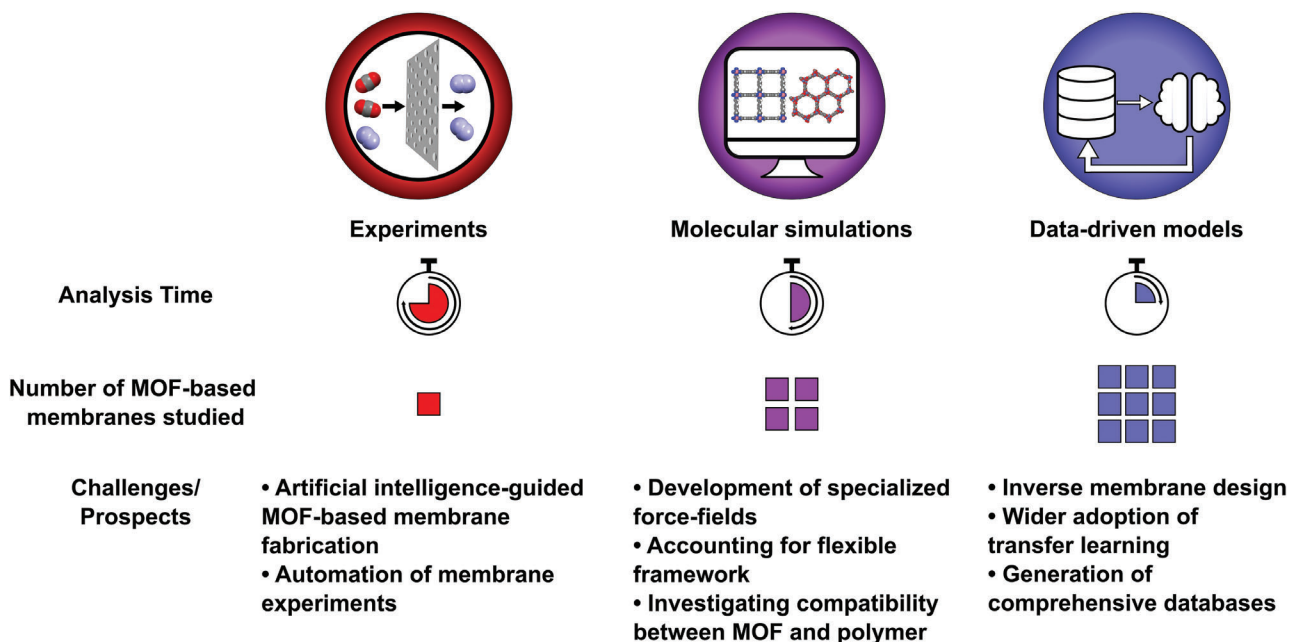
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Figure 1. An overview of different methodologies used to study MOF-based membranes summarizing typical analysis time of MOF-based membranes, number of MOF-based membranes that can be probed, and potential challenges/prospects.

ab initio force fields derived for CO_2 adsorption in M-MOF-74 could provide adsorption loadings in better agreement with experiments than those obtained using a generic force field.[55–58] Similarly, the widely adopted assumption of rigid frameworks could be relaxed by employing flexible force fields that can reveal drastic differences in adsorption and diffusion properties across simulations using rigid and flexible frameworks. For instance, comparing simulation results where rigid and flexible structures were employed, it was concluded that both Henry's constants and/or gas loadings at high pressures in MOFs could be considerably different where flexibility effects were typically more important for large adsorbates.[59,60] Similarly, it was previously demonstrated that the self-diffusivities of CH_4 in UiO-66 could differ significantly across frameworks modeled rigid and flexible where the self-diffusivities obtained using flexible force field were much closer to experimental values.[61] Recent works that developed force fields describing intramolecular interactions in ZIFs, MIL-88B demonstrated that using density-functional theory (DFT) calculations, accurate flexible force fields could be derived.[62–64] So far, one of the less probed areas in the simulation studies of the MOF structures is stability/phase transition, which is anticipated to attract more interest in the near future as many studies pinpointed potentially high-performing MOF membranes that can find use in practical separation applications.[65–69]

With the expansion of computational resources, generating computational data for large number of materials has become a much faster process enabling investigation ofthousands of MOFs for a particular gas separation of interest. Machine learning (ML) has recently appeared as a strong computational tool to make accurate predictions for the properties and performances of a large variety of materials. One of the earliest ML studies on MOF membranes, to the best of our knowledge, was about D_2/H_2 separation where the large-scale MOF data were used to generate ML mod-

els to identify the promising MOF membranes in terms of ideal selectivity showing the potential of ML models for the categorization of high- and low-performing MOF membranes.[70] Later, ML models predicting the separation performances of MOF membranes were developed for various gas separations.[71–75] For instance, Orhan et al.[74] calculated the Henry's constants, uptakes, and self-diffusivities of O_2 and N_2 in MOFs and subsequently developed ML models to predict selectivities of MOF membranes at infinite dilution conditions and 1 bar, 298 K.

This review specifically highlights the current state-of-the-art in the computational modeling of MOF-based membranes to identify the promising membrane materials and structure–property correlations, which can facilitate the design of high-performing membranes. We specifically focused on the very recent developments in fusing molecular simulation techniques and ML methods to unlock the potential use of MOF-based membranes in various gas separations. After reviewing the use of gas permeation models, atomistic-level simulations, process modeling, stability, and cost analysis of membranes, we discussed the integration of data science techniques and molecular simulations for predicting gas separation performances of MOF membranes and MOF/polymer composite membranes. We finally addressed the challenges listed in Figure 1 which can lead to great opportunities for the joint experimental/theoretical/data-driven efforts to generate new, robust, and high-performing MOF-based membranes.

2. Current State-of-the-Art in Modeling of MOF Membranes

MOF-based membrane modeling studies mainly focus on the determination of the two key membrane performance metrics (gas permeability and membrane selectivity), which are typically

obtained using force field-based classical molecular simulations. In these simulations, the intermolecular interactions are mostly represented by the combination of van der Waals and Coulombic interactions whose accuracies rely on multiple factors including but not limited to gas models, and partial charge assignment methods.[40] Among computational MOF-based membrane studies, the most commonly utilized techniques are grand-canonical Monte Carlo (GCMC), equilibrium molecular dynamics (EMD) and nonequilibrium molecular dynamics (NEMD), transition-state theory (TST), and DFT.[50] GCMC simulations have become a standard tool to determine the gas adsorption properties (i.e., gas uptakes or gas affinities) of MOF membranes while the gas diffusion properties in MOF membranes can be acquired via MD simulations or TST approach. Once the gas adsorption amounts and gas diffusivities are calculated, permeability and membrane selectivity (i.e., ratio of gas permeabilities) can be determined based on the solution-diffusion model.[76]

In the initial stages of modeling of MOFs, the crystallographic information of the experimental MOF structures was dispersed in the literature requiring manual/automated scraping of structures of interest. Today, more than 100 000 MOF structures have been deposited into the CSD[16] with reference codes for easy identification.[18] One of the first publicly available collections of experimental MOF structures aimed to collect and curate structures (MOFs without framework disorders and/or other complexities such as the presence of solvents) from the CSD to provide "computation-ready" structures that can ideally be used in molecular simulations without any modification.[77] The availability of computation-ready experimental MOF structures streamlined the investigation of hundreds/thousands of MOF membranes via GCMC and MD simulations for various gas separations such as CO_2/N_2,[78,79] and $CO_2/N_2/CH_4$.[65] The success of computation-ready MOF database prompted its recent expansion, which now includes more than 12 000 structures furthering the investigation of membrane-based separation performances of experimentally reported MOF structures.[80,81] Similarly, a recent effort has led to the creation of a curated CSD MOF subset with more than 60 000 structures that is regularly updated.[15] The introduction of hypothetical MOF databases enabled scrutiny into not yet synthesized MOFs that can elucidate the potential performance gains over the synthesized ones.[19,23–25] While some of these MOF databases were computationally screened for the membrane-based separation of H_2/CH_4,[41] CO_2/N_2,[79,82] CO_2/CH_4,[66,83] H_2/N_2,[84] CO_2/H_2,[67] H_2S/CH_4,[66] $CO_2/N_2/H_2O$,[78] and $CO_2/N_2/CH_4$,[42] the number of hypothetical structures and types of gas mixtures that have not been investigated yet constitute a rich domain, suggesting that there is a lot of room for studying MOF membranes using computational methods. Given the even larger number of structures that can be obtained through integrating MOFs with other porous materials and constructing mixed ligand structures, the opportunities for gas separation using MOF-based membranes are almost endless.[85–87]

Figure 2a displays the typical HTCS approach where structures of interest are first collected from MOF database(s) based on user-specified criteria such as the pore size of the MOFs and interactions between the gas molecules and MOF atoms in molecular simulations are defined through either quantum chemical calculations or force fields. As the separation performance is the key factor for the selection of a membrane material, in general,

HTCS studies have mostly investigated gas adsorption and diffusion properties of MOF structures.

Among the three main approaches (EMD, NEMD, and TST) to investigate the gas diffusion in MOF membranes, EMD is the most popular one whose results have been combined with GCMC results to obtain permeability of various gases (e.g., CO_2, N_2, CH_4) in MOFs.[50] Figure 2b shows the results of an HTCS where about 3806 MOF membranes were investigated for CO_2/N_2 separation under infinite dilution condition using GCMC and MD simulations. Almost 80% of the studied MOFs were found to surpass the Robeson's upper bound[78] because of their very high CO_2 permeabilities, showing the high potential of MOF membranes to replace the conventional polymer membranes in flue gas separation.

2.1. Modeling Permeation in MOF Membranes

Almost all HTCS of MOF membranes have computed gas adsorption and diffusion in a single MOF crystal via molecular simulations and the gas permeability computed through a single MOF crystal was used to describe the separation performance of a MOF membrane. To mimic the practical membrane-based gas separation, forming a MOF surface and computing gas permeation through the MOF layer can be useful, however, this may computationally be more demanding. NEMD approach was used to simulate gas permeation through MOF membranes since this simulation technique is ideally suited to represent an experimental membrane system in which an external driving force, such as pressure gradient, is applied to a membrane. Figure 2c shows an example of H_2 and CH_4 mixture permeation through a ZIF-8 membrane constructed in the NEMD simulation.[88] NEMD typically requires significantly longer simulation times than the computational approach that combines GCMC and EMD simulations to predict gas permeability, however, implementation of NEMD instead of EMD can provide more realistic results and better agreement with the experimentally measured gas permeations since it takes into account mass transfer resistance at the pore mouth of the membranes.[88] Ozcan et al.[89] developed a new NEMD method called concentration-gradient-driven MD (CGD-MD) and demonstrated that experimental gas permeability trend can be reproduced for hydrocarbons including methane, ethane, and ethylene and for the separation of an equimolar ethylene/ethane mixture in a ZIF-8 membrane.

We further discuss several important aspects related to the modeling of MOF membranes, since these issues may significantly change the studies' conclusion about the separation performances and material rankings. For example, there can be significant disparities across experimental and simulated gas separation performances of MOF membranes, which can be in part attributed to the presence of defects affecting gas adsorption and diffusion.[37] Kim et al.[37] performed preliminary screening of >800 MOF membranes for the separation of H_2/CH_4 mixture based on the Henry's constants (K_H^0) and self-diffusivities of gases computed at infinite dilution (D^0). It was shown that both adsorption and diffusion-related properties (K_H^0, D^0, permeability, membrane selectivity) could be significantly altered due to the presence of defects and different defect concentrations resulting in differently ranked top MOFs based on the
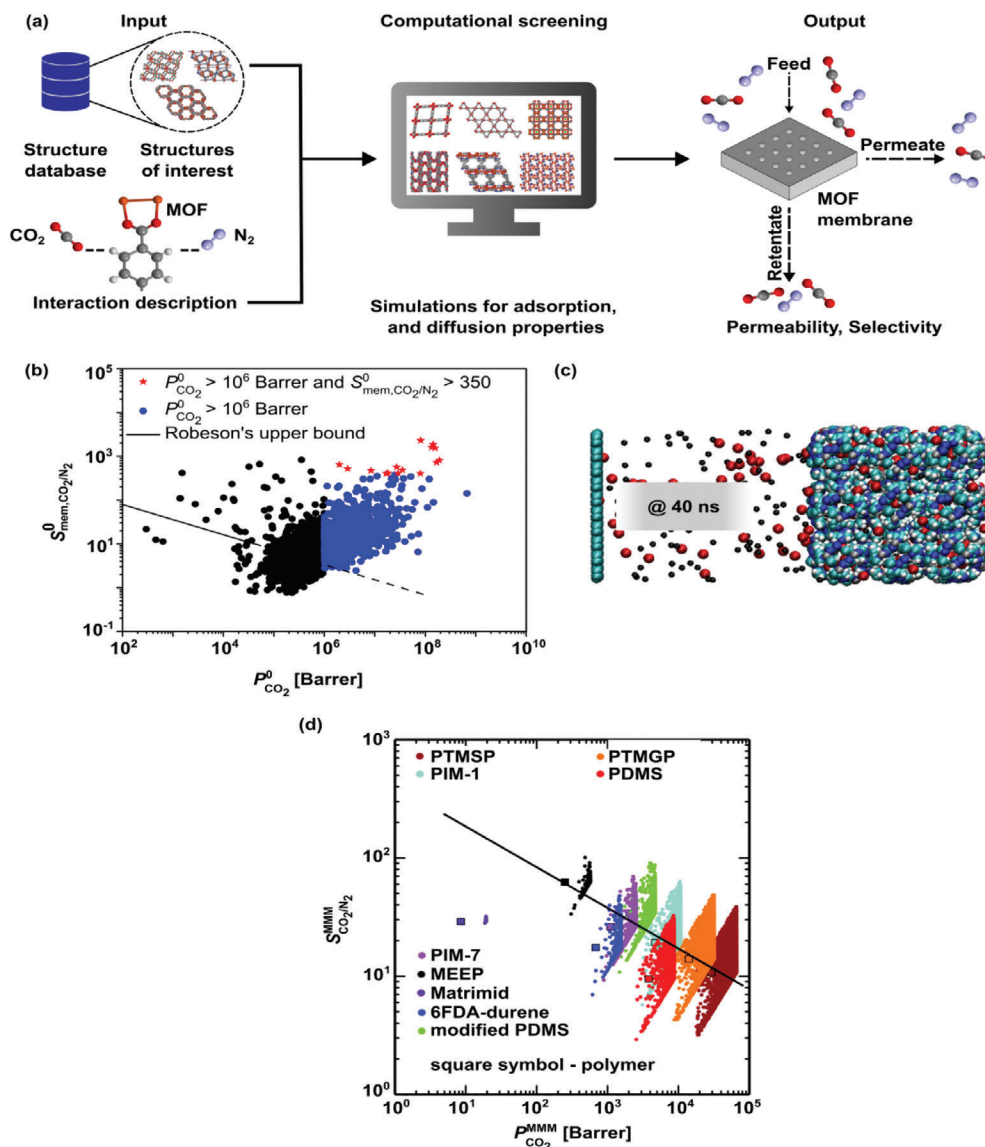
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Figure 2. a) Representation of HTCS approach for computational screening of MOF-based membranes. b) CO_2/N_2 selectivity and CO_2 permeability of 3806 MOF membranes computed by combining GCMC and MD simulations at infinite dilution at 298 K. Adapted with permission.[78] Copyright 2018, American Chemical Society. c) NEMD snapshot showing the feed side of the ZIF-8 membrane for CH_4 (red symbols) and H_2 (black symbols) mixture permeation. Adapted with permission under the terms of the CC BY-NC 3.0 license.[88] Copyright 2019, The Authors, published by Royal Society of Chemistry. d) CO_2/N_2 selectivity and CO_2 permeability of over 1 million MOF/polymer MMMs computed by combining molecular simulations and the Maxwell model. Adapted with permission.[79] Copyright 2019, Royal Society of Chemistry.

membrane selectivity. Combining the gas separation performance analyses of defective and pristine MOF membranes could be beneficial to estimate overall separation performances (over the initial and prolonged operation cycles) as pristine MOFs could start degrading over cycles.[37] Kallo and Lennox[90] constructed defective and defect-free 2D CuBDC MOFs and used external force NEMD simulations for CO_2/CH_4 mixture separation. Comparing the flux ratios, it was shown that 2D CuBDC had higher performances over bulk CuBDC across a large pressure drop range where strongly adsorbing CO_2 could block the passage of CH_4 leading to a pore blocking separation mechanism. While the defect-free structure was selective toward

CO_2, the presence of missing linkers could lead to having nonselective or CH_4 selective membranes depending on the missing linker concentration, attributed to weakened pore blocking due to created cavities. This implies that identifying promising membranes through computations needs to be complemented with the synthesis of membranes identical to computational models to observe the desired performance in practical use.

Another important aspect regarding the MOF membranes is the role of the MOF functionalization on membrane separation performance. By carrying out dual-force zone NEMD simulations for H_2/CH_4 separation in bare and functionalized IRMOF-1 membranes, Wang et al.[91] demonstrated that the

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incorporation of functional groups can lead to higher or lower gas permeabilities depending on the gas and functional group type. Wu et al.[92] also computationally investigated CO_2/CH_4 and CO_2/N_2 membrane separation performances of pristine UiO-66 and —$(COOH)_2$ functionalized UiO-66 using GCMC and EMD methods. It was shown that the incorporation of —(COOH) functional groups could dramatically raise the permeation selectivity of pure MOF membrane for both separations surpassing selectivities of many other commonly studied MOFs such as Cu-BTC.

While most of the studies focus on dry gas mixtures, in practice, there exists water vapor at different levels in the gas mixtures to be separated that can degrade the MOFs. Chen et al.[93] investigated the degradation of a Zn-based MOF due to water adsorption through MC simulations, which unveiled that the MOF degradation could happen due to the initial water uptake at defect sites followed by water molecule clustering. This signifies the importance of considering potential differences across experimental samples and ideal models and incorporating such structural differences in modeling as they can help elucidate the experimental observations. Daglar and Keskin[78] investigated humidity effect on flue gas separation performances of MOF membranes using GCMC and EMD simulations by comparing CO_2/N_2 and $CO_2/N_2/H_2O$ mixture simulation results and showed that the presence of water molecules in flue gas mixture could hamper the CO_2 permeability and CO_2/N_2 membrane selectivity.

One of the most widely studied gases for membrane-based separation is CO_2 due to its environmental and energetic relevance. Studying membrane separation of molecules with strong quadrupole such as CO_2 using the force field-based molecular simulations requires accurate partial charge assignments to the membranes. It is known that the use of different atomic partial charge assignment methods may lead to drastically different adsorption and/or diffusion properties.[94] Ongari et al.[95] compared highly accurate DFT-based density-derived electrostatic and chemical charge method (DDEC3)[96,97] charges with several other variants of charge assignment methods including Qeq,[98] EQeq,[99] MEPO-Qeq[100] and demonstrated that the latter can be systematically different than the former charges influencing adsorption of several gases (i.e., CO_2) in MOFs. This implies that the membrane-based separation performances of MOFs can also be influenced by the charge assignment schemes since they are governed by not only diffusion properties but also adsorption properties. Altintas et al.[94] employed different partial charge assignment methods for MOFs, DDEC3 as a DFT-based method and Qeq as an approximate method, to determine their role on the CO_2/CH_4 separation performances of MOF membranes. Results showed that depending on the gas mixture conditions, MOF rankings based on separation metrics calculated with DDEC3 and Qeq charges could be highly correlated. Yet, there were discrepancies in the top MOF lists underlining that approximate charges may not be sufficient to identify all the top performing MOFs and ab initio based accurate charges would be more appropriate for studies aiming not to miss any of the top-performing MOF membranes. It can be envisioned that determining pure MOF membrane performances through simulations would be more relevant for practical purposes as the progress in the fabrication of ultrathin MOF membranes can unlock the realization of more MOF membranes in the lab.[101]

2.2. MOF/Polymer MMM Modeling

Pure MOF membranes have been extensively studied yet, the challenges regarding the fabrication of pure, thin film MOF membranes such as creation of defects and prohibitive cost triggered the search for alternative membranes that can perform on par or better than the former. In this regard, MMMs have emerged as alternative and efficient membranes since the ease of fabrication of polymer matrices and high permeability/selectivity of MOF fillers can be capitalized on. As the unit cells of MOFs typically have in the order of 100 atoms, their fully atomistic modeling for gas adsorption and diffusion is rather straightforward. However, once MOFs are combined with polymer matrices (whose models could involve many more atoms than MOFs) to construct composite membranes (MMMs), performing fully atomistic simulations to determine gas permeabilities becomes computationally expensive. In such cases, generally, theoretical permeation models (e.g., Maxwell,[102] Bruggeman,[103] Felske[104]) are utilized to estimate gas permeabilities in MMMs. These models are built upon different assumptions and thus involve different levels of complexity (e.g., presence of defects, interfacial voids). They couple gas permeabilities in MOFs acquired by atomic simulations and gas permeability in polymer, which is generally collected from experimental literature. Thus, once gas adsorption and diffusion properties of MOFs are determined, permeabilities of MMMs in which MOFs are used as fillers could be obtained without any further simulations. However, as in all models, the success of permeation models relies on several assumptions such as fully dispersed and symmetric filler particles, no interaction between fillers, no agglomeration, ideal interface compatibility, etc.[105]

Initial computational studies utilized different permeation models to characterize the gas permeabilities of MOF/polymer MMMs.[106] In 2010, the estimation of CO_2, CH_4, H_2, and N_2 permeation in MOF/polymer MMMs via two mathematical models (i.e., Maxwell and Bruggeman) using simulated gas loadings and diffusivities in the MOF sparked much interest as the estimations were close to the experimental data, despite many simplifying assumptions.[106] Since then, several groups have probed the separation of CO_2/CH_4,[83] O_2/N_2,[107] and CO_2/N_2,[79] in ≈60, 80 000, and 1 000 000 MOF/polymer MMMs, respectively. As an example, Figure 2d represents CO_2/N_2 selectivity and CO_2 permeability of over 1 million MOF/polymer MMMs computed by combining molecular simulations mimicking infinite dilution conditions and the Maxwell permeation model.[79] It was shown that MOF/polymer MMMs can offer higher membrane selectivity and/or CO_2 permeability than the corresponding neat polymers and most of these MMMs could surpass the Robeson's upper bound hinting that the limitations of polymeric membranes can be overcome by incorporating MOF fillers. Recently, Daglar et al.[108] investigated more than 180 000 synthesized MOF/polymer MMMs using GCMC and MD simulations and the Maxwell model to study the separation of 11 different gas separations at 1 bar, 298 K where it was demonstrated that gas permeabilities could be improved upon MOF incorporation into different polymers, which can be attributed to the high permeability of largely porous MOF structures. By contrast, the selectivities of MMMs mostly remained in the ballpark of those of neat

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polymers hinting that permeability enhancements upon MOF incorporation into polymers were comparable for both gases in the gas mixture. Similar to the observations made for pure pristine and functionalized MOF membranes, the presence of functionalized MOFs in MMMs could provide membrane separation performance benefits over MMMs with pristine MOFs. For instance, Anjum et al.[109] experimentally demonstrated that the presence of amine-functionalized linkers in NH_2-UiO-66/polyimide (PI) MMM lead to both higher CO_2/CH_4 selectivity and CO_2 permeability compared to the unfunctionalized UiO-66/PI MMM. This suggests that similar enhanced membrane separation performances upon functionalization may be observed in many other MOF membranes that can be computationally investigated.

One caveat that should be noted for such HTCS studies on MOF/polymer MMMs is the neglect of MOF/polymer incompatibility, which can affect the separation performances of the MMMs. Depending on the polymer rigidity, and affinity between the MOF and the polymer, irregularities at MOF/polymer interface could occur influencing porous structure of the MMM in turn affecting separation performance.[110,111] To investigate such nonideal morphological effects on membrane performance, Ozcan et al.[112] established a MOF/polymer MMM model by combining a DFT optimized −OH and −H terminated ZIF-8 [011] surface and polymer of intrinsic microporosity (PIM-1) membrane obtained using an in silico polymerization approach.[113] ZIF-8/PIM-1 composite membrane was equilibrated using several MD simulations after which the ZIF-8 model was sandwiched between duplicated polymer slabs. They demonstrated that H_2/CH_4 separation performance of ZIF-8/PIM-1 MMM was lower than those of its constituents as the interfacial voids induced selectivity losses. Similarly, Fan et al.[114] addressed the effect of MOF/polymer interface on the CO_2/N_2 and CO_2/CH_4 separation performances of MMMs using several simulation techniques including quantum chemical calculations, force field-based MC, and MD (both EMD and NEMD) simulations. As a case study, a MMM composed of NUS-8(Zr) as the filler and PIM-1 as the polymer was constructed using DFT and MD simulations, which was determined to have interfacial void region. NEMD simulations resulted in comparable permeabilities and selectivities with the experimental ones.[115] CO_2/N_2 selectivity of the MMM was found to be identical with that of the polymer suggesting that not all interfacial voids are detrimental to selectivity, even though potential negative effect of the interfacial voids was mentioned earlier.[112] While atomically detailed simulations can provide high-fidelity results, they are computationally expensive computations.[116] As a computationally efficient alternative, Yuan and Sarkisov[116] described gas permeability in MMMs using lattice models and dynamic mean field theory. Unlike macroscopic models neglecting interfacial effects, the developed model can suggest that gas transport may be hindered due to pore blockage at the interface. While the model predictions are not at the resolution of molecular simulations for multiple reasons involving the omission of long-range interactions, such models could be used as a preliminary screening tool to investigate diffusion in many MOF-based MMMs followed by detailed molecular simulations for candidate MMMs identified.

There are several ways to adjust the MOF/polymer compatibility including introduction of noncovalent/covalent bonds, generation of MOF defects, etc. As the hydrogen bonding between the

MOF fillers and polymer matrix can enhance the MOF/polymer interface compatibility, MOFs with functional groups that can form hydrogen bonds with polymers (e.g., −NH_2) can be promising candidates to be blended with polymeric membranes to form selective MMMs.[117] In this respect, Ma and Urban[118] have shown that UiO-66 functionalized with −NH_2 group could have good interfacial compatibility with 6FDA-DAM:DABA matrix and the resulting MMM could achieve high CO_2/CH_4, H_2/CH_4, and H_2/N_2 separation performances surpassing Robeson's upper bounds. Similarly, it has been shown that −CN functionalized ZIF-8/PIM-1 MMM has better compatibility and superior C_3H_6/C_3H_8 separation performance than pristine ZIF-8/PIM-1 MMM.[119] In this context, the atomically detailed simulations (e.g., force field-based MD simulations, DFT calculations) can reveal the formation of noncovalent/covalent bonds between MOF and polymer that can provide guidance for the selection of MOF/polymer pairs that can lead to good interfacial compatibility and high gas separation performance. For instance, Sadeghi and Howe[120] have employed DFT to investigate adsorption of polymer fragments (Kapton and 6FDA-Durene) on MOF surface models (ZIF-8 and Co-BDC) and unraveled that unsaturated sites could lead to good MOF/polymer compatibility while the lack of undercoordinated surface species may result in poor adhesion of MOF and polymer where dispersion forces dominate.

Along with the presence/absence of defects, the type of defects in the MOF can also influence the MOF/polymer compatibility as exemplified by An et al.[121] where MD simulation results suggested ZIF-8 with Zn-alkyl amine point defects had better compatibility with 6FDA-DAM than ZIF-8 with Zn-OH point defects. Interestingly, it was found that Zn-alkyl amine defective sites hindered the framework flexibility and shrank the window size thereby increasing C_3H_6/C_3H_8 selectivity of MMM over that of MMM with ZIF-8 having Zn-OH point defects. The foregoing studies imply that there is much room for computations to reveal effects of MOF properties on MOF/polymer MMM interface compatibility and separation performance. Currently, the number of computational studies focusing on MOF/polymer compatibility at atomic detail is relatively less, however, its expansion will be of high value as it would facilitate the design of high-performing membranes.

2.3. Cost Analysis

Obtaining a specific property–performance relation for MOF-based membranes is important to understand the limits in which membranes could operate. However, the decisive factor for their use in practical applications would eventually be operation and capital costs. As part of efforts to determine the carbon capture cost, Budhathoki et al.[79] carried out techno-economic analyses of MOF/polymer MMMs for post-combustion carbon capture process where information gathered from atomistic simulations (e.g., gas diffusivity, Henry's constant) were linked with process models to obtain cost of carbon capture (CCC) in $/tonne CO_2 removed. The separation performances of both synthesized and hypothetical MOFs (>2000 synthesized MOFs and >110 000 hypothetical MOFs) were investigated using MC and EMD simulations. Combining the simulation results with the Maxwell model, CO_2/N_2 separation performances of MOF/polymer MMM were

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estimated. To estimate CCC, a three-stage process configuration with sweep was employed in process models where membrane area, pressure, temperature, and flowrate were optimized for different membranes to obtain the lowest electricity cost. Their analysis showed that while the overwhelming portion of MOF/polymer MMMs could provide lower CCC than that of pure polymer ($64 (tonne CO_2)$^{-1}$), several MOF/polymer MMMs (involving MOFs with lower permeability or selectivity than that of polymer membrane) exhibit higher CCC values. This suggests that selecting not sufficiently selective or permeable MOFs for MMM construction may not provide any economic benefit. One interesting finding of their work was that the lowest CCC values were not obtained by the MMMs with the most permeable or selective MOFs but rather by MMMs with MOF/polymer selectivity ratio larger than MOF/polymer permeability ratio by a factor of 10. These inferences about the selection of MOFs for cost-effective MMM construction are highly valuable, yet they rely on several factors including the use of generic force field, partial atomic charges based on empirical parameters, rigid MOFs, Maxwell permeation model, and a three-stage membrane-based capture process. With the use of specialized force fields, more accurate simulation results can be obtained. Similarly, rather than using a generic process configuration model, configurations optimized for materials could be considerably different than generic models and provide more economic benefits.[122] Thus, using a combination of material-specific force fields and process configurations could reveal new conclusions for constructing cost-effective MOF/polymer MMMs compared to those obtained through generic models. For instance, modeling flexible structures, using ab initio-based force fields and DFT-based methods for partial charge assignment, incorporating MOF/polymer interface effects through atomistic modeling, and refined process modeling could provide different correlations between gas separation performances and CCC.

3. Data-Driven Applications for MOF Membranes

To reduce the computational cost and allocate computational resources efficiently, the development of ML models has recently become a hot topic in the field of MOFs. **Figure 3**a depicts a typical workflow for the ML model development where a collection of input data (e.g., structure files) is first transformed into representations in different formats including but not limited to scalars, vectors, and strings to bring about ML model descriptors (e.g., structural, chemical, energetic, topologic properties of materials). Some of these descriptors could be obtained through crystallographic file parsing (e.g., enumerating atom types, numbers), geometric calculations, and/or molecular simulations. Ideally, these descriptors should be rapidly calculable quantities rather than those obtained via computationally expensive calculations, especially for large data sets. To this end, novel methods providing faster calculations of descriptors would be highly desired for faster ML model development. For instance, a recently introduced method to calculate adsorption enthalpy has been shown to be two orders of magnitude quicker than the conventional method, which can help widen the adoption of an energetic descriptor, adsorption enthalpy, in ML models for large data sets.[123] Once material representations are obtained (either from experimental or computational data), ML models (e.g., kernel-

based, neural network based) are developed mainly for two tasks, classification and regression.[124] The regression tasks are mostly about predicting their separation performance metrics (e.g., permeability, selectivity).

In the cases where regression models are not accurate enough due to several factors such as insufficient data, lack of physically relevant features, classification models could be used to categorize membranes (e.g., high-performing, low-performing). Besides, classification models could be of high use where the aim is to correctly label materials in terms of a specific property (e.g., stability) rather than provide exact figures. Based on the classification/regression model outputs, the identification of candidate MOF-based membranes could be expedited.

In principle, ML models can be developed based on experimental data, computational data, or a combination of both. However, due to the large time and cost requirements of experiments and immense computational power available to researchers today, many of the current ML studies use simulation data rather than experimental data. For instance, Bai et al.[71] first performed an HTCS of pure MOFs taken from computation-ready experimental (CoRE) MOF database[80] for membrane-based H_2 separation (from CH_4, N_2, H_2S, O_2, CO_2, He) and developed eight different ML models based on the generated computational data to predict H_2 permeability. ML models were also able to accurately estimate another performance metric of membranes, trade-off multiple selectivity and permeability (TMSP). While many features could be used to train accurate ML models for H_2 permeability and TMSP predictions, models with similar prediction accuracies were obtained using only two structural features, pore limiting diameter and porosity of MOFs. Figure 3b shows that most of the MOF membranes have relatively low H_2 permeabilities ($<10^3$ Barrer) and Gaussian process regression-based (GPR-based) ML model could provide H_2 permeability predictions close to the simulated values where the error between ML predictions and simulations can be more pronounced for more H_2 permeable MOF membranes.[71]

Accurate ML models for the separation performance predictions of pure MOF membranes are highly encouraging, which sparks the question whether similarly accurate ML models could be established for MOF-based composite membranes. To this end, for the CO_2/N_2 (15/85) separation at ambient conditions, Zhang et al.[73] computationally prepared 8167 ionic liquid-incorporated (IL-incorporated) MOF composites (IL@MOF) by placing an IL, [NH_2-Pmim][Tf_2N], into MOFs taken from CoRE MOF database[80] via MC trials after which GCMC and MD simulations were performed to determine membrane selectivity and gas permeability. ML models were developed using the combination of structural and chemical features including density, pore limiting diameter, accessible surface area to make predictions for CO_2/N_2 selectivity and CO_2 permeability. Figure 3c demonstrates that ML-predicted CO_2 permeability of IL@MOF membranes are close to the simulated values for many membranes but there can also be significant overpredictions in permeabilities at low-medium permeabilities ($<2 \times 10^6$ Barrer). The best IL@MOF composites were identified using the product of membrane selectivity and permeability based on simulation results. Given the high CO_2/N_2 separation performance of IL@ZIF-67 based on molecular simulations, [NH_2-Pmim][Tf_2N]@ZIF-67 composite was synthesized and incorporated into PIM-1. This

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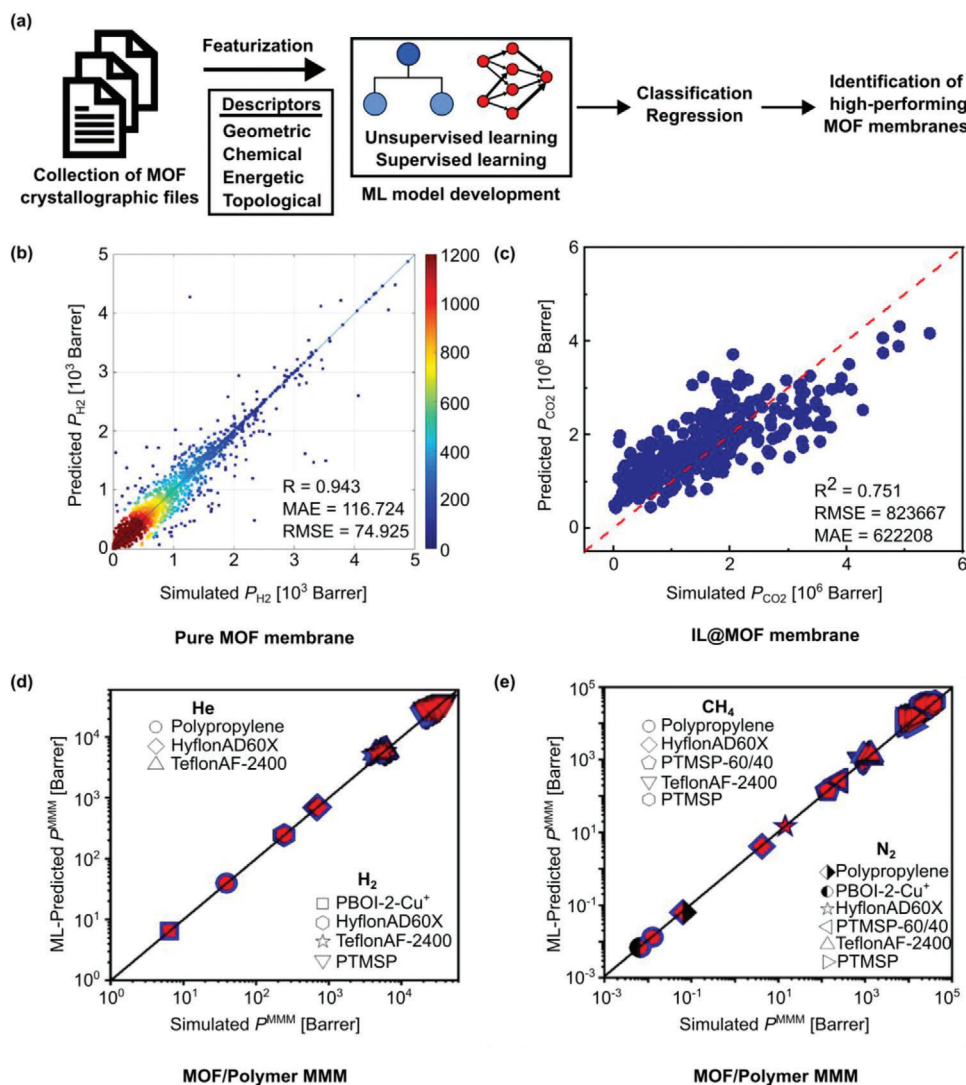Open Access
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Figure 3. a) A general representation of ML model development workflow for high-performing membrane discovery. Comparisons of ML model predictions with simulation results for b) H_2 permeabilities of pure MOF membranes. Adapted with permission.[71] Copyright 2022, Elsevier. c) CO_2 permeabilities of IL@MOF membranes. Adapted with permission.[73] Copyright 2022, Elsevier. d) He, H_2 permeabilities of MOF/polymer MMMs. Adapted under the terms of the CC BY 4.0 license.[72] Copyright 2022, American Chemical Society. e) CH_4 and N_2 permeabilities of MOF/polymer MMMs. Adapted under the terms of the CC BY 4.0 license.[72] Copyright 2022, American Chemical Society. Blue (red) symbols in (d) and (e) denote the training (test) set. He, H_2, CH_4, and N_2 permeabilities were shown for MMMs composed of combinations of 677, 2715, 5215, and 5224 MOFs, respectively, with indicated polymers. Note that many data points resembling different MOF/polymer MMMs lie on each other.

MMM offered higher CO_2/N_2 selectivity and CO_2 permeability than both pristine PIM-1 and ZIF-67/PIM-1 composite, surpassing the Roupper bound.[125] Those results obtained from the combination of HTCS and ML suggested that IL@MOF composites with favorable separation performances could serve as good filler materials for the fabrication of high-performing MMMs.

Identification of such high-performing MOF composite fillers through molecular simulations and ML algorithms is also vital to abandon the trial-and-error approach and adopt a data-driven approach for the design of MOF/polymer MMMs. In fact, considering the very large number of available MOFs and polymers, ML has a huge power to guide the experimental efforts and time to the best MOF-polymers pairs that can yield to high-performance MMMs. Daglar and Keskin[72] performed GCMC and MD sim-

ulations to calculate membrane selectivity and permeability of 5249 MOF membranes and 31 494 MOF/polymer MMMs for many gas separations including He/H_2, He/N_2, He/CH_4, H_2/N_2, H_2/CH_4, and N_2/CH_4 at ambient conditions. This large simulation data was then used to train ML models employing physical, chemical, and energetic features of MOFs and these models were employed to predict the gas separation performances of pure MOFs and MOF/polymer MMMs. As shown in Figure 3d,e, ML-predicted selectivities of MOF/polymer MMMs for several gas separations agreed with the simulated selectivities where the agreement was stronger for MMMs involving polymers with low or medium gas permeability (polypropylene, PBOI-2-Cu$^+$).[72]

Comparing the predictions of ML models, results of molecular simulations and experimentally measured gas permeabilities

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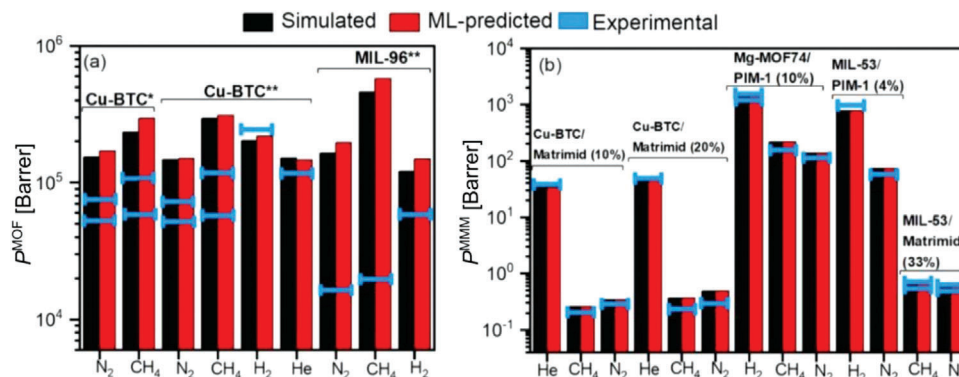Open Access
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Figure 4. Comparison of experimental, simulated, and ML-predicted gas permeabilities in a) MOF membranes and b) MOF/polymer MMMs. Blue lines refer to the experimental gas permeabilities at (a) 1 bar, 298 K in MOF membranes and (b) 0.5–5 bar, 298–308 K in MOF/polymer MMMs. Values in parentheses in panel (b) denote the MOF filler volume fraction. * and ** designate MOF(s) in the test and training sets, respectively. Adapted under the terms of the CC BY 4.0 license.[72] Copyright 2022, The Authors, published by American Chemical Society.

of MOF membranes and MOF/polymer MMMs is critical to develop and use accurate and efficient models that can direct the experiments. **Figure 4**a exhibits such a comparison for MOF membranes where the experimental gas permeabilities in the MOF membranes of interest were generally overestimated by molecular simulations and ML models, which could be attributed to the assumptions made for the molecular simulations including defect-free, and rigid framework, which might not be experimentally valid. Figure 4b displays the gas permeability benchmarks of experiments, simulations, and ML model predictions for the MOF/polymer MMMs where all three permeabilities were generally in good agreement. This hints that, despite the underlying assumptions, the simulation-based permeability could be closer to experimental permeability for MOF/polymer MMMs, compared to pure MOF membranes, which in turn enables ML models to predict values in agreement with experimental values. Such computational study combining HTCS and ML has the potential to discover promising MOF membranes and MOF/polymer MMMs that have not been synthesized before.

The foregoing examples show that molecular simulations could be employed to generate large-scale data for various types of membranes, which can be subsequently used for ML model development. Since obtaining experimental data could be more cumbersome and less time-efficient, the scale of experimental data is typically much more limited than computational data, especially in open sources. Yet, accurate ML models could still be developed after scraping the experimental data from the literature.[75] For instance, Guan et al.[75] demonstrated one of the first examples of ML models purely based on the experimental data to predict the membrane-based CO_2/CH_4 separation performances of MMMs involving MOFs. The polymer type, the pore size of the MOF, and the loading of the MOF in the MMM (pure polymer selectivity, pure polymer permeability, and MOF loading in the MMM) were found to be the most important descriptors for permeability (selectivity) predictions, in agreement with the theoretical models as their estimations rely on the foregoing factors as well. ML models predicted that MOFs having pore sizes >10 Å and surface areas ≈800 m² g⁻¹ could perform well in terms of CO_2 permeability and CO_2/CH_4 selectivity. Following these guidelines, two Cu-based MOFs (Cu-THQ and Cu-CAT-1) were

synthesized and incorporated into polymers (PIM-1 and Pebax 2533) to fabricate MMMs where Cu-CAT-1/PIM-1 MMM could surpass the upper bound. It was shown that ML predictions for selectivity and permeability were in line with the experimental data of MMMs based on those two MOFs demonstrating the success of ML predictions for the fabrication of high-performing membranes.

In general, computationally expensive simulations (e.g., prolonged MD runs) are performed only for a small subset of MOFs investigated, which may hinder revealing structure–property correlations and establishing ML models from large data. Leveraging transfer learning (TL) techniques can help quickly acquire MOF membranes' properties for which performing computations can be expensive. For example, TL approach was recently used to derive ML models for predicting CO_2/CH_4 separation performances of MOF/polymer MMMs and then CO_2/N_2 separation performance predictions were made based on these models.[75] The TL predictions were shown to be on par or better than direct learning predictions hinting that rather than deriving ML models from scratch for each gas separation of interest, knowledge transfer could be highly useful, especially in the cases where there is limited (experimental) data. Similarly, Lim and Kim[126] demonstrated that using the knowledge from a pretrained deep neural network model with computed CH_4 loadings in MOFs as the source data, the prediction accuracy (R^2 score) of CH_4 diffusion coefficients of MOFs can be enhanced by up to 25% compared to direct learning predictions. This suggests that using a large set of computationally more affordable calculations (CH_4 uptake in >20 000 MOFs), prediction accuracies for small sets of computationally more expensive self-diffusion coefficients (for <500 MOFs) can be considerably boosted alleviating the problem of not having access to large data sets for some ML tasks.

While there can be many MOFs in the databases offering efficient solutions to modern-day energy and environmental challenges, a nontargeted simulation-based investigation of millions/billions of MOFs would be computationally too expensive. This brings up the subject of efficiency in MOF design, which can be addressed by adopting inverse-design techniques where desired material properties are fed into a workflow to design

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materials. For example, Lim et al.[127] used a genetic algorithm (GA) to construct MOFs by targeting a specific Xe/Kr adsorption selectivity and demonstrated that their inversely designed MOFs were distributed around the desired selectivity value while the randomly generated MOFs were skewed toward lower selectivities. A similar approach was recently undertaken where MOF membranes were inversely designed for C_2H_4/C_2H_6 separation using GA with the aim of obtaining MOF membranes having high C_2H_4/C_2H_6 selectivity and C_2H_4 permeability.[128] It was shown that one of the designed MOFs exceeded the threshold values of membrane selectivity and permeability in the fitness function, which also surpassed the computed membrane-based separation performances of MOFs in CoRE MOF database.[80] That work also showed that the ideal MOF membrane for C_2H_4/C_2H_6 separation can be specified in much fewer attempts (8000 MOFs constructed) than a typical high-throughput screening approach that would enumerate all possible combinations of topologies, nodes, and linkers of MOFs.

4. Outlook

Given the highly tailorable structures of MOFs, membrane-based separation using MOFs holds much promise. Yet, considering the multiobjective nature of MOF development aiming to provide high-performing, stable, cost-effective structures, the discovery of promising MOF-based membranes is a multidimensional challenge requiring the integration of experimental, theoretical, and data-driven efforts. Thus, the major developments in the field of MOF-based membranes are expected to involve significant advances in all these three aspects. On the experimental side, two major developments whose wider adoption in the field could accelerate MOF development process are 1) AI-guided MOF-based membrane synthesis and 2) automation of experiments. Over time, many synthetic challenges were overcome and MOF membranes with diverse physical and chemical properties were realized in the lab.[129,130] However, the conventional experimental approach for MOF-based membrane studies mostly relies on heuristic or trial-and-error approach. AI-driven MOF-based membrane fabrication can significantly accelerate the membrane discovery process. Through the exploitation of ever-increasing large-scale MOF membrane data, accurate AI-driven models can be constructed that can rapidly provide the best fabrication conditions for MOF-based membranes in addition to predicting gas separation and stability/compatibility properties of membranes to guide the experimental efforts. Furthermore, recently introduced "synthesis" robots and automated material characterization/testing systems could provide an easier pathway to membrane synthesis, characterization, and testing.[131,132]

On the molecular simulations side, the accuracy of simulations performed to investigate MOF-based membranes could be taken to the next level by employing specialized and flexible force fields. For instance, DFT-based force fields can provide accurate description of gas-open metal site interactions for which generic force field-based interactions may be inaccurate.[133] The use of accurate ab initio force fields instead of generic force fields in gas adsorption and diffusion simulations can provide more accurate membrane performance metrics (e.g., selectivity, permeability) and material rankings for further computational scrutiny and/or experimentation. Likewise, the widely adopted assump-

tion of rigid MOFs in adsorption and diffusion simulations may lead to inaccurate results, especially when the gas molecule sizes are comparable to the pore sizes of MOFs.[59,83,134] Depending on the case, flexibility effects may lead to better or worse membrane performance.[135] Yet, the development of flexible force fields has its own challenges such as the choice of system size, and deficiency of efficient sampling of phase transitions.[136] Recently, employing ML methods for force field development has increasingly been popular and exemplary works on modeling diffusion in MOFs using ML force fields have appeared.[137,138]

Several recent studies[139–141] demonstrated that MOFs having the same reference code in the databases may have different chemical compositions depending on the structure curations (i.e., removal of solvents and charge-balancing ions, adding missing hydrogens) carried out prior to database construction. An important outcome of this issue is that the discrepancies in simulated gas uptakes across differently curated structures (with identical reference codes) may grow as lower pressures are employed.[139] This suggests that computational screening of materials for gas separation at subatmospheric pressures can result in different "promising" materials lists. As adsorption and diffusion properties of structures rely on the structure composition and atomic positions, analyzing the structures of top-performing membranes would be highly useful to identify potential structural problems and discard problematic structures.

Although almost all the current simulation studies on MOF-based membranes aimed to predict their gas separation properties, gaining insights into the stability of membrane materials is critical for practical use.[142] So far, the mechanical stability of MOFs has been studied using DFT and force field-based simulations.[143–145] Yet, the scale of MOFs for which mechanical properties were calculated is limited, and expanding those investigations, especially to high-performing membrane candidates, can provide insights into their potential use in practical separation operations. Regarding the water stability, performing water uptake simulations at low pressures can provide a qualitative idea about the extent of hydrophilicity of MOF structures. Besides, for the MOFs which appear to be hydrophilic, investigating their water degradation mechanisms via DFT simulations can be highly beneficial to elucidate the likelihood of structure degradation upon exposure to different extents of humidity. The MOF/polymer interface compatibility can improve or hinder the separation performance of MMMs. However, most of the current studies estimate separation performances of MOF/polymer MMMs based on the theoretical permeation models having disparate assumptions on interfaces. While some of those models could provide realistic results for some MMMs, a universal permeation model that applies to all MOF/polymer MMMs does not exist. Therefore, detailed molecular simulation should be carried out for the MOF/polymer MMMs of high interest as exemplified earlier to reveal the molecular insight behind their separation mechanism.[146,147]

The data-driven approaches have been very recently used in the field of MOF-based membranes. The rapid increase in the number of synthesized MOFs, production of the large amount of simulation data for MOF membranes and MOF/polymer MMMs, and the recent advancements in the development and implementation of AI methods in the material science have all contributed to the emergence of a new era for the computational

modeling of MOF-based membranes. AI approaches taking a desired material property/performance as input and providing structure as output is highly promising since this can significantly reduce the number of membrane materials investigated. So far, it has been shown that using secondary building units of MOFs and evolutionary algorithms, high-performing MOF membranes in terms of selectivity and permeability can be inversely designed.[128] This approach can be extended to the inverse design of other MOF membranes where a specific separation performance metric could be prioritized. Ideally, defining multiple objective metrics (e.g., mechanical stability, water stability, permeability, etc.) can be more beneficial although it would increase the complexity of the problem and require performing a greater scale of molecular simulations or development of new ML models whose outputs could be fed into the GA process. Since developing ML models from scratch for each application can take a lot of time and effort, TL approaches can also be beneficial to make predictions for a wide variety of applications in shorter time by transferring the knowledge from computationally more affordable simulations to the challenging ones. It was also shown that TL approaches can be used to transfer knowledge from a targeted gas separation to another gas separation.[75] Since both approaches reduce the number of molecular simulations that are computationally expensive, their wider implementation in the near future is anticipated to further accelerate the process of predicting the separation performances of MOF-based membranes.

As MOFs can be decomposed into their building blocks via recently developed tools like MOFid,[148] moffragmentor,[149] mBUD,[150] and MOFseek,[151] the MOF databases can be queried with the extracted building blocks to identify and probe MOFs with similar/identical building units of high-performing MOF-based membranes. These capabilities can be combined with ML models predicting MOFs with high thermal and solvent-removal,[152] mechanical,[143] water stability[153] to identify materials that can potentially find use in industrial applications. This suggests that combining the stability and separation performance of MOF-based membranes would allow for stability and performance targeted identifications/investigations of MOF-based membranes. Given the large number of MOFs, building experimental and computational MOF membrane databases following findable, accessible, interoperable, reusable (FAIR)[154] principles can significantly facilitate the reuse of existing data and the collaboration of experimentalists and theoreticians. Recently, a number of large open computational datasets regarding membrane properties started to emerge.[72,74,128] In the future, these datasets could be integrated into other computational studies where larger databases could be formed from which extraction of large-scale structure–property correlations would be possible.

As the HTCS and ML studies mostly identify promising MOF membranes, it could be anticipated that the subsequent synthesis efforts would be targeted at the best performing materials. Yet, many times, lower ranked materials are synthesized due to facile synthesis procedures of the material.[155] The determination of relative free energies of structures through simulations and/or ML models can reveal the structures that are highly unlikely to be synthesizable which can be discarded from the material list of interest. Among the materials that are determined to be synthesizable, those with low synthesis cost would be preferred in practical applications, thus MOF cost should be one of the selection criteria in addition to performance.[156]

To sum up, performing force field-based molecular simulations, DFT simulations, and establishing ML models can provide multiple benefits for advancing the understanding of MOF-based membrane structures and the underlying reasons behind their separation performances. The force field-based molecular simulations enable efficient sampling of the porous space in MOF-based membranes for gas adsorption and diffusion. Recently, machine-learned force fields[138,157] based on ab initio data were derived that can accurately describe the adsorption and/or diffusion of small molecules in MOFs with open metal sites. The expansion of such efforts where ab initio data and ML methods are combined to develop accurate force fields will be highly beneficial as it will enable obtaining molecular simulation results in line with experimental observations for a larger set of MOFs where generic force fields typically fail. The development of accurate force fields is also crucial for performing prolonged force field-based MD simulations for the investigation of relatively slowly diffusing species in MOF-based membranes where long ab initio MD runs would be highly costly. Besides providing reference data for force field development, DFT simulations are also vital to accurately characterize MOF-based membrane structures. While the application of DFT was initially mostly limited to partial charge assignment and optimization of pure MOF structures, protocols of DFT simulations have been established and applied for the modeling of MOF-based MMM structures as well.[114] This hints that fully atomistic simulations of MOF-based MMM structures could be performed more commonly in the near future which could help investigate interface effects at atomistic scale rather than employ permeation models, which may not provide a realistic description of the MMM structure.

The development of ML models can significantly speed up the prediction of structural properties and/or gas separation performances of MOF-based membranes. However, to have physically relevant predictions using ML models, the reference dataset to be used in the ML model development needs to be accurate. Depending on the system and target property, generic force field-based molecular simulation data could be considered accurate or not. Before developing ML models, the accuracy of simulation data should be validated using experimental data and/or computational data based on more accurate methods. Once data accuracy is validated, ML models can be trained using different classes of features (e.g., geometric, chemical). While there are some commonly used features (e.g., surface area, number of specific atoms) for ML model development, the introduction of new and preferably easily calculable features will be of high importance for the prediction of structural, adsorption, and diffusion properties of MOF-based membranes. All in all, the multidimensional MOF membrane discovery and development problem can only be effectively tackled by the cooperative implementation of the state-of-the-art experimental, theoretical, and data-driven methods as exemplified by the recent multiscale work[158] combining molecular simulation, ML, and process modeling to study CO_2/CH_4 separation using MOF-based membranes. With well-integrated experimental–theoretical–data-driven workflows, we anticipate that the discovery process of promising MOF-based membranes with superior properties than conventional membranes can be drastically expedited and many of the hurdles regarding the devel-

opment and use of high-performing, stable, and low-cost MOF-based membranes in the industry can be overcome.

Conflict of Interest

The authors declare no conflict of interest.

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