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Perspective

Accelerated Discovery of Metal−Organic Frameworks for CO_2 Capture by Artificial Intelligence

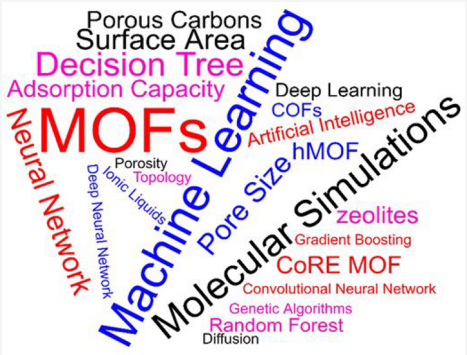
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ABSTRACT: The existence of a very large number of porous materials is a great opportunity to develop innovative technologies for carbon dioxide (CO_2) capture to address the climate change problem. On the other hand, identifying the most promising adsorbent and membrane candidates using iterative experimental testing and brute-force computer simulations is very challenging due to the enormous number and variety of porous materials. Artificial intelligence (AI) has recently been integrated into molecular modeling of porous materials, specifically metal−organic frameworks (MOFs), to accelerate the design and discovery of high-performing adsorbents and membranes for CO_2 adsorption and separation. In this perspective, we highlight the pioneering works in which AI, molecular simulations, and experiments have been combined to produce exceptional MOFs and MOF-based composites that outperform traditional porous materials in CO_2 capture. We outline the future directions by discussing the current opportunities and challenges in the field of harnessing experiments, theory, and AI for accelerated discovery of porous materials for CO_2 capture.



Fossil fuels will continue to provide a substantial portion of the world's energy needs in near future. However, this reliance comes at a cost; their combustion has caused a significant rise in atmospheric carbon dioxide (CO_2) levels from 320 parts per million (ppm) in 1960 to 417 ppm in 2022,[1] and an increase in the global average temperatures, reaching a 1 °C rise above preindustrial levels.[2] Consequently, the urgency of climate action has resonated across the globe, with countries committed to ambitious CO_2 emission reduction targets through new policies and international accords such as the Paris Agreement and the European Green Deal.[3−6] Traditional carbon capture technologies, amine-based scrubbing and cryogenic separation, have been commercially used for CO_2 separation.[7,8] Adsorption- and membrane-based separation techniques are better alternatives in the pursuit of sustainable CO_2 capture solutions since they can offer low operation costs, simplified operation, and easy scalability.[9,10] The main challenge of adsorption- and membrane-based separation technologies is to find the optimal materials to be integrated, as traditional ones such as zeolites, activated carbons, and polymers generally suffer from low CO_2 affinity/capacity/selectivity and stability concerns.[11]

Recent studies have focused on CO_2 capture with metal−organic frameworks (MOFs),[12] a unique class of porous materials composed of metal nodes and organic linkers that form crystalline structures. MOFs offer significant opportunities such as very large structural diversities and functionalities, exceptional porosities (up to 0.9), tunable pore sizes (3−100 Å), and record surface areas (up to 10,000 m^2/g) compared to classical porous materials. Inspired by the MOFs, many other MOF-like structures such as covalent organic frameworks (COFs),[13,14] zeolite imidazolate frameworks (ZIFs),[15] and porous polymer networks (PPNs)[16] have emerged, and all these materials have been widely investigated for CO_2 adsorption in the last two decades as shown in Figure 1(a), more than the adsorption of other gases such as CH_4, O_2, and H_2 as shown in Figure 1(b). Thanks to their large chemical varieties, high surface areas, and pore volumes, MOFs offer favorable adsorption sites for CO_2 molecules, and more importantly, their structures can be decorated with open metal sites and/or functional groups to achieve very high CO_2 uptakes.[17,18] For example, early experimental studies showed that several MOFs outperform commercial zeolite 13X (4.7 mol/kg)[19] and activated carbon Norbit RB2 (2.5 mol/kg)[20] because of their high CO_2 adsorption capacities in the ranges of 0.6−8.5 mol/kg at ambient conditions, even reaching record-breaking capacities of ∼50 mol/kg at 40 bar, 298 K.[21−23]

Motivated by these findings, more and more MOFs have been synthesized and tested for CO_2 capture. Structures of

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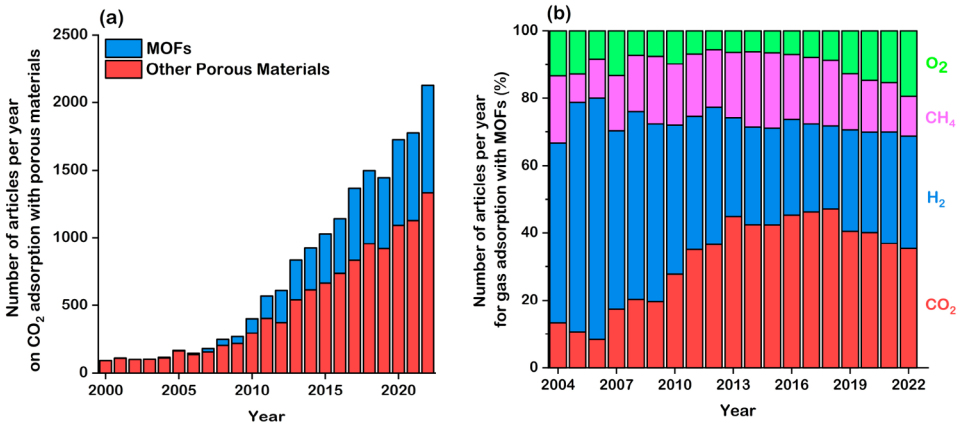


Figure 1. (a) The number of publications having keywords "metal−organic framework or MOF or zeolite or activated carbon" and "carbon dioxide or CO_2" and "adsorption or uptake or capture" in their titles and abstract. For simplicity, MOF subfamilies, including ZIFs, PPNs, and COFs, were also referred to MOFs in the figure. (b) The percentage of published papers having keywords "methane or "CH_4", "oxygen or O_2", and "hydrogen or H_2" in addition to the keywords listed in part (a) in their titles and abstracts. Search was performed using Scopus, accessed on October 15, 2023.

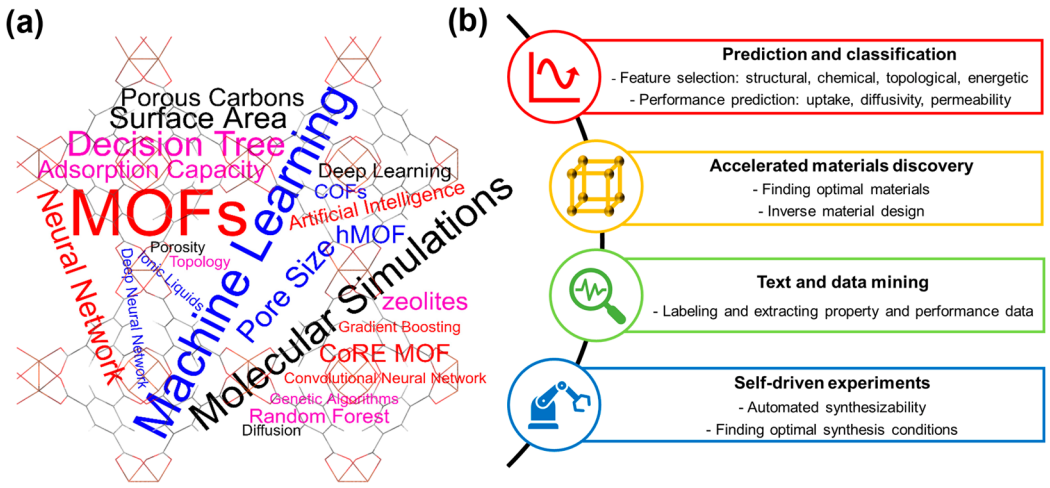


Figure 2. (a) Word cloud analysis of 85 publications in 2014−2023 collected from the literature by using the keywords of "artificial intelligence or machine learning" and "metal−organic framework or MOF or zeolite or activated carbon" and "carbon dioxide or CO_2" and "adsorption or uptake or capture". Search was performed using Scopus, accessed on October 15, 2023. The sizes of the words reflect the frequency of the relevant words appearing in publications. For example, pore size appeared in 8 of 85 studies. (b) The four main fields where AI has been beneficial.

synthesized MOFs are deposited into the Cambridge Structural Database (CSD),[24] and our search of this data center using ConQuest software[25] resulted in 122,738 MOFs as of October 2023. In addition to MOFs, 648 synthesized COFs were reported.[26] Beyond the synthesized structures, hypothetical MOFs[27−30] and COFs[31−33] (hMOFs and hCOFs), consisting of trillions of structures generated by using metals, linkers, and topological nets observed in synthesized structures, have recently emerged. Evaluating the CO_2 adsorption performance of each material present in this large material spectrum through experimental methods is unfeasible due to extensive time and resource needs. High-throughput computational screening (HTCS) uses classical molecular simulations to rapidly assess MOFs for adsorption of target gas molecules, accelerating the identification and development of materials for specific adsorption and separation purposes.[34,35] For example, almost 4000 MOFs were examined for adsorption-based separation of a CO_2/H_2 mixture using Grand Canonical Monte Carlo (GCMC) simulations, and MOFs were shown to exhibit superior performance compared to many zeolites.[36] 10,995 MOFs, which were computationally constructed by addition of functional groups (−F, $-NH_2$, and/or $-OCH_3$) into multivariate MOFs, were studied using GCMC simulations for CO_2/N_2 separation, and the results showed increases up to 3-fold in CO_2 selectivities and capacities of MOFs.[37]

With the number of MOFs increasing at an unprecedented rate, even using the HTCS approach remains insufficient to examine the entire MOF spectrum for the identification of the most promising materials for CO_2 capture. More importantly, analyzing the very large amount and high-dimensional data belonging to this large material world requires the usage of data science to reveal the hidden materials' structure−performance relations to gain a fundamental understanding of the molecular features leading to high-performing materials. As a result, we have recently witnessed significant efforts to combine artificial intelligence (AI) methods with classical molecular simulations and experiments to unlock the CO_2 capture performance of MOFs.

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In this perspective, we address the state-of-the-art technologies in integrating AI, molecular modeling, and experiments for accelerating the design and discovery of MOFs and MOF-based composite materials that outperform traditional porous materials in CO_2 capture. We focus on pioneering contributions that have used the combination of AI and theory to design novel MOF adsorbents and membranes for CO_2 capture and then validated the designed materials with experimental studies. We finally outline the directions we see as most critical for further advances by addressing the current opportunities and challenges in this field.

2. AI APPLICATIONS OF POROUS MATERIALS FOR CO_2 CAPTURE

We start by reviewing the current state of emerging AI applications and their benefits in the field of CO_2 capture with porous materials. Including the first machine learning (ML) study focusing on predicting CO_2 capture properties of 100 different MOFs,[38] almost all AI-based studies aiming to assess porous materials for CO_2 capture focused on MOFs, hMOFs, and COFs while a very limited number of studies examined porous carbons and zeolites, as shown in Figure 2(a). To the best of our knowledge, two AI studies exist for porous carbons and one for zeolites. By collecting 1000 experimental data points for CO_2 adsorption in porous carbons, an ML algorithm was developed to predict CO_2 adsorption capacity of unknown porous carbons based on their textural properties such as surface area and pore volume.[39] A convolutional neural network algorithm trained on experimental N_2 isotherms of porous carbons measured at 77 K was utilized to predict CO_2/N_2 separation performance of 1 million hypothetical porous carbons.[40] An artificial neural network (ANN) constructed based on the molecular simulation data of 245 zeolites was used to evaluate the significance of various structural descriptors in determining CO_2 adsorption, and surface area was found to be the most important descriptor.[41] Many studies recently utilized AI to explore MOFs and their composites, which are addressed in detail in sections 2.1 and 2.2.

The literature predominantly focuses on supervised learning algorithms for classification and regression in specific data sets. These algorithms use various descriptors, like structural- and energy-based, to predict metrics such as CO_2 adsorption capacities. Supervised models need large labeled data sets, and they may face issues such as overfitting. Unsupervised algorithms, free from the need for labeled data, face challenges in interpretation of the results and require high-quality data.[42] Both types of algorithms are crucial in materials genomics for predicting properties and identifying patterns, but their limitations must also be considered. Figure 2(a) shows that ML algorithms, such as decision trees, random forests, gradient boosting, and ANN, have been used to predict CO_2 adsorption capacities[43−45] and CO_2 diffusion rates[46] in porous materials based on materials' structural properties, such as pore size, surface area, porosity, and topology. More complex algorithms, including convolutional neural networks, genetic algorithms, deep learning, and deep neural networks, have also recently been implemented in MOF research.[47−50] Achieving accurate ML predictions requires training the models based on a high-quality data set obtained for a large number and diversity of materials. CO_2 adsorption and diffusion data of MOFs have been generally obtained from HTCS of thousands of materials and then used to train predictive ML models, while experimental CO_2 uptake data of MOFs are utilized to optimize the material synthesis procedures.[51−53]

Figure 2(b) shows the four important aspects of AI in the discovery of novel MOFs:

(i) ML algorithms are used to estimate the materials' performance metrics related to CO_2 capture and separation, such as CO_2 uptake,[54] diffusivity,[46] and permeability,[55] by reducing the need for complex simulations and time-consuming experiments through classifying high- or low-performing materials.[45,56,57] For example, the quantitative structure−property relationship (QSPR) classifiers generated based on support vector machines accurately identified the promising materials offering high CO_2 adsorption capacity (>1 mmol/g at 0.15 bar and >4 mmol/g at 1 bar, 298 K) among 292,050 different types of hMOFs.[57] These QSPR models found 945 (905) out of the top 1000 structures with the highest CO_2 uptakes at 0.15 (1) bar, 298 K, which were identified based on the results of GCMC simulations.

(ii) AI-based algorithms can extend the current reach of experimental and computational studies by efficiently identifying the optimal materials having the desired CO_2 capture performance among millions of candidates and describing the most important features of the best materials. For example, a ML algorithm was developed to predict CO_2 uptake capacities of 70,433 hMOFs at 0.5 and 2.5 bar, 298 K, using their structural and chemical properties such as pore size, surface area, density, atom types, and building blocks, and ML predictions were shown to be in a very good agreement with the direct GCMC simulations.[54]

(iii) AI-based text and data mining algorithms enable us to rapidly extract data from the vast MOF literature. For example, important data on materials' pore sizes and surface areas, which are the two key structural properties for determining the gas uptakes,[51,58−60] or experimental binary mixture adsorption data[61] can be collected using AI. Text and data mining was recently used to search, filter, and summarize synthesis conditions of MOFs from the publications into structured data sets and used to construct predictive models for the outcomes of MOF synthesis reactions.[51]

(iv) ML algorithms further help optimizing the current synthesis conditions such as temperature, concentration, and time to formulate the novel synthetic pathways for MOFs.[62,63] For example, the usage of the genetic algorithm, a computational technique inspired by the principles of natural selection and evolution to optimize large and complex search areas where an exhaustive search would be impossible, is useful for the optimization of synthesis conditions of MOFs offering high CO_2 capture performance. For instance, conditions of failed and successful experiments, reaction time, temperature, solvent composition, and reactants ratio were fed to a genetic algorithm to develop a more efficient synthetic pathway to synthesize the well-known MOF, HKUST-1.[64] Similar approaches have also been used for the synthesis of ZIF-67[65] via developing fully automated MOF synthesis platforms using robotics to reduce the expenses and time requirements associated with experimental efforts and to expedite the synthesis of

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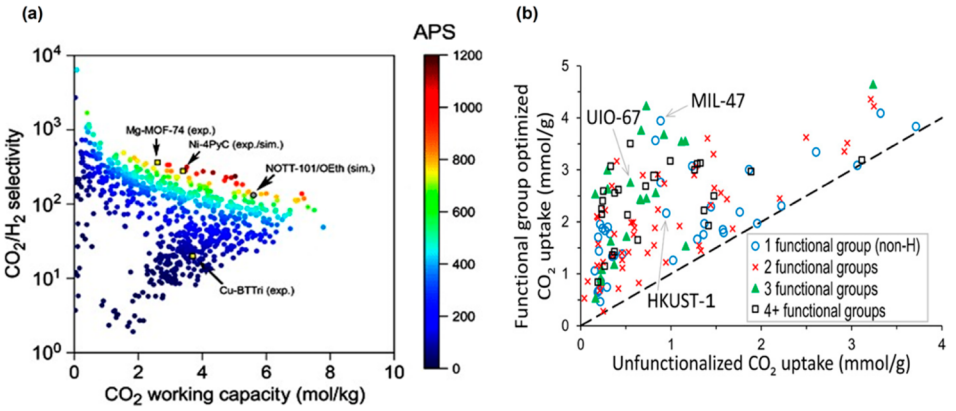


Figure 3. (a) Simulation results for 730 hMOFs identified using genetic algorithm among 51,163 structures for precombustion CO_2 capture at 20 bar, 313 K. Reprinted with permission from ref 49. (b) CO_2 uptakes acquired from molecular simulations at 0.15 atm and 298 K for 141 experimental MOFs with the genetic algorithm-optimized functional groups compared to the uptakes of the unfunctionalized parent MOFs. Reprinted with permission from ref 66.

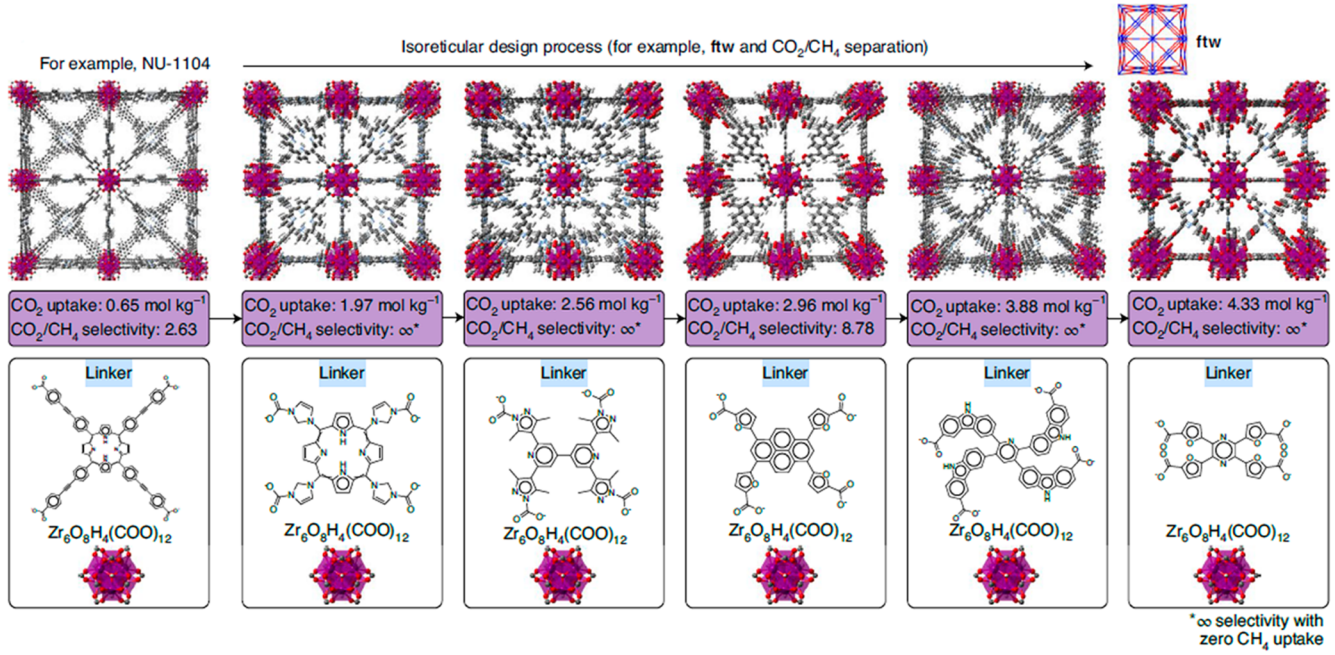


Figure 4. Isoreticular design process of a new hMOF, starting from NU-1104, offers significantly higher CO_2 uptake and selectivity. Readapted with permission from ref 67.

new and innovative MOFs discovered through AI-based algorithms.

2.1. MOFs. *Discovery of MOFs for CO_2 Capture.* The key benefit of integrating AI with molecular simulations is the ability to study the very large MOF spectrum in a quick and efficient manner as opposed to the brute-force computational screening of every single material. In one of the pioneering works, a genetic algorithm was employed to discover a high-performing MOF for CO_2 capture from the precombustion mixture (CO_2/H_2:20/80) and required only 1% of time that would have been spent if the brute-force computational screening had been used for all hMOFs in the database.[49] First, a screening approach based on the materials' chemical similarity was used to refine 51,163 unique hMOFs out of 137,193 structures, and then, the genetic algorithm identified 730 hMOFs as the top candidates offering the highest CO_2 working capacities, CO_2/H_2 selectivities, and adsorbent performance scores (APS), which is the multiplication of the first two. Figure 3(a) shows the relationship between CO_2 selectivity and working capacity of 730 hMOFs calculated from the gas uptakes obtained from GCMC simulations at an adsorption condition of 20 bar, 313 K. Computations predicted a very high CO_2 working capacity (5.6 mol/kg) for one of the hMOFs, NOTT-101/OEt, which outperformed several well-known MOFs, Mg-MOF-74 (2.6 mol/kg) and Ni-4PyC (3.4 mol/kg). This MOF was then synthesized, and experimental tests resulted in a CO_2 working capacity of 3.8 mol/kg, still higher than widely studied MOFs.

Functionalization of MOFs is a strategy to enhance their CO_2 capture properties by creating new adsorption sites attracting more CO_2 molecules. Numerous functional groups exist even for a single MOF; therefore, identifying the most effective functional groups for improving the CO_2 adsorption capacity of thousands of MOFs is a very challenging work,

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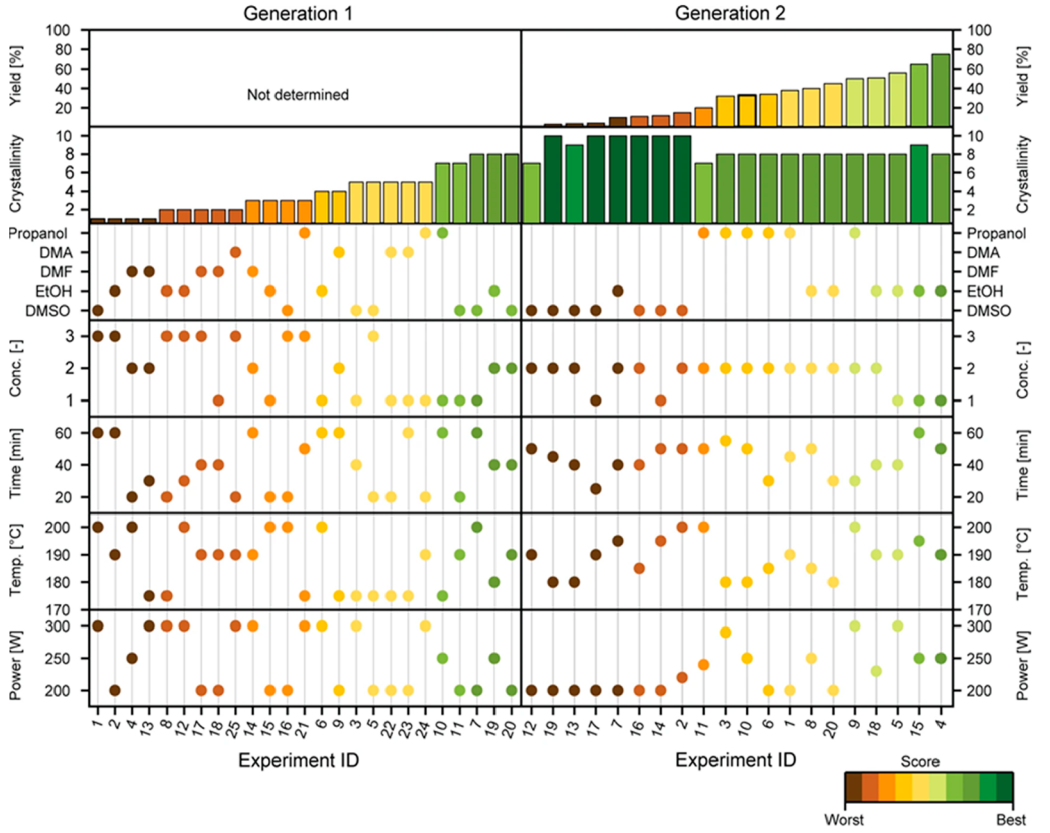


Figure 5. Experimental variables (microwave power, reaction temperature, time, concentration, and solvents) identified from the genetic algorithm for optimizing Al-PMOF synthesis are depicted by circles, while the bar graphs illustrate the ranking of each reaction in terms of crystallinity and yield. The good samples (green) have crystallinity scores larger than 6 out of 10 with yields larger than 50%, while the poor and bad samples (yellow/orange and brown) have crystallinity scores less than 6 out of 10 and yields less than 50%. Readapted with permission from ref 62.

which requires one to search for a very large space of material−functional group combinations. The MOF functionalization genetic algorithm (MOFF-GA) was utilized to identify 1035 novel MOFs with high CO_2 uptakes (>3 mmol/g) obtained from the GCMC simulation results among 581,278 unique and viable structures derived from 141 MOFs and 26 functional groups including aldehyde (−HCO), ethene ($-CHCH_2$), propoxy (−OPr), nitro ($-NO_2$), and hydroxyl (−OH), which are promising for optimizing the CO_2 uptake, volumetric surface area, and parasitic energy of materials.[66] As shown in Figure 3(b), optimizing functional groups resulted in an average 3.7-fold increase in CO_2 capacities of 141 MOFs. Functionalized versions of widely studied, well-known MOFs, such as MIL-47, HKUST-1, and UiO-67, exhibit very high CO_2 uptakes (up to 4.6 mol/kg), a notable three times enhancement compared to those of their original versions. As a result, MOFF-GA represents the importance of using AI-driven screening methods to examine very large material spaces that cannot be fully explored through purely experimental approaches.

Design of New MOFs for CO_2 Capture. AI is not only useful for screening the material databases to identify promising MOFs among already available structures but also very valuable for generating new materials with improved CO_2 capture properties. A deep learning algorithm was employed for the automated design of materials offering high CO_2 capture, and ∼2 million new hMOFs were generated by using metal nodes, organic linkers, and topologies of ∼14,000 synthesized MOFs.[67] Here, 45,000 hMOFs were randomly selected to study CO_2/CH_4 separation at 5 bar, 300 K, by using GCMC simulations, and gas uptake results were fed to the deep learning algorithm together with the structural properties of these hMOFs to obtain the optimized structures with improved CO_2 uptakes. Figure 4 shows the isoreticular design process starting from a previously synthesized MOF, NU-1104, having a ftw topology, Zr node, and CO_2 uptake of 0.65 mol/kg. A peak CO_2 uptake of 4.33 mol/kg, with more than six times increase compared to the CO_2 uptake of the original material (NU-1104), and infinite CO_2/CH_4 selectivity were achieved after utilizing six different linkers extracted from experimental MOFs. This study proved that AI-based platforms grounded in chemical and structural knowledge significantly aid in the design of new, novel MOF materials with improved CO_2 capture properties at predefined operating conditions.

AI-Driven MOF Synthesis. A systematic approach combining AI, molecular simulations, and experiments is very useful for the design and discovery of new MOFs specifically tailored for effective CO_2 capture from wet flue gas. Smit's group[68] computationally generated 325,000 hMOFs and examined for CO_2/N_2 separation by using GCMC simulations. Here, 8325 hMOFs with high CO_2 selectivities (>50) and working capacities (>2 mol/kg) were identified as high-performing materials. Based on the chemical property information acquired by data mining on CO_2 binding sites of these high-performing materials, 35 isoreticular hMOFs with frz topologies, Al metal nodes, and tetra-carboxylate-based organic linkers were generated. Molecular simulations showed that one

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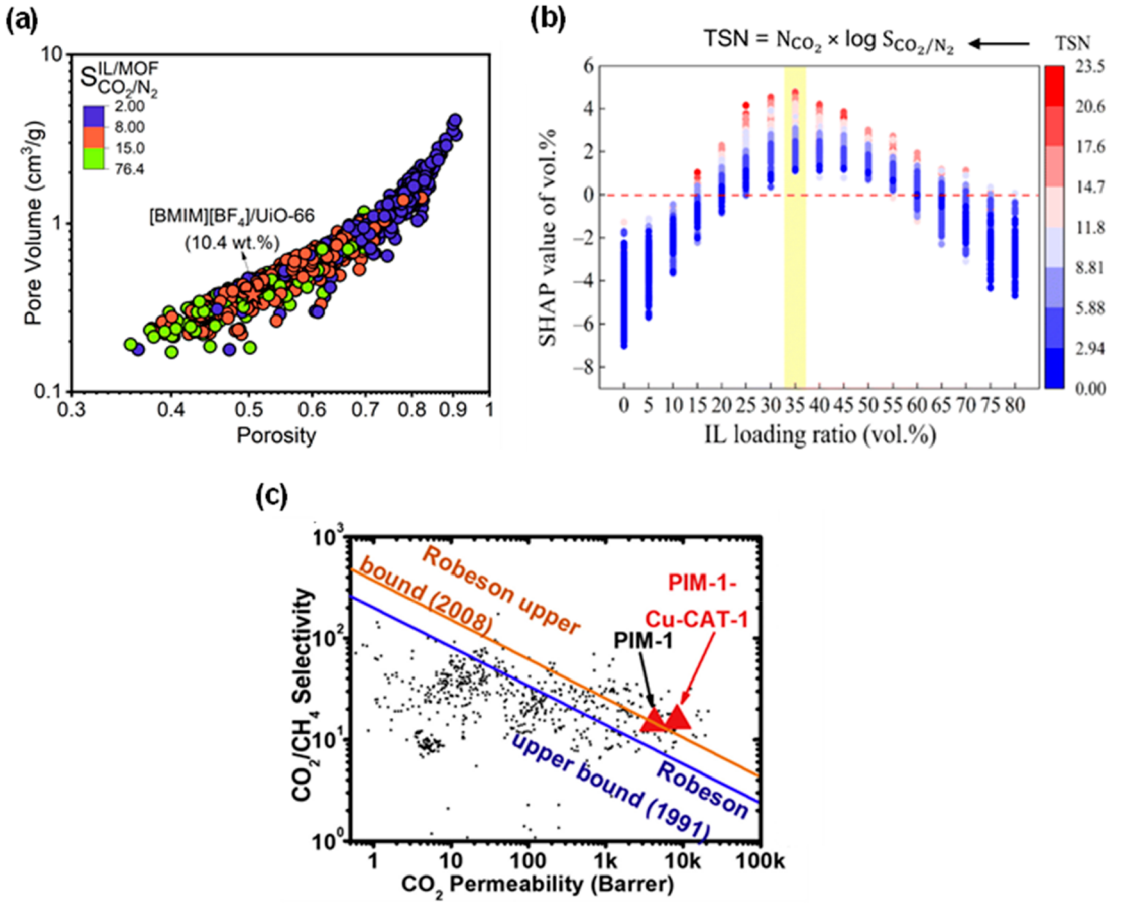


Figure 6. (a) 941 different types of [BMIM][BF_4]-incorporated IL/MOF composites and the relationships between their pore volume, porosity, and ML-predicted selectivities at 1 bar, 298 K. Readapted with permission from ref 73. (b) SHAP value analysis showing the relations between volumetric [MMIM][BF_4] loading (vol %) and ML-predicted TSN values for 15,410 different types of [MMIM][BF_4]-incorporated IL/COF composites at 1 bar, 298 K. Readapted with permission from ref 74. (c) Experimentally reported CO_2/CH_4 selectivities as a function of CO_2 permeabilities for PIM-1-Cu-CAT-1 membrane, which was selected to be synthesized based on insights of ML model. Readapted with permission from ref 75.

of these hMOFs, Al-PMOF, can achieve a CO_2 uptake of 1.75 mol/kg under dry conditions and 1.65 mol/kg under humid conditions at 1 bar, 313 K. This hMOF was selected for synthesis, and breakthrough experiments determined its high CO_2 working capacity up to 0.95 (0.86) mol/kg under dry (humid) conditions, surpassing those of activated carbon (0.55 and 0.35 mol/kg) and zeolite 13X (0.74 and 0.50 mol/kg) under both dry and humid conditions, respectively.

Although Al-PMOF was proven to be exceptional in CO_2 capture and was successfully synthesized, it had low yields (38%−88%) and required a long reaction time (16 h). To tackle this inefficiency problem, synthesis conditions for Al-PMOF were optimized using the parameters of both failed and partially successful experiments.[62]

Figure 5 shows the main experimental variables such as the power of the microwave used for synthesis, reaction temperature and time, the concentration of substrates, and the type of organic solvent. According to these variables, 25 different synthetic pathways were identified, and through experiments, two different generations were employed by genetic algorithm to optimize both the crystallinity and the yield, which define the success of a valid and stable MOF synthesis. Results showed that very high yields (>%80) in Al-PMOF synthesis were acquired from the optimized synthetic pathway with a reaction time of only 50 min, almost 20 times more time efficient compared to the original synthesis methodology. These results demonstrate that the integration of molecular simulations, AI, and experiments will enable researchers to efficiently synthesize novel MOFs with desired CO_2 capture performances.

2.2. MOF-Based Composites. Opportunities for enhancing the gas adsorption and separation performance of a high-performing MOF persist, even after its synthesis, by generating MOF-based composites. The two most widely studied MOF-based composites are ionic liquid (IL)/MOF composites, where an IL is incorporated into a MOF via postsynthesis modification, and MOF/polymer composites where MOFs are incorporated into polymers to generate composites with enhanced CO_2 adsorption and/or separation properties.[69,70] AI will perhaps be much more useful for the design and discovery of MOF-based composites rather than pristine MOFs since selecting the most appropriate IL among 10^{18} different available chemicals,[71] and the most appropriate polymer among hundreds of available structures[72] for a given MOF, would be critical.

To find a novel IL/MOF composite for CO_2/N_2 separation, ML models were developed using structural-, chemical-, and energy-based descriptors of 941 MOFs and their composites

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with [BMIM][BF_4] (1-*n*-butyl-3-methylimidazolium tetrafluoroborate).[73] Figure 6(a) shows the distribution of ML-predicted CO_2 selectivities of [BMIM][BF_4]/MOF composites with respect to the two most important molecular features, porosity and pore volume, identified from the feature importance analysis of a ML model. A computationally designed [BMIM][BF_4]/UiO-66 composite was then successfully synthesized and tested for CO_2/N_2 separation. Experimentally measured selectivity matched well with the ML-predicted value, highlighting the great value of using ML in accurately assessing CO_2/N_2 separation performances of any [BMIM][BF_4]/MOF composite within minutes compared to extensive time and effort requirements of purely experimental studies. The CO_2 capture properties of the composites are not only determined by the type of IL but also its loading in the composite. Here, 15,410 different types of IL/COF composites, derived from 557 COFs and an IL, [MMIM][BF_4] (1,3-dimethyl-imidazolium tetrafluoroborate), at 18 different loadings, were studied to identify the optimal IL loading ratio to maximize the adsorption-based CO_2/N_2 separation performance of composites.[74] Structural features of COFs and IL loading ratios were used in ML models to predict the trade-off (TSN) between CO_2 selectivity and uptake in [MMIM]-[BF_4]/COF composites. Shapley additive explanation (SHAP) analysis that quantifies the magnitude of each feature's impact on the ML predictions was used to analyze the relation between TSN and IL loadings. Figure 6(b) shows that composites offering the highest TSN have an IL loading ratio of 35 vol %, an important result that can accelerate the experimental efforts toward the synthesis of the most useful IL/COF composites with the optimal IL loadings. A similar approach can be used to determine the optimum IL loadings for IL/MOF and IL/MOF/polymer composite membranes to guide the experimental efforts.

IL/MOF composites are not only used as adsorbents for CO_2 separation but also used as fillers in polymers to generate mixed matrix membranes (MMMs) with the aim of making novel membranes exceeding the upper bounds[76,77] established for pure polymer membranes. In a recent work, 8167 different types of [NH_2-PMIM][Tf_2N]@MOF composites ([NH_2-PMIM][Tf_2N]:1-aminopropylimidazolium bis-(trifluoromethylsulfonyl) imine) were computationally generated, and ML models were developed to predict their CO_2 permeabilities and CO_2/N_2 membrane selectivities based on the structural (accessible volume, density, pore size, surface area, etc.) properties.[55] ML-predicted separation performance of the [NH_2-PMIM][Tf_2N]@ZIF-67 composite was shown to be above the upper bound, and it was incorporated into the polymer, PIM-1, to make IL@ZIF-67/PIM-1 MMM. This MMM also surpassed the upper bound with a CO_2/N_2 selectivity of 31.1, higher than that of PIM-1/ZIF-67 MMM, showing the potential of using IL@MOF composites as fillers in MMMs to make membranes with outstanding CO_2 capture performance.

Data for a large variety of MOF/polymer MMMs composed of 36 MOFs and 41 polymers studied for CO_2/CH_4 separation were collected and used to develop ML models predicting CO_2 permeabilities and CO_2/CH_4 membrane selectivities of MMMs.[75] Pore size, polymer type, and MOF loading were found to be the most significant descriptors to predict the CO_2 permeability of MOF/polymer MMMs among descriptors that include surface area, MOF type, pressure, filler size, aperture size, temperature, and thickness. According to the results of the ML model, Cu-CAT-1 was found to have the optimum structural features for high CO_2 separation; it was synthesized and incorporated into polymers Pebax 2553 and PIM-1. The resulting Cu-CAT-1/PIM-1 membrane surpassed the upper bound with a CO_2/CH_4 selectivity of 15.4, as shown in Figure 6(c). ML models constructed for predicting CO_2/CH_4 separation performance of MOF/polymer MMMs were then extended for CO_2/N_2 separation by applying a transfer learning approach. These extended models made more accurate predictions compared to the models developed by using the limited experimental data for MOF/polymer MMM for CO_2/N_2 separation. This result highlights a very important capacity of AI: making accurate predictions for a target application by learning from the predictions made for another application. Considering the fact that the majority of MMM studies focus on well-known MOFs such as ZIF-8, UiO-66, Cu-BTC, and MIL-53[78,79] for CO_2 separations, the discovery of a Cu-CAT-1/PIM-1 membrane demonstrates a significant shift toward the identification of promising MMMs from unexplored MOF material space. AI can play a pivotal role in decision-making processes by assessing critical factors like separation performance, durability, and costs associated with the utilization of MOF membranes versus MOF-based composite membranes. AI can use the results of simulations and experiments to show whether a pure MOF or a MOF-based composite exhibits better gas separation performance. In addition, AI can provide thermal and mechanical stability predictions for a very large material spectrum which are crucial to assess the materials' applicabilities for target gas separation.

3. OUTLOOK

In this perspective, we discuss the recent works showing how AI can guide experimental works to discover an existing porous material from thousands of candidates for CO_2 capture or to design an entirely new MOF that offers high CO_2 adsorption property. Believing that we will witness rapid and continuous growth in the number of studies combining AI, molecular simulations, and experiments for the design and discovery of new porous materials, we now present the current opportunities and challenges we see as the most critical for the further advancement of the field.

Most of the ML studies in this field primarily center around removal of CO_2 from flue gas (CO_2/N_2), natural gas (CO_2/CH_4), and precombustion gas (CO_2/H_2) mixtures since many computational research groups generated very large amounts of data for the adsorption of these three gas mixtures by molecular simulations which were then used in training ML models. Separation of CO_2 from other gases such as acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propane (C_3H_8), and hydrogen sulfide (H_2S) is also critical for industrial and environmental reasons, but the literature data are limited for them.[80−82] This can be attributed to several reasons such as (i) the challenge in computational modeling of large, polar gas molecules in addition to the difficulty of accurately defining the interactions in multicomponent gas mixtures and (ii) the experimental challenges posed by toxic or flammable gases like hydrogen sulfide and acetylene when testing CO_2 capture. The available literature on processes like pervaporation indicates that performing such molecular simulations for these systems, especially for separating very large molecules, is also computationally expensive.[83,84] Thus, the usage of low-data effective AI-based models can be useful to study MOFs as adsorbents and membranes in this regard. Future studies in this field may also

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identify the porous adsorbents and membranes that will show superior performance in separating CO_2 from multiple different gas mixtures.

Current studies used molecular simulation results for training ML models to predict the CO_2 adsorption properties of porous materials, but a lot of experimental data also exist, especially for CO_2 adsorption in zeolites and MOFs. However, extracting these large data from the vast literature and classifying them based on the operating conditions, process type, etc. is not straightforward. AI-based data and text mining algorithms can be used to extract, clean, and organize experimental data related to CO_2 adsorption and separation performances of porous materials in addition to complementing these data with structural (pore size, surface area, etc.) and chemical (metal, linker types, topologies, etc.) properties. The development of accurate, clean, easily accessible, standardized data sets on experimental CO_2 adsorption and separation properties of various types of porous materials will significantly accelerate the integration of experiments with ML and provide important collaboration opportunities between experimental and computational researchers.

ML models are generally trained by using the results of GCMC simulations for CO_2 adsorption. GCMC is a well-established technique in quantifying gas adsorption properties of various porous materials, but it relies on many assumptions, such as using rigid frameworks, generic force fields, and partial charge assignment for framework atoms, to screen several thousands of MOFs in a time-efficient manner. Several MOFs are known to be flexible upon guest adsorption, and many have open metal sites or special functional groups or defects that may require specially tailored force fields to accurately describe the interactions between the framework and CO_2 molecules. Of course, all these issues may affect the simulated CO_2 adsorption capacity, diffusivity, selectivity, and permeability of materials. On the other hand, performing flexible MOF simulations and developing material-specific force fields are computationally very demanding when thousands of materials are considered. AI has a huge potential in solving this bottleneck. For example, running computationally demanding flexible simulations for a representative set of materials and then training AI models based on these data can assist the researchers to make highly accurate predictions for CO_2 capture properties of MOFs that have special features such as flexibility, defects, etc. Assigning accurate partial atomic charges is critical for CO_2 molecules to model their electrostatic interactions with the MOF atoms during the adsorption simulations. Partial charges are not experimentally observable, and ab initio calculations to compute them are very time demanding. A recent work used the power of AI to develop software that assigns the partial atomic charges in MOFs with similar accuracy and 40% faster than the density functional theory (DFT)-based methods.[85] These AI-driven tools will accelerate the molecular simulations of adsorption and diffusion of CO_2 in porous materials.

Molecular simulation studies focusing on IL/MOF and MOF/polymer composites also have several assumptions, such as perfect interaction between the composite constituents and homogeneous distribution of the fillers in the MMMs.[86] Several studies investigated the specific interactions in the MOF−polymer interface to gain insights into the stability and feasibility of MMMs.[87−89] A similar approach can be applicable to IL-incorporated MMMs as well because ILs can improve the MOF−polymer interactions in IL/MOF/polymer MMMs.[90,91] However, studies investigating the interactions between ILs, MOFs, and polymers on an atomistic scale are limited due to high computational cost required to define all complex interactions.[92] AI-based methods using the descriptors acquired from the DFT calculations for IL-incorporated MMMs can help in developing force fields to define these complex interactions accurately and efficiently for several different combinations of MOFs, polymers, and ILs. AI-based methods will enable the exploration of a wider variety of ILs and polymers for integration of these novel MOF-based composite adsorbents and membranes into CO_2 capture processes.

ML studies on zeolites, porous carbons, MOFs, COFs, and their composites generally predicted materials' CO_2 adsorption and separation properties based on the easily accessible structural features of materials, such as surface areas and element types. New tools were developed to predict guest accessibility of any given MOF from the chemical features, the organic linkers, and the metal ions.[93,94] Recent efforts showed that introducing new descriptors can offer time efficiency and more accurate predictions. For example, energy-based descriptors, including Gibbs free energy and Boltzmann weighted energy distributions of xenon (Xe) and krypton (Kr) gases, were demonstrated to be more important for determining Xe/Kr selectivities of MOFs compared to their structural and chemical features.[95] Another new descriptor, effective point charge, was recently introduced and used together with the Henry coefficients of CO_2 in ML models to predict CO_2 capture properties of MOFs at very low-pressure conditions mimicking direct air capture.[96] Development and usage of new features in the future will lead to much accurate ML models.

AI studies to date have been used to predict CO_2 adsorption and separation performance metrics of porous materials, such as selectivity, working capacity, APS, and permeability, and then to rank the materials based on these metrics for identifying the top performing candidates. However, the fact that a material captures a very high amount of CO_2 does not guarantee that the material can be easily synthesized or is stable or feasible to use in real applications. AI tools that can predict the synthesizability of MOFs,[97] the optimal synthesis conditions of MOFs,[64] and their expected thermal and mechanical stabilities[98−100] have recently appeared. Heat capacity is a fundamental descriptor defining the heat required to regenerate an adsorbent, and a ML model was developed to accurately predict heat capacities of MOFs, COFs, and zeolites using DFT-based chemical descriptors.[101] These capacities were then used to calculate the performance metrics identifying the best materials for a temperature swing CO_2 capture process. In addition to performance metrics related to the material itself, metrics focusing on the efficiency of a process, such as CO_2 recovery, purity, productivity, and parasitic energy, are also important.[102−104] However, finding a material that meets all requirements of material- and process-based metrics is difficult using molecular simulations or experiments alone. For example, MOFs offering high CO_2 purity, recovery targets and having parasitic energies lower than the one required for a solvent-based CO_2 capture were identified for a CO_2/N_2 separation process using a genetic algorithm.[105] AI-based methods can also be useful for techno-economic analysis of MOF-based CO_2 capture processes to evaluate the efficiency of MOFs for an industrial-scale process by computing the cost of carbon capture.

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Material discovery, particularly in the field of MOFs, faces challenges in aligning computational predictions with laboratory experiments. The hesitancy to invest in uncertain experiments and the complexity of synthesis procedures are major hurdles. Computational models also struggle with data imbalances, usually omitting unsuccessful attempts. Integrating AI and automated systems into existing lab workflows and scaling experiments for industrial applications are other significant challenges. Therefore, enhanced collaboration between computational and experimental researchers is vital in this field. With the rapid developments in AI, the increase in computer power, the realization of experimental studies with novel robotic systems, the increase in the number and variety of new porous materials, and perhaps most importantly, the cooperation of expert researchers in these fields, a very exciting future awaits us for the design and discovery of new adsorbents and membranes that will efficiently capture CO_2 and hopefully solve one of the most important challenges of our world, global warming.

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Notes

The authors declare no competing financial interest.

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