In Silico Design and Analysis of Microporous Polymers for Chemical Separations and Gas Storage

Dylan M. Anstine[1,2], David S. Sholl[3,4], J. Ilja Siepmann[5], Randall Q. Snurr[6], Alán Aspuru-Guzik[7,8,9,10], and Coray M. Colina[1,2,11,*]

[1] Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA
[2] George & Josephine Butler Polymer Research Laboratory, University of Florida, Gainesville, FL, USA
[3] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, USA
[4] Oak Ridge National Laboratory, Oak Ridge, TN, USA
[5] Department of Chemistry and Chemical Theory Center, University of Minnesota, Minneapolis, MN, USA
[6] Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL, USA
[7] Department of Chemistry, University of Toronto, Toronto, Ontario, Canada
[8] Department of Computer Science, University of Toronto, Toronto, Ontario, Canada
[9] Vector Institute for Artificial Intelligence, Toronto, Ontario, Canada
[10] Lebovic Fellow, Canadian Institute for Advanced Research, Toronto, Ontario, Canada
[11] Department of Chemistry, University of Florida, Gainesville, FL, USA
[*] Corresponding author: colina@chem.ufl.edu

Highlights

- Atomistic modeling techniques for microporous feature analysis.
- *In silico* predictions of adsorption with flexible frameworks.
- Data-driven methods are positioned to accelerate PIM discovery and design.

Keywords

intrinsic microporosity • molecular simulation • polymer modeling • machine learning • adsorption

Abstract

Polymers of intrinsic microporosity (PIMs) are a family of materials with potential to be effective and scalable solutions for challenging adsorbent and membrane applications. The broad range of repeat unit chemistry, microporous structural features, and polymer processing makes exploration of the expansive PIM design space inefficient via chemical and materials intuition alone. Computational techniques such as molecular simulations and machine learning can provide a leap in capabilities to address this polymer design challenge and will be central to the future development of PIMs. We highlight recent microporous material studies that arrived at key results by employing computational techniques and provide our perspective on the prospects for *in silico* design and development of PIMs.

1. Introduction

Polymers of intrinsic microporosity (PIMs) are constructed from repeating units that typically have ladder-like backbones and appreciable internal molecular free volume [1,2]. Forming polymer chains from these rigid and sterically constrained building units yields inefficiently packed materials that can have persistent microporosity (*e.g.*, pores up to 2.0 nm in diameter [3]). A PIM's performance for adsorbent or membrane applications is a function of factors that define material microporosity, such as polymer chemistry and processing steps. Surpassing current performance limits that arise from known property tradeoffs is a defining challenge for PIM materials [4•]. For example, membrane selectivity and membrane permeability are observed to be inversely related, result in a performance ceiling, *i.e.*, the so-called Robeson upper bound [5]. Many PIM practitioners are driven by the concept that these types of performance ceilings can be overcome through innovative monomer design and novel fabrication techniques [6,7]. A key goal in the application of PIMs to chemical separations and storage applications is to discover low-cost, processable, scalable, mechanically robust, aging-resistant polymers with either large uptake capacity or high selectivity and permeability. The path to such PIMs is understandably elusive. As a result, computational efforts are emerging that are aimed at expedited PIM development through adopting molecular simulation (MS) and machine learning (ML) techniques.

In this review, we summarize MS approaches that have been used to predict PIM performance, properties, and structure for separation and storage applications. The results of applying simulation techniques that account for guest-induced polymer restructuring (for example, swelling) are emphasized. We also provide a perspective on aspects of emerging data-driven methods that have conceivable application to PIM materials. Breakthroughs in ML, materials informatics, and cheminformatics are creating opportunities to rapidly accelerate the discovery of new polymers, which we envision will become a core component of forthcoming PIM development. We offer an outlook on the challenging areas that future computational efforts need to address to enable development of exceptional PIM adsorbents and membranes.

2. Molecular Simulations

2.1 Predictive PIM *In Silico* Synthesis and Characterization

Molecular simulation studies of PIMs are mainly performed using atomistic/united-atom models (the latter combines CH_x units into a single site) because adsorption processes and, in particular, chemical selectivity are governed at the (sub-) angstrom scale. Force-field-based molecular modeling and simulation techniques [8] can be applied to provide predictions of PIM material characteristics *a priori* or alongside an experimental study if an appropriate molecular model (or force field) is available. A core advantage of atomistic/united-atom modeling is the possibility to predict the molecular packing of polymer chains from knowledge of the repeating unit chemistry [9,10••,11•]. Unlike simulations of crystalline (defect-free) materials,

construction of *in silico* models of porous polymers is a challenging task. Powerful tools and the necessary validation steps for this task now exist and have been reviewed by Kupgan *et al.* [10••]. The benefit of *in silico* structural and trajectory analyses, which are performed as a function of atomic coordinates, is that it yields insight into polymer microporosity, amorphous structure, and motion of polymer and adsorbate molecules that is difficult to obtain experimentally. Simulations of PIM structures have been used in several combined experimental-computational studies [11•–14]. For example, Figure 1 shows computational results from the 2017 work of Rose *et al.*, which used molecular modeling and experimental characterization to describe structural features of PIM-TMN-Trip [11•]. The authors' molecular modeling approach was able to connect the inefficiently packed polymer conformations with pore structure and the experimentally observed ultrapermeability.

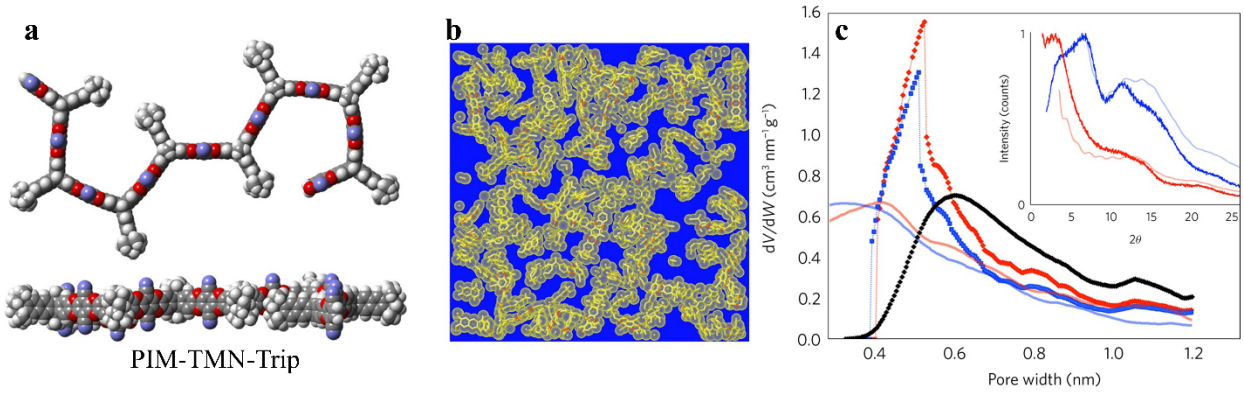

Figure 1 Results from predictive molecular simulations of PIM-TMN-Trip. a) 2D shape of a chain fragment of a PIM-TMN-Trip 8-mer. b) illustration of molecular packing of PIM-TMN-Trip polymer chains from molecular simulations. The polymer pore space is highlight in blue, whereas polymer occupied space is shown by the yellow isosurfaces. c) comparison of polymer structure, for PIM-TMN-Trip and PIM-TMN-SBI, and textural features with experimentally obtained values. The large frame demonstrates additional pore size distribution description obtainable from molecular modeling (red and blue lines), corresponding to nitrogen probe excluded regions, which are not observed in the experimental measurement (filled symbols). The inset plot shows that the simulated and experimental wide-angle X-ray scattering spectra reasonably agree. This figure is adapted by permissions from ref [11].

2.2 Adsorption and Framework Flexibility Predictions

Beyond investigation of polymer packing, MS is useful for predicting the adsorption of single- and multi-component adsorbate systems, notably providing an opportunity to screen materials as adsorbents. Approaches to simulate adsorption in glassy polymers are summarized in the reviews by Vergadou and Theodorou [15] and Anstine and Colina [16]. It is important to mention that MS procedures are typically straightforward to generalize to multi-component mixtures, whereas the availability of broadly applicable mixed-gas adsorption equipment is an ongoing experimental challenge [17].

Quantifying adsorptive properties and their relationship to guest uptake driven polymer restructuring is essential. Recent physisorption simulations with polymeric adsorbents apply

computational techniques that incorporate the critical role of adsorbate-induced polymer restructuring [18•–22••]. One technique to examine polymer swelling, pore restructuring, and microporous feature rearrangement is the adsorption-relaxation protocol (ARP). The ARP consists of iterative transitions between Monte Carlo simulations (to predict uptake) and isothermal-isobaric molecular dynamics simulations (to incorporate framework flexibility). One of the earliest applications of ARP to a PIM material was performed by Kupgan *et al*. in 2018, where the degradation of PIM-1 performance with adsorption-induced swelling of common gases was demonstrated [18•]. Compared to rigid framework approximations, the authors' ARP results showed better qualitative agreement with the experimental CO_2 adsorption isotherm shape and superior quantitative agreement at elevated uptake (> 3-5 mmol g^{-1}).

A limitation for exploring new PIM materials for separation or storage applications, both computationally and experimentally, is that studies typically focus on unary isotherms for a handful of common small adsorbate species, such as CO_2, N_2, and CH_4. This simplification has led to open research questions regarding the function of chemical diversity in adsorption-induced polymer restructuring. To address the role of adsorbent and adsorbate identity in the flexible adsorption of PIMs under swelling/plasticizing conditions, Anstine *et al.* recently reported an *in silico* screening of 24 different adsorbates in 15 different PIMs using the ARP [22••]. The adsorbate species and polymer repeating units were chosen to have variations in size, molecular geometry, and chemical functionality. It was demonstrated that swelling as a function of gas uptake can be described using a piecewise quadratic (swelling < 15%) and linear relationship (swelling > 15%), see Figure 2. The shape of the linear and quadratic regions is unique to the PIM-adsorbate pair and can be rapidly estimated using routinely characterized values: the critical temperature and molar mass of the adsorbate, and the surface area and helium void volume of the polymer.

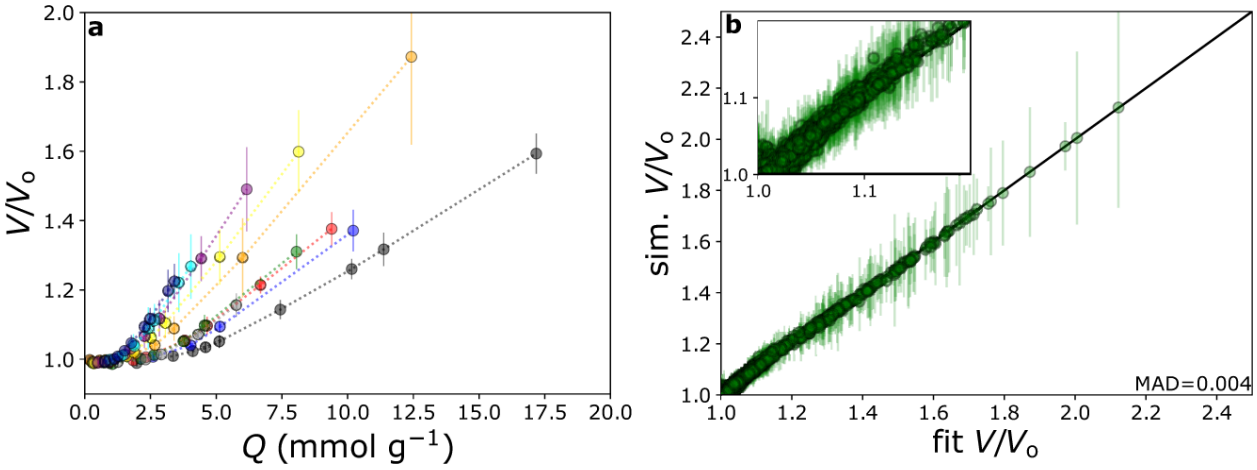

Figure 2 Demonstration of molecular simulation screening of loading-induced polymer swelling in PIMs with diverse adsorbate species. A) Simulated relative swelling (equilibrated PIM volume with adsorbates / initial adsorbate free PIM volume) as a function of uptake (Q) using the adsorption-relaxation protocol. Different colored curves represent the adsorption of distinct single-component gases in the same PIM material. B) Parity plot demonstrating

that loading-induced swelling can be described using a piecewise quadratic ($V/V_o < 1.15$) and linear ($V/V_o > 1.15$) fit. This figure is reproduced with permissions from ref [22].

3. Accelerating PIM Exploration

3.1 Data-Driven PIM Discovery

Wang *et al.* noted in 2018 that 50 PIM materials have been developed in the last 3 years [23]. At this rate, it will take several hundred years to study 10^3-10^4 novel PIMs using current strategies. It is possible that only a few of these PIM structures will have scale up value outside of a laboratory setting. Importantly, a few thousand polymer systems cover a small fraction of the vast PIM design space composed of, for instance, copolymers, polymer blends, and undiscovered homopolymers. This point emphasizes the need for expedited screening through data-driven computational techniques. Applications of big-data and ML methods to porous materials have been reviewed by Jablonka *et al*. [24••]. In short, microporous materials scientists are increasingly adopting ML techniques for structure exploration and rapid adsorption predictions, although studies for structurally disordered materials such as polymers remain limited. For PIM discovery, the lack of data-driven methods is limited by two factors: (1) structural/textural characterization for experimental PIMs is sparsely reported, and (2) systematic construction of a database of amorphous PIM models is computationally challenging. In 2020 Thyagarajan and Sholl created and characterized a database of 205 atomistic models of amorphous microporous materials aggregated from existing literature [25]. Their database represents progress toward curating a repository of amorphous microporous models. However, this is significantly smaller than collections of crystalline materials; for example, the CoRE MOF database contains 14,000+ metal-organic frameworks [26]. The largest dataset of PIM structures was created in the 2021 study of Anstine *et al.*, where simulations of 15 polymer chemistries produced over 240,000 fresh and swollen polymer structures [22••]. Large-scale exploration of PIM chemistry is an ongoing need.

The power of ML-driven discovery of microporous polymers is emphasized in the 2020 works of Barnett *et al.* [27•] and Zhu *et al.* [28•]. Barnett *et al.* sought to overcome the Robeson upper bound by using existing polymer membrane data to train ML models that predict permeability and selectivity from a fingerprint representation of repeating unit chemistry. Their workflow (see Figure 3) was applied to 11,325 previously synthesized polymers with unknown permeability and selectivity. Following the identification of several membrane materials that were predicted to exceed the CO_2/CH_4 Robeson upper bound, the authors experimentally synthesized two polymers and confirmed their ML predictions of performance. Future efforts can be oriented toward exploring unknown polymer systems, for example, using generative models. The study by Zhu *et al*. aimed to develop a predictive ML permeability model with applicability to broad classes of polymers. The authors leveraged a fingerprint representaition of repeat unit chemistry to train a Gaussian process regression model on existing data from

literature to predict permeability/permselectivity of 6 common gases. A noteworthy aspect of the Zhu *et al*. work is that their models are made available via an online platform.

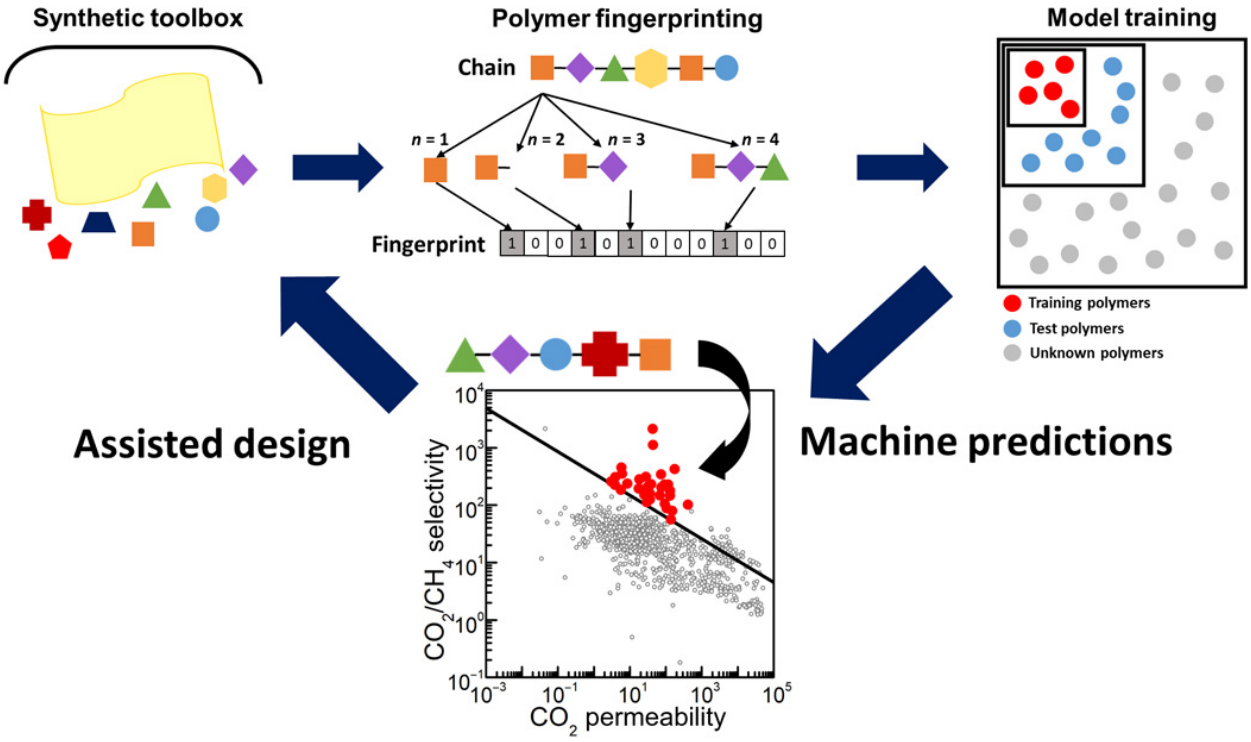

Figure 3 Workflow of computer-aided design of polymeric membranes with exceptional selectivity and permeability. The synthetic toolbox consists of a collection of known polymeric materials that can be represented with a fingerprint of the polymer repeating unit. These fingerprints are used in machine learning models to predict performance of previously synthesized microporous polymers. Polymers that exceed the permeability-selectivity tradeoff ceiling (diagonal line in the lower plot) are identified in red, two of which were experimentally tested to confirm the machine learning prediction. This figure is reproduced with permissions from ref [27].

3.2 Rapid Predictions of Adsorption

Screening materials via MS for adsorption properties can be computationally laborious. Assessing uptake of mixtures or complex adsorbates (*i.e.*, hydrogen bonding or with high degree of conformational flexibility) in databases containing thousands of candidate adsorbents can require millions of hours of compute resources [29]. This has led to efforts to reduce the computational expense of evaluating large material datasets [30•]. One approach to rapidly predict adsorbate uptake is to replace Monte Carlo simulations with ML-based predictions [31–32]. The strategy is to translate microporous adsorbent models into a set of descriptors containing sufficient detail to predict adsorption. It is worth noting that studies of this kind are not yet widespread for PIMs (due to limited data). However, methods applied to other families of microporous systems are conceivably extendable to polymeric adsorbents. An example approach, reported by Bucior *et al.*, used an energy-based descriptor, namely a 1-dimensional potential energy histogram, to efficiently predict hydrogen and methane uptake in metal-organic frameworks (MOFs) [32]. A summary of their workflow for hydrogen uptake predictions

is shown in Figure 4. The authors employed a strategy to represent atomistic MOF models as a collection of equally spaced 3-dimensional grid points. At each grid point position, the potential energy of a probe particle is calculated as the sum of all nonbonded interactions with the framework. An energy histogram from the grid point calculations was used to predict hydrogen and methane uptake using a least absolute shrinkage and selection operator regression with an accuracy of better than 4 g L^{-1}. We comment that alternatives to least absolute shrinkage and selection operator regression, such as neural networks, are equally applicable.

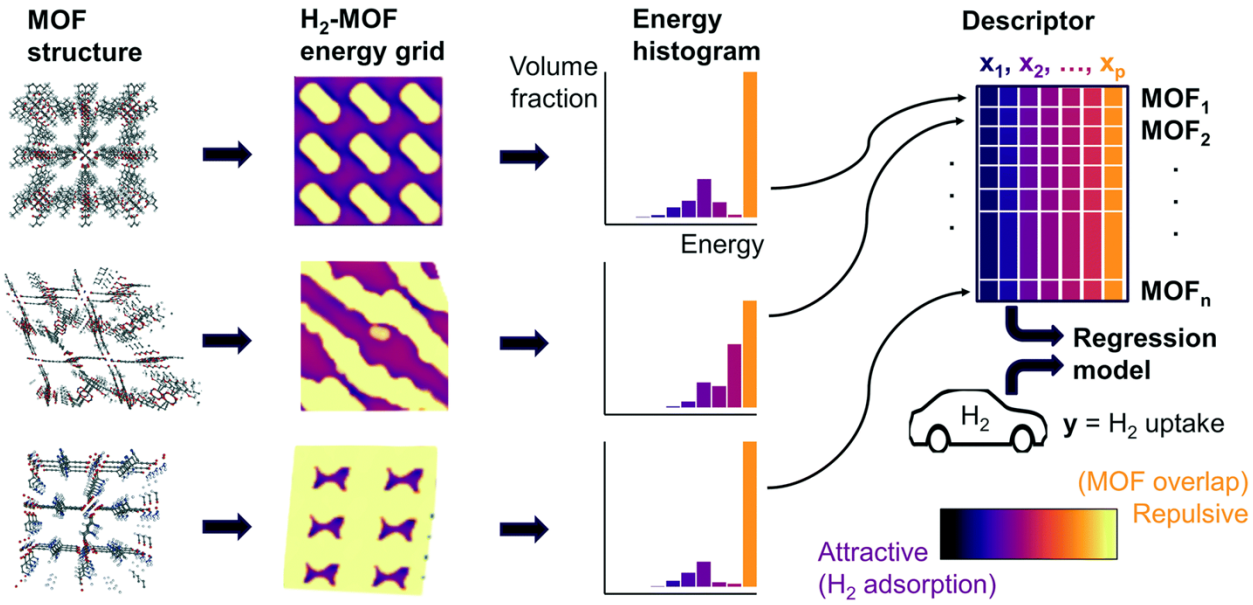

Figure 4 Workflow of rapid hydrogen adsorption predictions using grid point energy histograms as an adsorbent material descriptor. The potential energy of a hydrogen probe particle is calculated at regularly spaced grid points of the metal-organic framework (MOF) unit cell. A histogram of the grid point energies is used in a data-driven regression model to predict hydrogen uptake. This figure is reproduced with permissions from ref [32].

Other recent works focusing on accelerated adsorption predictions have successfully used ML approaches with multiple energy probe descriptors [33], fingerprinting [34,35], and textural properties [36]. To date, several studies have trained accurate species-specific models without designing for extensibility. Moreover, most ML models reported are designed to predict for a given set of conditions, *e.g.*, specific working pressure range at fixed temperature for a storage application, but progress has been made toward applicability over a wide range of temperatures and pressures [35]. Development of an openly available ML approach for rapid adsorption predictions of PIMs with accuracy across many thermodynamic states and species transferability is needed.

4. Challenges and Outlook

Simulations of PIMs have proven valuable for studying amorphous structures and screening gas physisorption properties. There are many PIM applications that are computationally unexplored. For example, Jung *et al.* reported experimentally post-synthetically modified PIMs

for toxic gas uptake [37]. Accurate simulations of these systems need to account for chemisorption phenomena, which requires further force field validation and methodology development. A major challenge facing the field of membrane science is to develop microporous polymeric materials for liquid purifications, such as reverse osmosis [38,39]. MS techniques to evaluate liquid separation performance of PIMs are needed, and interested readers are directed to the work by Bai *et al.* for zeolites [29]. There is a growing trend for integrating PIMs into multi-component material systems such as mixed matrix membranes [40-43]. Workflows to build structures, force fields with compatibility between PIMs and crystalline materials, and standardized equilibration procedures are topics to address for these composite systems.

This review also highlighted data-driven computational techniques, such as ML, for accelerated PIM screening and rapid adsorption predictions. A limitation for applying ML methods to amorphous PIMs is to find a high-quality input representation. Interestingly, the previously discussed studies of Barnett *et al.* and Zhu *et al.* found success in exceeding the Robeson upper bound using only monomer-level fingerprint descriptors [27•,28•]. We highlight that mapping monomer structure to the anticipated polymer properties is attractive because it can avoid the computational labor of building atomistic/united-atom PIM models. However, for unknown PIMs, models are likely to be more extensible if microporous textural descriptors (*e.g.*, fractional free volume) and/or polymer-level inputs (*e.g.,* elastic moduli) are added. It is also of interest to compare the fingerprinting approach against text-based input representations such as BigSMILES or SELFIES [44,45]. A long-term strategy for efficient and creative PIM development is to employ a generative model, for example, variational autoencoders, to derive optimal repeating units for a target property [46]. Other methodologies include generational adversarial networks and reinforcement learning [47]. Such methods typically require expansive datasets to properly function; as a result, accelerating the development of new PIMs to construct large microporous polymer databases is of immediate importance.

As we approach two decades of PIM chemistry and material science, it is worth considering how best to optimize our future allocation of experimental and computational efforts. The development of exascale high-performance computing systems is providing computational power nearly 3 orders of magnitude greater than when the first PIM was experimentally synthesized. Thus, simulation codes that can take full advantage of exascale computing resources need to be developed. Considering increased computer speed in combination with versatile open-source software and workflow managers, for example, pysimm [48], LAMMPS [49], and RASPA [50], MS methods for adsorbent material research are becoming faster, more reproducible, and generalizable to diverse systems. Even though new PIMs have been discovered predominately through experimental research, computational tools now exist that will allow an exponential discovery of new PIMs. Modern MS and ML techniques are positioned to enable computer-guided optimization of PIMs. MS studies have mainly focused on gaining fundamental understanding into the amorphous PIM structures and adsorption-induced polymer restructuring, which is a small fraction of their potential. We believe that leveraging a

unified approach of MS, data-driven techniques, and experimental studies will be the defining feature of the next two decades of PIM chemistry and material science.

Conflict of Interest Statement

A.A.-G. is co-founder and Chief Visionary Officer of Kebotix, Inc. an AI-driven materials discovery company based in Boston, MA.

R.Q.S. has a financial interest in the startup company NuMat Technologies, which is seeking to commercialize MOFs. The authors declare that they have no other competing interests.

References and Recommended Reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

Acknowledgment

The authors acknowledge funding provided by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under award DE-FG02-17ER16362. The authors also thank Dai Tang, Salah Boulfelfel, Zhenzi Yu, Zhao Li, Roshan Patel, and Saumil Chheda for helpful discussions on the topics addressed on this review.

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