

Feasibility of zeolitic imidazolate framework membranes for clean energy applications†

Aaron W. Thornton,^{*a} David Dubbeldam,^b Ming S. Liu,^c Bradley P. Ladewig,^d Anita J. Hill^a and Matthew R. Hill^{ae}

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Gas separation technologies for carbon-free hydrogen and clean gaseous fuel production must efficiently perform the following separations: (1) H₂/CO₂ (and H₂/N₂) for pre-combustion coal gasification, (2) CO₂/N₂ for post-combustion of coal, (3) CO₂/CH₄ for natural gas sweetening and biofuel purification, and (4) O₂/N₂ for oxy-combustion of coal. By utilizing a molecular simulation approach, Monte Carlo procedures, free volume analysis, and continuum modeling, we predict the intrinsic gas permeability and separation properties of several new Zeolitic Imidazolate Frameworks (ZIFs), a family of the Metal–Organic Frameworks (MOFs). The well defined pore sizes in conjunction with high surface areas make ZIFs prime candidates for molecular sieving. In this work, our calculated intrinsic properties are compared with current experimental results where ZIFs are either grown in dense layers to form pure inorganic membranes on porous supports or dispersed within a polymer phase to form mixed matrix membranes. Consequently, this paper assesses current membrane development according to industrial feasibility targets and highlights the achievable superior separation results for ideal membrane configurations. For example, ZIF-11 is discovered to be capable of sieving H₂ from all of its larger gas counterparts at a remarkable H₂/CO₂ selectivity of 262 and H₂ permeability of 5830 Barrer, well within the target area for efficient hydrogen production.

Introduction

Gas separation technology is set to become a key enabling technology in an economy where a cost is placed on carbon waste emissions. Applications such as removal of CO₂ from pre- and post-combustion flue gas streams at coal-fired power plants or the isolation of clean fuels such as hydrogen or methane will be the beneficiaries of the economic drivers in a low carbon environment.^{1–3} Fig. 1 illustrates three approaches to carbon-reducing power generation with their corresponding separation challenges, including H₂/CO₂ and H₂/N₂ for hydrogen production from gasified coal typically after a water–gas shift reaction,^{4–6} CO₂/N₂ for decarbonization of coal combustion exhaust streams,^{7–9} CO₂/CH₄ for natural gas sweetening and biofuel purification,^{10,11} and O₂/N₂ for oxy-combustion of coal that

^aCSIRO Materials Science and Engineering, Process Science and Engineering, Private Bag 33, Clayton Sth MDC, Victoria, 3169, Australia. E-mail: aaron.thornton@csiro.au; Fax: +61 03 9545 2837; Tel: +61 03 9545 8018

^bVan't Hoff Institute for Molecular Sciences, University of Amsterdam, 904 Science Park, 1098, XH, Netherlands

^cCSIRO Mathematics, Informatics and Statistics, Private Bag 33, Clayton Sth MDC, Victoria, 3169, Australia

^dDepartment of Chemical Engineering, Monash University, Clayton, Victoria, 3800, Australia

^eSchool of Chemistry, University of Melbourne, Parkville, Victoria, 3800, Australia

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Broader context

Small molecule transport cycles are critical for sustainable closed-loop energy-waste systems. Here we explore the role of materials design in the efficient separation of gas molecules in the quest for clean energy from fossil fuels. Zeolitic Imidazolate Frameworks (ZIFs) are highly porous, chemically functional and size-selective crystals that offer almost resistant-free gas separation properties. ZIFs are predicted to be capable of satisfying industrial performance targets necessary for clean energy from fossil fuels as we transition to renewable sources of clean energy.

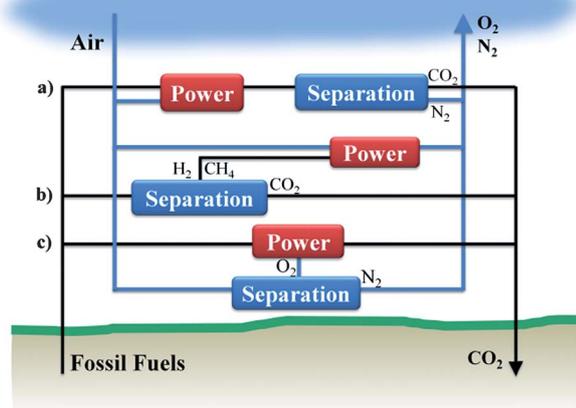


Fig. 1 Carbon-reducing power generation approaches with separation technologies: (a) post-combustion separation for the removal of CO_2 from flue streams, (b) pre-combustion separation for H_2 production after gasification and reformation of coal or CH_4 production from natural gas sources, and (c) oxygen separation from air for oxy-combustion of fossil fuels.

produces high CO_2 -concentrated emissions for immediate sequestration.^{9,12}

Material-based separations can occur either as a membrane system,^{13–16} where the material is chosen to selectively allow one gas to pass through preferentially over another, or an adsorbent system,¹² where the material is chosen to selectively capture one gas preferentially. Membranes have served the gas separation industry for over 30 years, offering an efficient flow-through system that is typically run at thermodynamic equilibrium.^{14,17} Adsorbents on the other-hand offer remarkable gas storage capabilities which have translated to the field of gas separation.

However, adsorbent-based separations require switching adsorption and desorption environments such as vacuum and pressure swing adsorption, thermal swing adsorption, electric swing adsorption, simulated moving bed and purge displacement, which pose engineering challenges that membranes do not encounter.^{18–21} Further, the majority of membranes have utilized the differences in gas diffusion rates to efficiently achieve high selectivities which are yet to be matched by adsorbents that rely on differences in adsorption uptakes.^{12,22} Overall, membranes offer an efficient means of separating gases.^{6,21}

Membrane materials have included polymers, inorganics and mixed matrix membranes (MMM), Fig. 2. Polymer membranes, though cheap, scalable and robust, have remained limited by a separation property trade off performance, as pointed out by Robeson.^{23,24} This trade off behaviour has been explained by solution–diffusion theory.²⁵ The wide pore size distributions and the dynamic nature of the porosity within polymers are factors that limit their size-sieving capabilities. Moreover, polymers commonly suffer from thermal degradation and plasticization, when exposed to service environments in clean energy applications.^{26–29} Therefore, other materials which are comprised of rigid and definable pores need to be developed in order to overcome the upper bound and hence deliver superior performance whilst minimizing costs related to pressurization and multi-stage capital equipment.

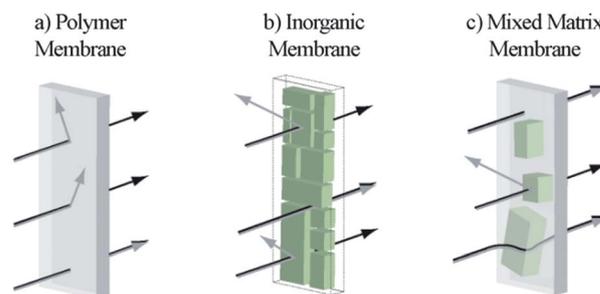


Fig. 2 Schematic of membrane configurations: (a) polymer only membrane where separations are governed by the solution–diffusion mechanism, (b) inorganic only membrane with elevated sieving and sorption characteristics, and (c) mixed matrix membrane (MMM) where inorganic particles are dispersed within a continuous polymer phase.

A particle (or material) with rigid pores of a size between two target gases could exhibit close to a perfect selectivity.^{30,31} Inorganic materials are attractive candidates in this regard due to their well defined, rigid pore sizes that offer greatly enhanced selectivity.^{32,33} Zeolites in particular have found application as they possess such well defined pore sizes in combination with good surface areas of up to several hundred square metres per gram.^{32,34–38} However, there are inherent limitations to zeolites. The low pore connectivity common in zeolites can often lead to blockage by larger diameter gases, a problem not seen in flexible polymer membranes.¹⁴ Another possible solution to this “plumbing problem” is to find or design a pore network such that there is a high degree of pore connectivity, providing alternate routes for transport should a blockage develop.³⁹

Metal–organic frameworks (MOFs) are an emerging class of materials with exceptional porosity on the molecular and mesoscale and represent a possibly disruptive technology in the separations area.^{40,41} Consisting of metal atoms or clusters linked in a periodic fashion *via* organic linker molecules, MOFs exhibit pores of 0.3–5 nm diameter, walls of just one atom thickness, and surface areas of several thousand square metres per gram.^{42,43} Previously MOFs have been investigated for their exceptional gas adsorption properties^{44–46} whereby gas molecules enter the framework and adsorb upon the extremely large internal surface with a tunable enthalpy. Use of nitrogen heterocycle imidazolate organic linkers has been found to result in MOFs with points of pore constriction due to the asymmetric connectivity of the imidazolate ring.⁴⁷ The resultant framework commonly has a zeolitic topology and as a result has become known as a Zeolitic Imidazolate Framework (ZIF) which shows promise for gas separation.^{39,48–52} Typically these materials consist of high volume cavities linked by points of constriction – ideal for gas separation, with the points of constriction providing selectivity, and the cavities provide a passing lane for small molecules to overtake trapped gases of larger radii.

It is evident that certain inorganic materials, in particular ZIFs, have attractive intrinsic properties though major challenges remain for the membrane configurations necessary to utilize these advantages. In this instance, theory can guide experimental work where ZIFs are screened and membrane configurations are then designed to exploit the ZIF characteristics.^{53,54} Therefore in this paper we determine the intrinsic properties of a series of ZIFs (-7, -8, -11, -69, -71, -77 and -90),

and compare our predictions with experimental results^{13,39,50–52,55,56} in light of industrial feasibility targets. This comparison offers insights and guidance for the development of ZIF-based membranes focusing on applications in clean energy generation. A remarkable discovery from this work is the super H₂-sieving characteristics of ZIF-11 that could significantly revolutionize the hydrogen production industry if incorporated within a cheap and robust membrane configuration that maximizes gas–ZIF contact.

Prediction and computational details

To predict the permeability and selectivity properties of the membrane systems we follow the methodology outlined by Krishna and van Baten⁵⁷ for predicting the intrinsic ZIF crystal properties and Keskin and Sholl⁵⁴ for predicting the mixed matrix membrane properties. Both methods have been tested through comparison with numerous experimental results. It is important to note that these predictions are based on ideal situations within the limits of the model, though with rigorous simulation–experiment examinations as presented in this study, these models will continue to improve.

Permeability is commonly represented as the product of solubility, a measure of gas concentration within the membrane, and diffusivity, a measure of gas mobility within the membrane. Recently, Krishna and van Baten^{57–59} presented a simulation methodology for screening zeolitic crystals for CO₂ capture that utilized the following approximation for the intrinsic permeability of a perfect ZIF crystal (P_{ZIF}),

$$P_{\text{ZIF}} = D_{\text{self}} \phi \frac{c}{f} \quad (1)$$

where D_{self} is the self-diffusivity ($\text{m}^2 \text{s}^{-1}$), ϕ is the void fraction, c is the equilibrium gas concentration (mol m^{-3}) at an operating fugacity f (Pa). All permeability calculations were made at a pressure of 10 bar (= 1 million Pa).⁵⁷ In this form, permeability is in SI units of $\text{mol m m}^{-2} \text{s Pa}$, which is then converted to non-SI units of Barrer according to the following relation, 1 Barrer = $3.35 \times 10^{-16} \text{ mol m m}^{-2} \text{s Pa}$. In summary, with permeability as a product of diffusivity and solubility, we perform Molecular Dynamics (MD) simulations for predicting diffusivities and Monte Carlo (MC) procedures for predicting solubilities, as detailed below.

Equilibrium gas concentration is calculated from the Grand Canonical Monte Carlo (GCMC) scheme with fixed atom coordinates for each ZIF, downloaded from the Cambridge Crystallographic Data Centre (CCDC).^{49,60–66} GCMC simulations were carried out with the RASPA package developed at the Northwestern University, USA.⁶⁷ Forcefield (FF) values vary throughout the literature with Quantum Mechanics (QM)-based FFs from Han *et al.*,⁶² modified Universal Forcefields (UFFs) from Pérez-Pellitero *et al.*⁴⁹ utilized by Battisti *et al.*,⁶⁰ and charges from Xu and Zhong⁶⁸ utilized by Krishna and van Baten.⁵⁷ A standard practice for FF development is to start with a generic database and scale the FF values to fit experimental isotherms for the framework of interest. In this work we are interested in a variety of ZIFs, though in particular ZIF-11, because of its promising H₂ sieving capability observed from selective adsorption isotherms by Park *et al.*⁴⁷ Consequently we

modify the Dreiding FF according to a parameterization algorithm developed by Dubbeldam *et al.*⁶⁹ Fig. 3a shows the resulting isotherm which agrees well with experimental results and is also close to the results obtained by using modified UFF.⁴⁹ All FF values are summarized in Table S1 of ESI†. No electrostatic charges were included as the accuracy at high pressures is sufficient and it has been shown that charges are not necessary for room temperature calculations which is the region of interest for this work.⁷⁰ The number of gas molecules per cell at 10 bar

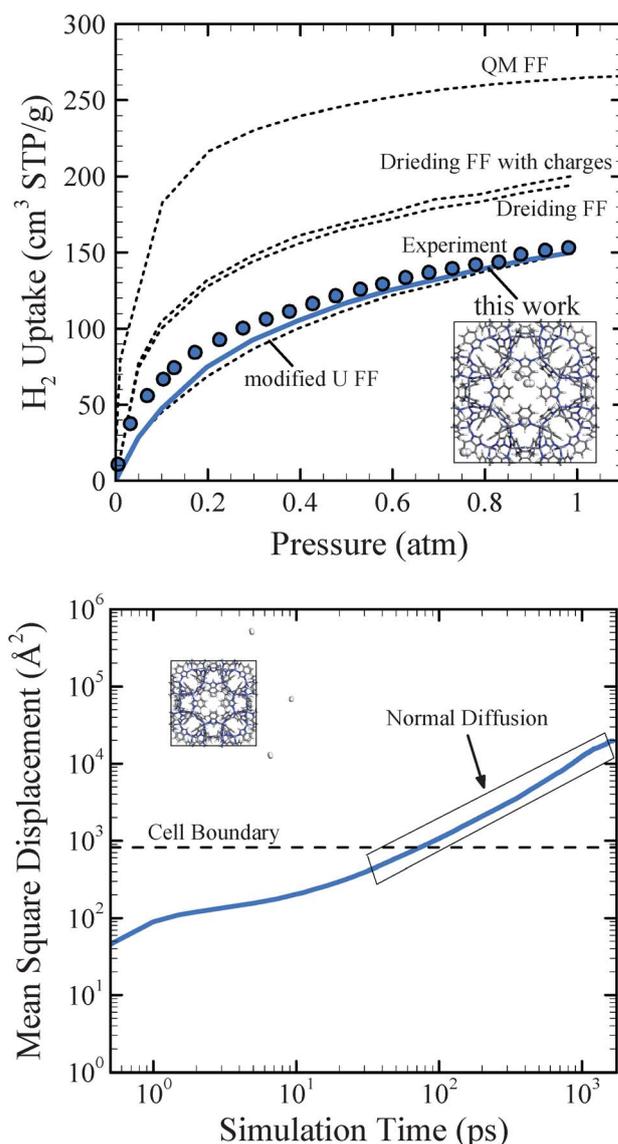


Fig. 3 Verification of Forcefield (FF) parameter values for hydrogen within ZIF-11. (a) Adsorption isotherm at 77 K with experimental results⁴⁷ (solid circles) versus Monte Carlo predictions (lines) with QM calculated FF,⁶² Dreiding FF with charges,^{68,73} Dreiding FF with no charges,⁷⁴ modified UFF^{49,60} and modified Dreiding FF determined in this present work (emphasized in solid blue) following the FF parameterization technique.⁶⁹ Solubility is predicted as the ratio of gas concentration over pressure at 10 bar and 298 K. (b) Molecular dynamics results represented as the mean squared displacement (MSD) using Dreiding FF at 10 bar and 298 K. Diffusivity is calculated from MSD according to eqn (2).

were then packed into each ZIF structure for MD simulations described below.

Self-diffusivity is estimated from MD simulations where molecular motion is determined by solving Newton's laws of motion for each atom, hence gas mobility can be monitored and quantified as the diffusivity coefficient defined below.⁶⁵ Previous simulations have treated the ZIF crystals as either a rigid framework, by Krishna and van Baten,⁵⁷ or a flexible framework, by Battisti *et al.*⁶⁰ For ZIF-8, the rigid framework simulation estimated a H₂ permeability of 5000 Barrer and a H₂/CO₂ selectivity of 2, while the flexible framework simulation estimated a H₂ permeability of 29 000 Barrer and a H₂/CO₂ selectivity of 1.04. The order of magnitude difference in permeability is a result of higher diffusivity within the flexible framework for both gases, as the fluctuating constriction (or window) size within the structure offers a higher acceptance rate for gas transport. It was further shown that a rigid model for ZIF-7 depicted no diffusion for any gas, which is in contradiction to experimental observations.⁶⁰ Therefore the windows critically control gas transport in a gating fashion⁷¹ which we also have observed in a copper-based MOF.⁷² With these considerations in mind, we believe it is important to incorporate framework flexibility into the simulation especially for predicting the sieving effect of light gas molecules of similar dimension. Therefore we have adopted the Dreiding force field for bond stretching, angle bending and dihedral torsions, and due to the approximate nature of the force fields we have fixed the cell geometry to that obtained by X-ray diffraction to minimize deviation from the actual structure.⁶⁰ Each structure was subject to geometrical optimization steps until the following convergence tolerances were reached, 1.0×10^{-4} kcal mol⁻¹ for energy, 5.0×10^{-3} kcal mol⁻¹ Å⁻¹ for forces and 5.0×10^{-5} Å for displacement, followed by MD steps within the NVT ensemble, Nosé thermostat and a step size of 1 fs up to a total of 4 ns. The Forcite module within Materials Studio, a product from Accelrys,⁷⁵ was used for all MD calculations. Finally, the diffusion coefficients were calculated from the mean squared displacement (MSD) over an average of three simulations, providing a reliable estimate of self-diffusivity according to the following Einstein relationship,

$$D_{\text{self}} = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N \langle [r_i(t) - r_i(0)]^2 \rangle \quad (2)$$

where N is the number of gas molecules and $r_i(t)$ is the vector position at time t for gas molecule i . Fig. 3b demonstrates normal diffusion of hydrogen within ZIF-11 at 298 K and 10 bar where the slope at large times is translated to diffusivity according to eqn (2).

Accessible surface area, pore volume, and helium void fraction calculations were performed on the ZIF structures. Accessible surface area calculations using a probe of similar size to a nitrogen molecule have been shown to match experimental surface areas *via* BET adsorption described by Duren *et al.*⁷⁶ Void fraction calculated according to the Widom insertion method is known to provide good estimates to the experimentally determined helium void fraction.⁷⁷⁻⁷⁹ The framework atomic coordinates are fixed during these calculations. By probing the accessible free volume with various probe sizes we have determined window sizes and cavity sizes.

Keskin and Sholl⁵⁴ recently verified a modeling framework for predicting mixed matrix membrane (MMM) properties by incorporating the intrinsic permeability properties of MOFs from molecular simulation within either Maxwell's model⁸⁰ (accurate up to 20% volume fraction) or Bruggeman's model⁸¹ (accurate up to 40% volume fraction). In this paper we will compare predictions against experimental work up to a volume fraction of 60%, hence the Bruggeman theory is adopted as follows,

$$\left(\frac{P_{\text{MMM}}}{P_{\text{p}}}\right)^{-1/3} \left[\frac{(P_{\text{MMM}}/P_{\text{p}}) - (P_{\text{ZIF}}/P_{\text{p}})}{1 - (P_{\text{ZIF}}/P_{\text{p}})}\right] = (1 - \phi_{\text{ZIF}}) \quad (3)$$

where P_{MMM} is the total permeability within the mixed matrix membrane, P_{ZIF} is the simulated permeability within the ZIF crystals according to eqn (1), ϕ_{ZIF} is the volumetric fraction of ZIF crystals dispersed within the continuous polymer phase and P_{p} is the experimental permeability of the polymer phase.

Results and discussion

The utility of a gas separation material possessing points of constriction joined by sizeable cavities, a pseudo hour-glass morphology, has been demonstrated previously to be a superior utilization of structure both synthetically and biologically.⁸²⁻⁸⁵ The cavities allow for smaller, permeating molecules to bypass larger species and hence avoid pore blockage.³¹ Very recently there has been some demonstration of this efficient transport within ZIF gas membranes.^{39,51} Here we show that many ZIFs possess an hour-glass pore architecture with a systematic variation in window sizes (2.90–3.74 Å depicted in Fig. 4 and quantified in ESI†). ZIF-11 has the most promising pore dimensions with window cut-offs ranging between 3.08 and 3.10 Å, which are ideal hydrogen sieving dimensions. In this section we discuss our predicted intrinsic ZIF properties within the framework of current technologies needed for carbon-free energy production.

Hydrogen production from coal gasification (H₂/CO₂ and H₂/N₂)

There have been a number of studies demonstrating the feasibility of hydrogen production from gasified coal streams for direct combustion or use in electro-chemical fuel cells.^{4-6,12,86,87} This process involves the gasification of coal into hydrogen (H₂) and carbon monoxide (CO) which is then converted by a water-gas shift reaction into hydrogen (H₂) and carbon dioxide (CO₂), and separated into fuel and waste respectively. This separation *via* conventional liquid solvents is projected to increase the cost of electricity by 30–40%,^{6,88} hence there is a commercial driven development of more efficient separation technologies. Membrane-based gas separation is one of the most efficient technologies.²¹ Recently, Ku *et al.*⁶ calculated the membrane performance requirements for the feasible use of hydrogen-selective membranes in integrated gasification combined cycle power plants. These requirements include a H₂ permeance of 1000 GPU (= 1000 Barrer assuming a 1 μm selective layer), a H₂/CO₂ selectivity greater than 20 and a H₂/N₂ selectivity greater than 290 (as N₂ is commonly used as a sweep gas for the H₂/CO₂ separation). Here we indicate these target areas in Fig. 5a and 6, and compare our predictions for ZIF-based membranes (filled symbols) and the experimental results (empty symbols) achieved

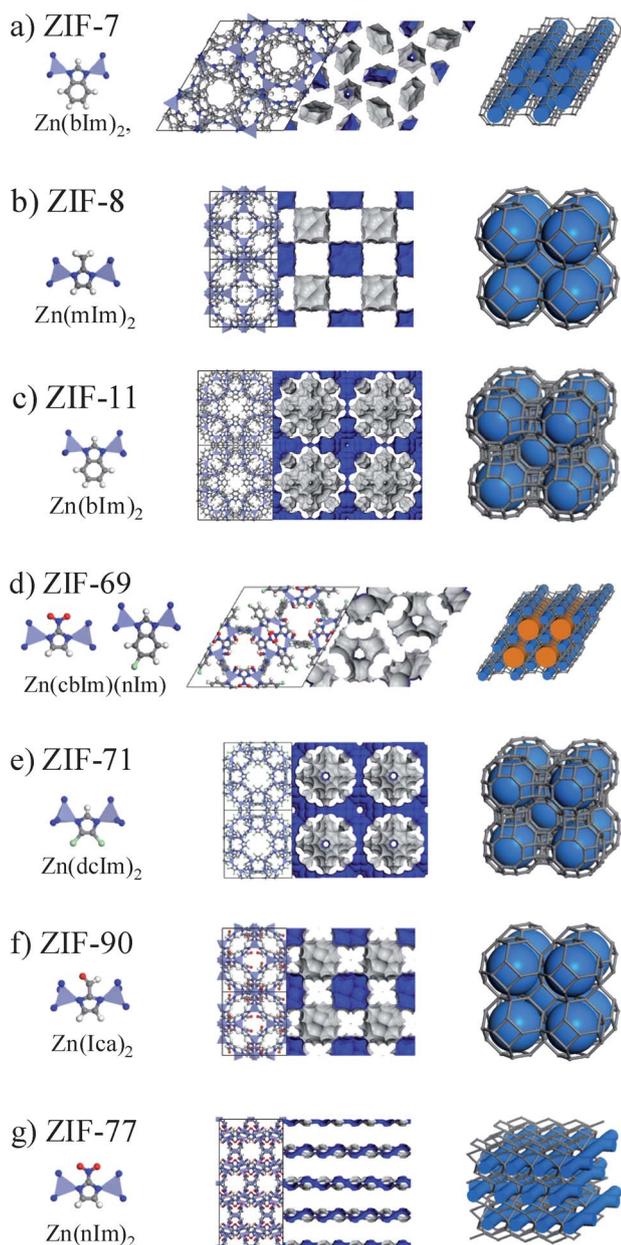


Fig. 4 ZIF structures with building blocks, topology and accessible surface area for a probe diameter of 2 Å. Images generated with Materials Studio, Accelrys.

to date along with the Robeson polymer upperbound representing the current limit for polymer membranes.²⁴

At first observation, all results demonstrate excellent hydrogen sieving capabilities for both the predicted and experimental data, utilizing either a pure inorganic layer or a MMM configuration. Our predicted intrinsic results for perfect ZIF crystals all surpass the performance achieved experimentally to date. In many cases the discrepancy between prediction and measurement is one or greater order of magnitude in permeability and selectivity. For example, in Fig. 5, ZIF-7 shows about an order of magnitude difference in the predicted properties and properties measured on ZIF-only inorganic membrane. With careful consideration we conclude that this difference is due to membrane configuration

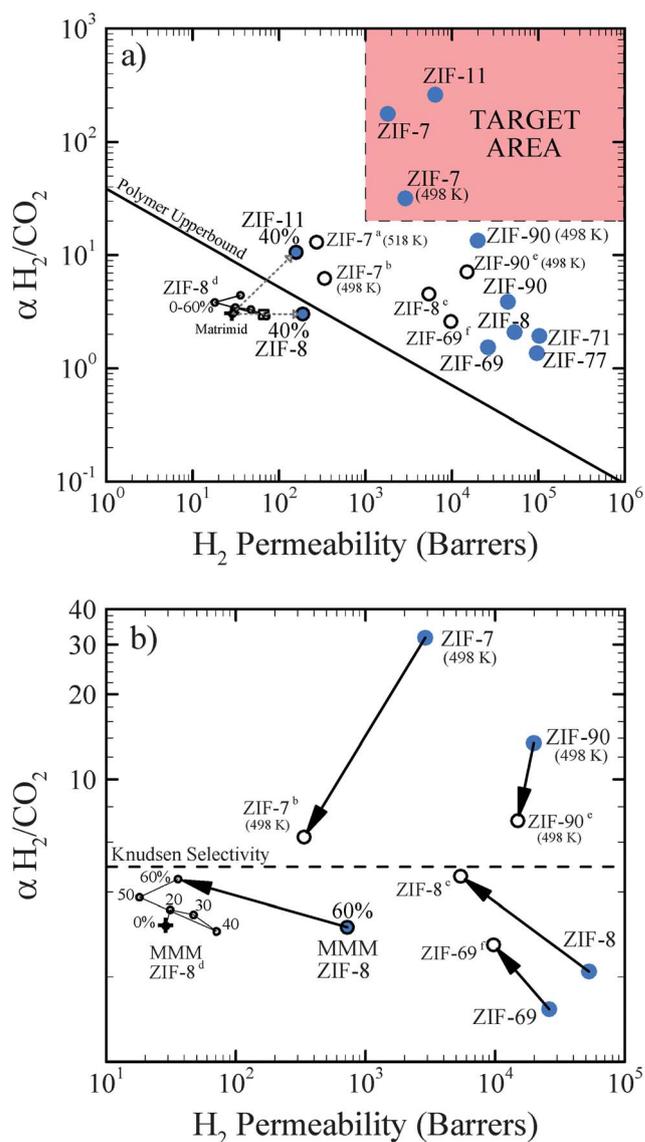


Fig. 5 (a) Our predicted intrinsic H₂/CO₂ properties (filled symbols) with experimental results (empty symbols) for ZIF membranes. Matrimid (cross) with connecting lines for our Mixed-Matrix Membranes (MMM) predictions (dotted lines) and experiment (solid line). Superscripts are used for experimental references, (a) Li *et al.*,⁹² (b) Li *et al.*,⁵¹ (c) Bux *et al.*,³⁹ (d) Ordoñez *et al.*,⁵² (e) Huang *et al.*,⁵⁵ and (f) Liu *et al.*,⁹³ Target area for industrial feasibility by Ku *et al.*⁶ (b) Closer comparison of our predicted intrinsic results (filled symbols) with experimental results (empty symbols). Arrowed lines emphasize the transition from the intrinsic predictions for the material to the experimental results for the membrane configurations, indicating a trend towards Knudsen separation properties in the membranes.

effects. See Fig. 5b for a closer examination that reveals that all experimental results tend towards Knudsen separation properties from their intrinsic predictions, indicative of non-selective transport through inter-crystal gaps or grain boundaries. Further logic for this difference is as follows, experimental adsorption results confirm that ZIF-7 (ref. 89) (and ZIF-11 (ref. 47)) are size selective. Size selective permeability should increase with temperature;^{31,90} predicted permeability increases with

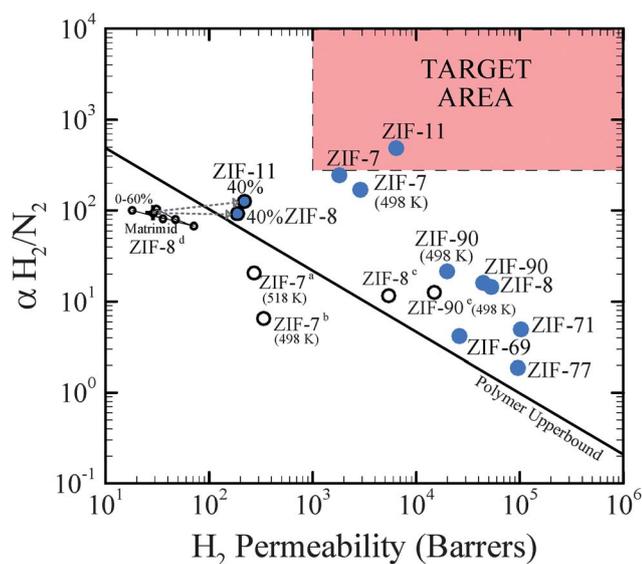


Fig. 6 Our predicted intrinsic H_2/N_2 properties (filled symbols) with experimental results (empty symbols) for ZIF membranes. Matrimid (cross) with connecting lines for our MMM predictions (dotted lines) and experiment (solid line). Superscripts are used for experimental references, (a) Li *et al.*,⁹² (b) Li *et al.*,⁵¹ (c) Bux *et al.*,³⁹ (d) Ordoñez *et al.*⁵² and (e) Huang *et al.*⁵⁵ Target area for industrial feasibility by Ku *et al.*⁶

temperature while experimental permeability does not increase with temperature. Therefore the ZIF-only results (experimental adsorption and simulated predictions) agree, while the experimental ZIF membrane, that is subject to many other factors such as imperfect crystallization, remaining solvent or grain boundaries, shows inferior properties. Indeed the ability to examine the difference between ideal prediction and experimental results gives additional guidance for membrane design.

The MMM samples of ZIF-8 embedded within Matrimid reported by Ordoñez *et al.*,⁵² show interesting behavior as ZIF volume fraction increases. Up to a volume fraction of 40%, the results are consistent with theory, though possessing a lower H_2 permeability than our prediction according to the Bruggeman model. However, at volume fractions of 50 and 60% the experimental results significantly deviate from the theory which predicts consecutive steps towards the intrinsic ZIF-8 results.⁵⁴ This deviation is consistent with the disruption of polymer chain packing at the ZIF-polymer interface. In previous work on nanocomposite MMM, the comparison of predicted and experimental transport results suggested the actual mechanism of transport which was shown to be due to the particles causing a disruption of polymer packing near the interface.⁹¹ This comparison of experiment and theory and elucidation of the transport mechanism in nanocomposite MMM has stimulated a multitude of subsequent research activity in the field. Ordoñez *et al.* performed experiments with impermeable ZIF crystals (non-activated ZIF-8 filled with solvent) to isolate the effect of the polymer-ZIF interface. We have plotted this data in Fig. 5a (empty square) which is almost identical to that for activated ZIF-8, illustrating that polymer-ZIF interface effects govern the separation performance of this membrane configuration. Efforts to overcome this interfacial transport include the strengthening

of polymer-particle interactions.³³ Alternatively, Bux *et al.*³⁹ have grown dense ZIF-8 layers on a porous support, consequently achieving superior results. With further optimization these results will improve towards our predicted intrinsic properties though falling short of application targets. Similar results are observed for the other pure ZIF membranes including ZIF-7,⁹² ZIF-69 (ref. 93) and ZIF-90.⁵⁵

Most importantly our calculations indicate that ZIF-11 reaches the industrial feasibility targets with ZIF-7 not far behind. Our molecular dynamics study reveals that over a total of 5 ns of simulation time not a single gas molecule, other than hydrogen, exhibit self-diffusion. As demonstrated in Fig. S1 in ESI†, completely confined motion is observed for CO_2 , O_2 , N_2 and CH_4 from the calculated mean squared displacements, while H_2 freely diffuses throughout the framework. As MD simulations are performed over a timescale of nanoseconds, it is possible that jump diffusion of the confined gases may occur over larger timescales. Therefore from the current study, it is reasonable to conclude that the diffusivities of these gases are less than $10^{-12} m^2 s^{-1}$, resulting in a H_2/CO_2 selectivity of 262. Therefore we predict that ZIF-11 is capable of achieving the greatest sieving of hydrogen. Moreover, the hydrogen diffusivity predicted by the mixed gas simulations compared to the single gas simulations are equal (see Table S3†). This demonstrates that the fast transport of hydrogen is not hindered by the presence of slow and constricted gases, an advantageous effect also observed experimentally.^{39,51,92} Additionally, *ab initio* calculations by Han *et al.*⁶² estimate a heat of adsorption for H_2 of $15 kJ mol^{-1}$, which translates to a favorable hydrogen solubility,¹⁸ another advantage of this ZIF, also verified by Assfour *et al.*⁹⁴ In the application of hydrogen production and purification technologies, these results place ZIF-11 as a promising candidate for membrane-based hydrogen separation.

Post-combustion carbon capture from coal flue streams (CO_2/N_2)

Coal power plants generate around 20% of the world's energy.⁹⁵ It is estimated that in 2009 approximately 43% of carbon dioxide emissions from fuel combustion were produced from coal.⁹⁶ The impact of these emissions on the rising atmospheric carbon dioxide levels, and the subsequent environmental effects have made technologies that prevent these emissions highly sought after.^{2,21,97,98} Without replacing plant infrastructure, carbon capture units are being added at post-combustion stages, mainly by means of chemisorption through amine liquid columns.¹² Membrane technologies offer a lower energy and higher efficiency means of capture, though with a 30% increase in cost with current membrane properties.⁷ The major cost components include gas compression equipment for achieving the driving-force for separation.⁸ This cost can be reduced by developing more favorable membrane properties such as permeability and selectivity. Here in Fig. 7, we indicate the target areas for these membrane properties according to industrial feasibility calculated by considering two sources of driving-force, namely, feed-side compression by Merkel *et al.*⁹ and permeate-side vacuum by Ho *et al.*⁷

Our simulated ZIF properties fall outside of the target areas and do not exceed the upperbound for polymers. High permeability has often been held as a more important property for

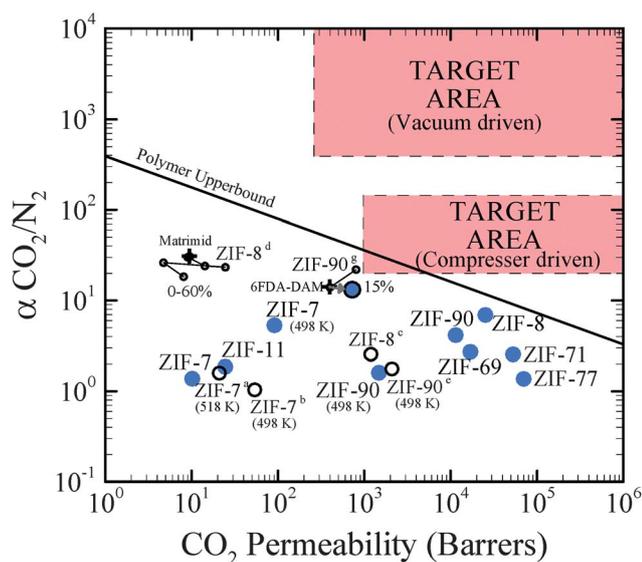


Fig. 7 Our predicted intrinsic CO_2/N_2 properties (filled symbols) with experimental results (empty symbols) for ZIF membranes. Matrimid (cross) with connecting line for MMM experiments (solid line). Superscripts are used for experimental references, (a) Li *et al.*,⁹² (b) Li *et al.*,⁵¹ (c) Bux *et al.*,³⁹ (d) Ordoñez *et al.*,⁵² (e) Huang *et al.*,⁵⁵ and (g) Bae *et al.*¹³ Target area for industrial feasibility with feed compression by Merkel *et al.*⁹ and permeate vacuum by Ku *et al.*⁶

operation than selectivity, and most of the ZIFs in this study satisfy the criterion of high CO_2 permeability.⁹ According to our feasibility studies for post-combustion capture with feed compression, a selectivity of at least 20 remains unachieved by the ZIFs. The Polaris™ membrane recently developed at Membrane Technology and Research Ltd. meets these requirements, though it is unclear what separation mechanism this membrane utilizes.⁹ With a closer look at the components of permeability from our simulations (ESI†), it is evident that all ZIFs have a higher affinity for CO_2 over N_2 from the concentration component but show no significant diffusion rate differences. CO_2 is found to exceed N_2 diffusivity only within ZIF-7, -8 and -11 which possess tight constrictions where size sieving occurs. Without size-sieving regions, CO_2 and N_2 compete by means of surface diffusion (sorption or solubility), where strong adsorption translates to slow diffusion, and Knudsen diffusion (at high temperatures), where heavy molecular mass translates to slow diffusion.⁹⁹ Therefore a ZIF adsorbent-based system utilizing differences in affinity may be more achievable for this application, currently an active area of research.^{70,89,100}

An alternative approach is to combine the favourable ZIF characteristics with other materials that have complimentary characteristics, hence combining mechanisms. Bae *et al.* demonstrated this by incorporating ZIF-90 particles within various polymers.¹³ The most impressive results for this separation using 6FDA-DAM, a glassy polymer, are shown in Fig. 7. With the intrinsic properties of ZIF-90 now predicted, we can interpret the behaviour observed experimentally. According to the mixed matrix model of Bruggeman, adding 15% of ZIF-90 to 6FDA-DAM should increase permeability though with a loss in selectivity, therefore we conclude that additional mechanisms are at work in the experimental MMM configuration. The observed

permeability increase suggests interfacial diffusion routes, due to a disruption of chain packing around the polymer–ZIF interface, which we comment further on in the next separation section for CO_2 over CH_4 .

Natural gas sweetening and biofuel purification (CO_2/CH_4)

Natural gas purification has been an active industrial operation since the 1980's with separations involving removal of N_2 and CO_2 from CH_4 for natural gas enrichment (or sweetening).^{14,17} In 2005 natural gas provided 17% of the world's energy and is growing.⁹⁵ With CO_2 emissions as an environmental concern, next generation technologies for efficient CO_2/CH_4 separations are critical for clean gaseous fuel production. If successful, this technology will become a critical component of the Power Generation Vision for 2050, generating 5% of the world's clean energy.¹⁰¹ Additionally, there has arisen interest in biofuel gas production from microalgae requiring H_2 and CO_2 separation from CH_4 .¹⁰² Here we consider ZIF-based membranes for advanced CO_2/CH_4 separation technology, Fig. 8.

Our intrinsic predictions reveal promising results for ZIF-8 and ZIF-77 which exceed the polymer upperbound. This result has been confirmed experimentally as Venna and Carreon have successfully synthesized pure dense ZIF-8 layers that perform CO_2/CH_4 separations and are close to our intrinsic predictions.⁵⁶ This is a promising result as the superior ZIF properties can be exploited within a membrane configuration.

Further, ZIF-90 is predicted to have promising separation properties, which has also been confirmed experimentally by Bae *et al.* by incorporating ZIF-90 within a MMM configuration.¹³ Three polymers namely Matrimid, Ultem and 6FDA-DAM were investigated by Bae *et al.* as the continuous matrix and here we

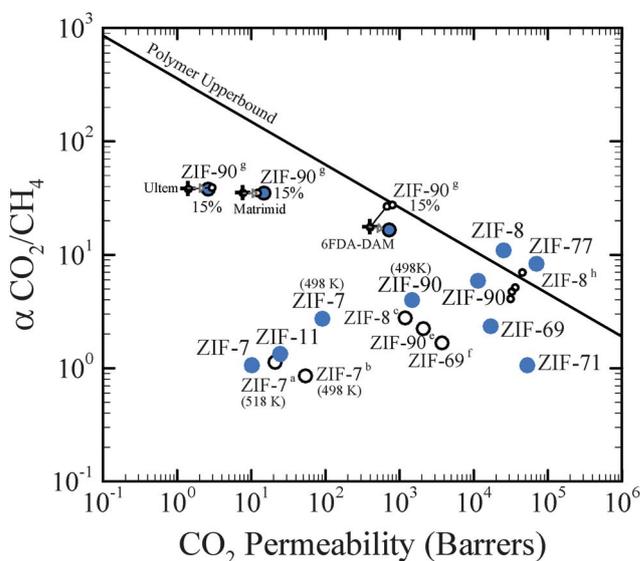


Fig. 8 Our predicted intrinsic CO_2/CH_4 properties (filled symbols) with experimental results (empty symbols) for ZIF membranes. Polymers (crosses) with connecting lines for our MMM predictions (dotted lines) and experiment (solid line). Superscripts are used for experimental references, (a) Li *et al.*,⁹² (b) Li *et al.*,⁵¹ (c) Bux *et al.*,³⁹ (e) Huang *et al.*,⁵⁵ (f) Liu *et al.*,⁹³ (g) Bae *et al.*¹³ and (h) Venna and Carreon.⁵⁶

predict this outcome, Fig. 8. Our results match well with experiment for the Ultem and Matrimid MMM at 15 wt% of ZIF-90, although a fundamental deviation occurs for the high free volume polymer 6FDA-DAM. Similar to the case discussed previously for Ordoñez *et al.*, it is likely that the polymer chain packing is frustrated nearby the ZIF particles consequently offering gas transport pathways that significantly differ from those within the ZIF. This effect has been shown to be enhanced within polymers composed of rigid chains⁹¹ as is the case for this glassy polymer 6FDA-DAM.

This conclusion relies on the accuracy of our intrinsic predictions for ZIF-90 which in future will be tested as alternative methodologies are developed by the research community. Indeed, according to Bae *et al.* an extrapolation of the experiment using the Maxwell model predicts an intrinsic CO₂/CH₄ selectivity of 250, compared to our intrinsic CO₂/CH₄ selectivity of 4. By considering the molecular structure and our simulation results we are in doubt as to whether ZIF-90 can achieve such a high selectivity, though further modelling that includes electrostatic charges could be used to test this hypothesis.

Interestingly, ZIF-77 is found to separate CO₂/CH₄ the most efficiently (highest permeability) whilst still achieving a selectivity above that of polymer only membranes. With similar equilibrium gas concentrations, see Table S3 and S4†, ZIF-77 appears to exploit diffusivity differences to separate the mixture. Fig. 4 reveals the 2-D channels within ZIF-77 which are from 3.6 to 4.7 Å in size, listed in Table S2†, capable of inhibiting CH₄ transport by means of constriction. Another point worth noting is that these 2-D channels do not connect in the normal (90°) direction, hence if the crystals were oriented uniformly, barrier properties could be observed. Overall our study has shown that ZIF-8, -77 and -90 are the most promising candidates for clean gaseous fuel production with both membrane configurations achieving remarkable results.

Air separation for oxy-combustion of coal (O₂/N₂)

Separating air has proved a useful operation since 1881 for metal manufacturing and has now grown to meet demands in many other industries such as healthcare, chemicals, environment, electronics and more importantly energy production and conservation.¹⁰³ In the interest of this study, coal and gas are found to combust more efficiently within pure O₂ than air (21% O₂, 78% N₂, *etc.*) and further produce emissions of high CO₂ concentration for direct sequestration, avoiding the difficult CO₂ separations required *via* other routes, as shown Fig. 1.¹² In Fig. 9, we depict the intrinsic O₂/N₂ separation properties for ZIFs calculated in this study.

Once again, ZIFs are predicted to be capable of efficiently separating small molecules, in particular ZIF-8, -90 and -71. There has been little experimental work for this separation, although according to these results this is an area worth pursuing. Compared with the conventional Matrimid polymer, our model predicts that four orders of magnitude improvement in efficiency may be achieved by utilizing ZIF particles in an ideal membrane configuration. As illustrated by previous examples in this work, membrane configuration will be of critical importance to achieve experimental performance matching our predictions.

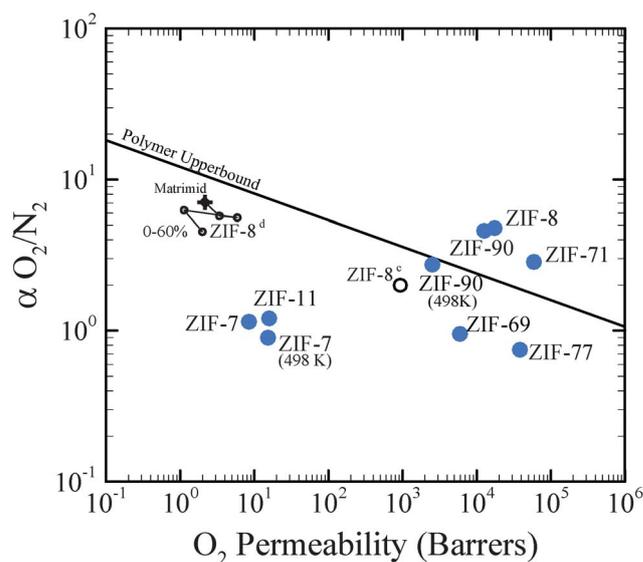


Fig. 9 Our predicted intrinsic O₂/N₂ properties (filled symbols) with experimental results (empty symbols) for ZIF membranes. Matrimid (cross) with connecting line for MMM experiments (solid line). Superscripts are used for experimental references, (a) Bux *et al.*³⁹ and (b) Ordoñez *et al.*⁵²

Conclusions

To summarize, we have investigated a systematic series of ZIF membranes for their gas separation properties in the interest of carbon-free energy generation. By utilizing free volume algorithms, molecular dynamics simulation, Monte Carlo schemes and transport theory, we have demonstrated that all of these ZIFs achieve remarkable H₂ selectivity, with ZIF-11 and ZIF-7 achieving the highest predicted separation factors of 487 and 245 (H₂/N₂) at room temperature, respectively. Further, we show that ZIF-11 meets industrial feasibility targets for H₂/CO₂ and H₂/N₂ separations, a critical operation for pre-combustion carbon capture. Our predictions also suggest that ZIF-8, -90 and -77 are attractive candidates for natural gas purification (CO₂/CH₄) and that ZIF-8, -90 and -71 are attractive candidates for air separation for oxy-combustion (O₂/N₂). This methodology has proved to be an effective method for screening and exploring the separation outcomes within ZIF membranes. We have established the accuracy of the model and shown that the ideal prediction can be used to guide the design of new MOF materials, and we have shown that differences between the ideal prediction and the experimental results provide insight that can assist in the translation from material synthesis to membrane fabrication and application. Further work will include predicting performance based only on structural and chemical considerations. It is hoped that future development of ZIF membranes, with the guidelines and insights of this study, will accelerate the production of low carbon energy.

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References

- 1 R. S. Haszeldine, *Science*, 2009, **325**, 1647.
- 2 M. Z. Jacobson, *Energy Environ. Sci.*, 2009, **2**, 148.
- 3 N. V. Rees and R. G. Compton, *Energy Environ. Sci.*, 2011, **4**, 1255.
- 4 C. A. Scholes, K. H. Smith, S. E. Kentish and G. W. Stevens, *Int. J. Greenhouse Gas Control*, 2010, **4**, 739.
- 5 L. de Lorenzo, T. G. Kreutz, P. Chiesa and R. H. Williams, *J. Eng. Gas Turbines Power*, 2008, **130**, 031401.
- 6 A. Y. Ku, P. Kulkarni, R. Shisler and W. Wei, *J. Membr. Sci.*, 2011, **367**, 233.
- 7 M. T. Ho, G. W. Allinson and D. E. Wiley, *Ind. Eng. Chem. Res.*, 2008, **47**, 1562.
- 8 M. T. Ho, G. Leamon, G. W. Allinson and D. E. Wiley, *Ind. Eng. Chem. Res.*, 2005, **45**, 2546.
- 9 T. C. Merkel, H. Lin, X. Wei and R. Baker, *J. Membr. Sci.*, 2010, **359**, 126.
- 10 H. Lin, E. Van Wagner, R. Raharjo, B. D. Freeman and I. Roman, *Adv. Mater.*, 2006, **18**, 39.
- 11 H. B. Park, S. H. Han, C. H. Jung, Y. M. Lee and A. J. Hill, *J. Membr. Sci.*, 2010, **359**, 11.
- 12 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058.
- 13 T.-H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones and S. Nair, *Angew. Chem., Int. Ed.*, 2010, **49**, 9863.
- 14 Y. Yampol'skii, I. Pinnau and B. D. Freeman, *Materials Science of Membranes for Gas and Vapor Separation*, John Wiley & Sons, Ltd, 2006.
- 15 A. Brunetti, F. Scura, G. Barbieri and E. Drioli, *J. Membr. Sci.*, 2010, **359**, 115.
- 16 S. Basu, A. Cano-Odena and I. F. J. Vankelecom, *J. Membr. Sci.*, 2010, **362**, 478.
- 17 R. W. Baker, *Membrane Technology and Applications*, Wiley, West Sussex UK, 2004.
- 18 S. K. Bhatia and A. L. Myers, *Langmuir*, 2006, **22**, 1688.
- 19 A. C. Dillon and M. J. Heben, *Appl. Phys. A: Mater. Sci. Process.*, 2001, **72**, 133.
- 20 B. Metz, O. Davidson, H. D. Coninck and M. Loos, *IPCC Report: Carbon Dioxide Capture and Storage*, CB2 2RU: Cambridge, 2005, p. 53.
- 21 J.-R. Li, Y. Ma, M. C. McCarthy, J. Scully, J. Yu, H.-K. Jeong, P. B. Balbuena and H.-C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791.
- 22 P. Bernardo, E. Drioli and G. Golemme, *Ind. Eng. Chem. Res.*, 2009, **48**, 4638.
- 23 L. M. Robeson, *J. Membr. Sci.*, 1991, **62**, 165.
- 24 L. M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390.
- 25 B. D. Freeman, *Macromolecules*, 1999, **32**, 375.
- 26 S. R. Reijerkerk, K. Nijmeijer, C. P. Ribeiro Jr, B. D. Freeman and M. Wessling, *J. Membr. Sci.*, 2011, **367**, 33.
- 27 C.-H. Lo, W.-S. Hung, M. De Guzman, S.-H. Huang, C.-L. Li, C.-C. Hu, Y.-C. Jean, K.-R. Lee and J.-Y. Lai, *J. Membr. Sci.*, 2010, **363**, 302.
- 28 G. Dong, H. Li and V. Chen, *J. Membr. Sci.*, 2011, **369**, 206.
- 29 M. M. Dal-Cin, K. Darcovich, S. Saimani and A. Kumar, *J. Membr. Sci.*, 2010, **361**, 176.
- 30 R. S. A. de Lange, K. Keizer and A. J. Burggraaf, *J. Membr. Sci.*, 1995, **104**, 81.
- 31 A. W. Thornton, T. Hilder, A. J. Hill and J. M. Hill, *J. Membr. Sci.*, 2009, **336**, 101.
- 32 J. Caro, M. Noack, P. Kölsch and R. Schäfer, *Microporous Mesoporous Mater.*, 2000, **38**, 3.
- 33 T. T. Moore, R. Mahajan, D. Q. Vu and W. J. Koros, *AIChE J.*, 2004, **50**, 311.
- 34 D. L. Gin and R. D. Noble, *Science*, 2011, **332**, 674.
- 35 M. Yu, H. H. Funke, R. D. Noble and J. L. Falconer, *J. Am. Chem. Soc.*, 2011, **133**, 1748.
- 36 Y. C. Hudiono, T. K. Carlisle, J. E. Bara, Y. Zhang, D. L. Gin and R. D. Noble, *J. Membr. Sci.*, 2010, **350**, 117.
- 37 Y. C. Hudiono, T. K. Carlisle, A. L. LaFrate, D. L. Gin and R. D. Noble, *J. Membr. Sci.*, 2011, **370**, 141.
- 38 S. G. Sorenson, E. A. Payzant, R. D. Noble and J. L. Falconer, *J. Membr. Sci.*, 2010, **357**, 98.
- 39 H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebecke and J. Caro, *J. Am. Chem. Soc.*, 2009, **131**, 16000.
- 40 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
- 41 J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.
- 42 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
- 43 S. R. Batten, S. M. Neville and D. R. Turner, *Coordination Polymers: Design, Analysis and Application*, CB4 OWF: Cambridge UK, 2008.
- 44 L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.
- 45 K. Sumida, M. R. Hill, S. Horike, A. Dailly and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 15120.
- 46 A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill and M. R. Hill, *J. Am. Chem. Soc.*, 2009, **131**, 10662.
- 47 K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186.
- 48 J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- 49 J. Pérez-Pellitero, H. Amrouche, F. R. Siperstein, G. Pirngruber, C. Nieto-Draghi, G. Chaplais, A. Simon-Masseron, D. Bazer-Bachi, D. Peralta and N. Bats, *Chem.-Eur. J.*, 2010, **16**, 1560.
- 50 Y.-S. Li, F.-Y. Liang, H. Bux, W. Yang and J. Caro, *J. Membr. Sci.*, 2010, **354**, 48.
- 51 Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang and J. Caro, *Angew. Chem., Int. Ed.*, 2010, **49**, 548.
- 52 M. J. C. Ordoñez, K. J. Balkus Jr, J. P. Ferraris and I. H. Musselman, *J. Membr. Sci.*, 2010, **361**, 28.
- 53 S. Keskin and D. S. Sholl, *J. Phys. Chem. C*, 2007, **111**, 14055.
- 54 S. Keskin and D. S. Sholl, *Energy Environ. Sci.*, 2010, **3**, 343.
- 55 A. Huang, W. Dou and J. Caro, *J. Am. Chem. Soc.*, 2010, **132**, 15562.
- 56 S. R. Venna and M. A. Carreon, *J. Am. Chem. Soc.*, 2010, **132**, 76.
- 57 R. Krishna and J. M. van Baten, *J. Membr. Sci.*, 2010, **360**, 323.
- 58 R. Krishna and J. M. van Baten, *Sep. Purif. Technol.*, 2012, **87**, 120.
- 59 C. Chmelik, J. van Baten and R. Krishna, *J. Membr. Sci.*, 2012, **397–398**, 87.
- 60 A. Battisti, S. Taioli and G. Garberoglio, *Microporous Mesoporous Mater.*, 2011, **143**, 46.
- 61 H.-C. Guo, F. Shi, Z.-F. Ma and X.-Q. Liu, *J. Phys. Chem. C*, 2010, **114**, 12158.
- 62 S. S. Han, S.-H. Choi and W. A. Goddard, *J. Phys. Chem. C*, 2010, **114**, 12039.
- 63 S. Keskin, *J. Phys. Chem. C*, 2011, **115**, 800.
- 64 B. Liu and B. Smit, *J. Phys. Chem. C*, 2010, **114**, 8515.
- 65 E. Pantatosaki, F. G. Pazzona, G. Megariotis and G. K. Papadopoulos, *J. Phys. Chem. B*, 2010, **114**, 2493.
- 66 R. B. Rankin, J. Liu, A. D. Kulkarni and J. K. Johnson, *J. Phys. Chem. C*, 2009, **113**, 16906.
- 67 D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, *RASPA, 1.0*, Northwestern University, Evanston, 2008.
- 68 Q. Xu and C. Zhong, *J. Phys. Chem. C*, 2010, **114**, 5035.
- 69 D. Dubbeldam, S. Calero, T. J. H. Vlugt, R. Krishna, T. L. M. Maesen, E. Beerdsen and B. Smit, *Phys. Rev. Lett.*, 2004, **93**, 088302.
- 70 D. Farrusseng, C. Daniel, C. Gaudillere, U. Ravon, Y. Schuurman, C. Mirodatos, D. Dubbeldam, H. Frost and R. Q. Snurr, *Langmuir*, 2009, **25**, 7383.
- 71 D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons and T. Duren, *J. Am. Chem. Soc.*, 2011, **133**, 8900.
- 72 M. Arif Nadeem, A. W. Thornton, M. R. Hill and J. A. Stride, *Dalton Trans.*, 2011, **40**, 3398.
- 73 R. Krishna and J. M. van Baten, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10593.
- 74 S. L. Mayo, B. D. Olafson and W. A. Goddard III, *J. Phys. Chem.*, 1990, **94**, 8897.
- 75 *Materials Studio, 5.0*, Accelrys Inc., San Diego, CA, USA, 2009.
- 76 T. Duren, F. Millange, G. Ferey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, 2007, **111**, 15350.

- 77 A. L. Myers, Thermodynamics of Adsorption, in *Chemical Thermodynamics for Industry*, ed. T. M. Letcher, Royal Society of Chemistry, Cambridge, 2004.
- 78 A. L. Myers and P. A. Monson, *Langmuir*, 2002, **18**, 10261.
- 79 D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, San Diego, 2002.
- 80 R. H. B. Bouma, A. Checchetti, G. Chidichimo and E. Drioli, *J. Membr. Sci.*, 1997, **128**, 141.
- 81 G. Bánhegyi, *Colloid Polym. Sci.*, 1986, **264**, 1030.
- 82 T. A. Hilder, D. Gordon and S.-H. Chung, *Small*, 2009, **5**, 2183.
- 83 H. B. Park, C. H. Jung, Y. M. Lee, A. J. Hill, S. J. Pas, S. T. Mudie, E. van Wagner, B. D. Freeman and D. J. Cookson, *Science*, 2007, **318**, 254.
- 84 B. Bolto, M. Hoang and T. Tran, *Water*, 2010, **37**, 80.
- 85 D. Kozono, M. Yasui, L. S. King and P. Agre, *J. Clin. Invest.*, 2002, **109**, 1395.
- 86 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int. J. Greenhouse Gas Control*, 2008, **2**, 9.
- 87 Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 5664.
- 88 J. M. Klara, *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Final Report*, 2007.
- 89 S. C. Reyes, N. Zheng, C. S. Paur, P. Kortunov, J. Zengel and H. W. Deckman, *Separation of Carbon Dioxide from Nitrogen Utilizing Zeolitic Imidazolate Framework Materials*, 2009.
- 90 A. W. Thornton and A. J. Hill, Modelling Gas Separation, in *Membrane Gas Separation*, ed. Y. Yampolskii and B. D. Freeman, Wiley & Sons, 2010.
- 91 T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin and A. J. Hill, *Science*, 2002, **296**, 519.
- 92 Y. Li, F. Liang, H. Bux, W. Yang and J. Caro, *J. Membr. Sci.*, 2010, **354**, 48.
- 93 Y. Liu, E. Hu, E. A. Khan and Z. Lai, *J. Membr. Sci.*, 2010, **353**, 36.
- 94 B. Assfour, S. Leoni and G. Seifert, *J. Phys. Chem. C*, 2010, **114**, 13381.
- 95 B. Metz, O. R. Davidson, P. R. Bosch and R. Dave, *Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, IPCC, Cambridge, United Kingdom and New York, NY, USA, 2007.
- 96 I.E. Agency, *CO₂ Emissions from Fuel Combustion – Highlights*, 2011, <http://www.iea.org/co2highlights/CO2highlights.pdf>.
- 97 S. A. Rackley, *Carbon Capture and Storage*, Elsevier, Oxford, UK, 2010.
- 98 M. Duke, B. Ladewig, S. Smart, V. Rudolph and J. Diniz da Costa, *Front. Chem. Eng. China*, 2010, **4**, 184.
- 99 R. Krishna and J. M. van Baten, *Ind. Eng. Chem. Res.*, 2011, **50**, 7083.
- 100 A. O. Yazaydan, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198.
- 101 World Business Council for Sustainable Development, *Vision 2050*, 2010, ISBN: 978-3-940388-56-8.
- 102 S. Amin, *Energy Convers. Manage.*, 2009, **50**, 1834.
- 103 R. Prasad, F. Notaro and D. R. Thompson, *J. Membr. Sci.*, 1994, **94**, 225.