

# Current Status of Metal–Organic Framework Membranes for Gas Separations: Promises and Challenges

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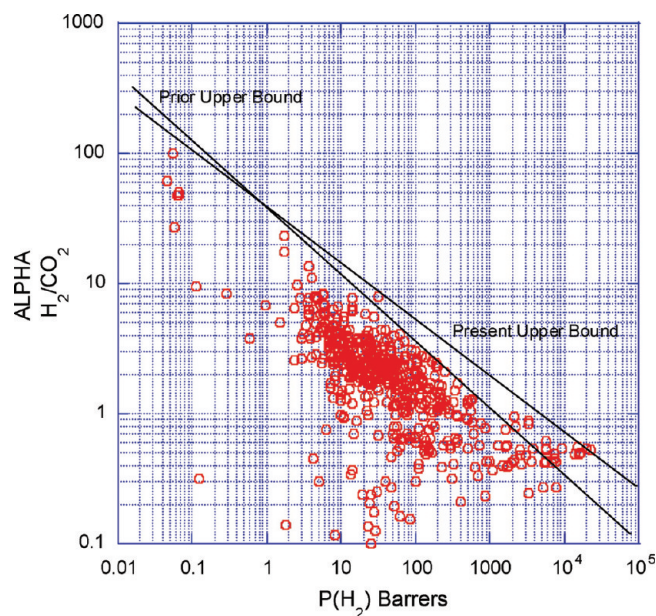
**ABSTRACT:** Metal–organic frameworks (MOFs) are hybrid organic–inorganic nanoporous materials that exhibit regular crystalline lattices with relatively well-defined pore structures. Chemical functionalization of the organic linkers in the structures of MOFs affords facile control over pore size and chemical/physical properties, making MOFs attractive for a variety of industrial applications including membrane-based gas separations. A wealth of reports exists discussing the synthesis and applications of MOFs; however, relatively few reports exist discussing MOF membranes. This disparity owes to challenges associated with fabricating films of MOF materials, including poor substrate–film interactions, moisture sensitivity, and thermal/mechanical instability. Since even nanometer-scale cracks and defects can affect the performance of a membrane for gas separation, these challenges are particularly acute for the fabrication of MOF membranes. Here, we review recent progress on MOF membranes with an emphasis on their fabrication techniques, challenges involved in membrane synthesis, reported strategies to address these challenges (issues), and gas separation performance. Finally, we conclude with our perspectives on future research directions in this area.

## 1. INTRODUCTION

In spite of the maturity of the petrochemical and commodity chemical industries, there are still tremendous needs for improving a variety of technologically relevant separations.<sup>1</sup> Traditional separation methods, such as distillation and condensation, are highly energy intensive. Membrane-based separations offer great potential in terms of their lower energy consumption and smaller carbon footprint.

The current membrane market for gas separation is dominated by polymeric membranes partially due to the fact that polymer membranes have low production costs and exhibit high gas fluxes and mechanical flexibility.<sup>2</sup> However, polymer membranes in general have short membrane lifetimes, low thermal and chemical stabilities, and low selectivities. Robeson<sup>3</sup> defined an upper bound for polymer membranes delineating a limit on their selectivity/permeability performance (see Figure 1). Although this limit has been adjusted since its inception,<sup>4</sup> it still indicates that there is a limiting trade-off between a polymer membrane's selectivity and permeability. Besides, some of these challenges make polymer membranes generally limited to the separation of noncondensable gases ( $H_2/N_2$ ,  $CO_2/CH_4$ ,  $N_2/air$ , etc.).<sup>2</sup> Condensable gas separations such as olefin/paraffin or butane isomer separations are an important area into which membrane technology can expand.<sup>2</sup> Unfortunately, few polymer membranes are capable of olefin/paraffin separation in an economically viable way, and none can do so without difficulty with issues such as durability and longevity.<sup>2,5</sup> This is particularly troublesome for polymer membranes, as the operating conditions to which these membranes are exposed often result in membrane plasticization.<sup>2</sup>

Zeolite molecular sieves have been investigated for application in membrane separations because of their well-defined, regular pore structure and thermal and chemical stability.<sup>6</sup> Their well-defined pores allow zeolite membranes to achieve gas separation



**Figure 1.** Upper bound correlation for  $H_2/CO_2$  separation. Reproduced with permission from ref 4, Copyright Elsevier, 2008.

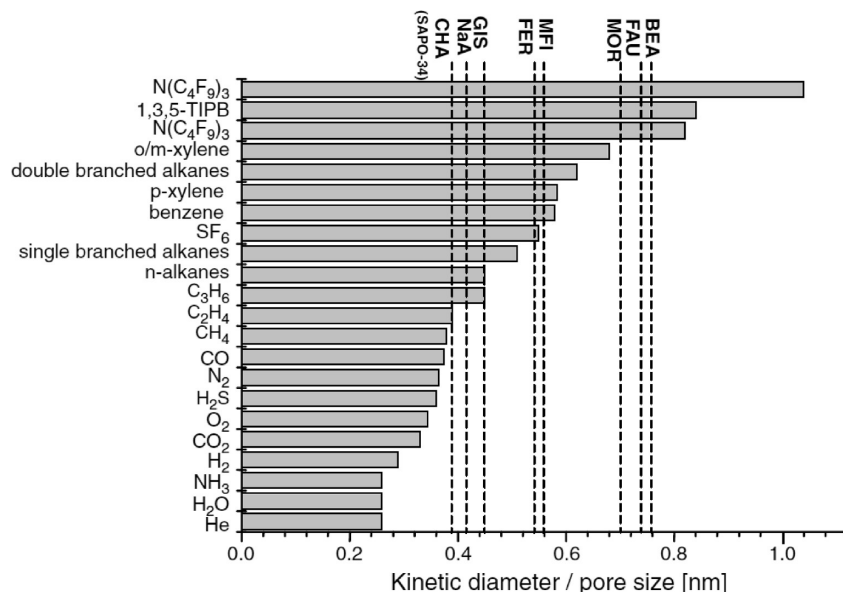
with high selectivity due to the molecular sieving effect.<sup>6d,7</sup> The high thermal and chemical stabilities of these materials also make them attractive for separation applications under high temperatures and harsh chemical environments. However, zeolites also have

**Received:** September 6, 2011

**Accepted:** December 7, 2011

**Revised:** November 29, 2011

**Published:** December 07, 2011

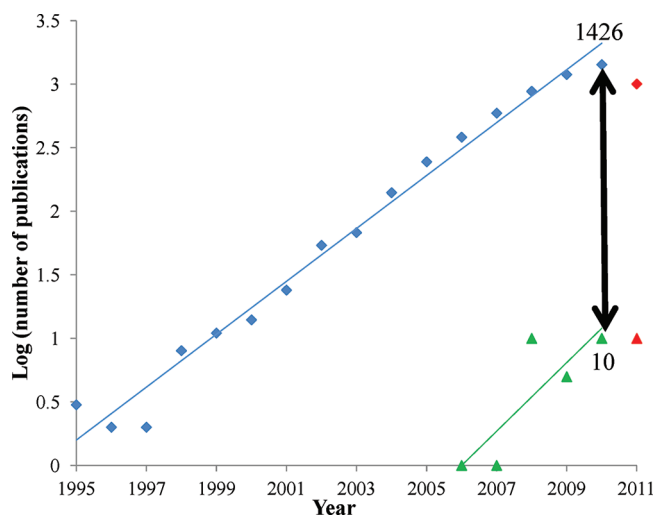


**Figure 2.** Comparison of effective zeolite pore sizes with kinetic diameters of common gases. Reproduced with permission from ref 98, Copyright Elsevier, 2006.

a discontinuous and limited range of available pore sizes (i.e., zeolites of proper pore sizes may not be available for gas mixtures of certain sizes). Figure 2 shows the kinetic diameters of various gases and the effective pore sizes of a few well-known zeolites. Apart from the high cost of production,<sup>8</sup> limited chemical tailorability of zeolites is another issue for wider applications of zeolite membranes in gas separations.

Another avenue of membrane research is focused on mixed matrix membranes.<sup>9</sup> These membranes are generally polymer/inorganic composites consisting of a primary polymer phase and a secondary phase of dispersed inorganic particles. The intention for these types of membranes is to combine the advantages of the materials of both phases such as the high flux of polymer membranes and the high selectivity of the inorganic phase (e.g., zeolite phase). In general, it is however difficult to achieve a close interface between the two phases.<sup>10</sup> If there is a repulsive interaction between the phases, then the interstitial space acts as a nonselective diffusion path. This creates difficulties in achieving permeability/selectivity performance greater than that of the polymer phase. Another issue is to incorporate inorganic particles in the submicrometer-thick selective skin layers.

Metal–organic frameworks (MOFs),<sup>11</sup> a relatively new class of hybrid materials consisting of organic and inorganic moieties in crystalline lattices, have the potential to answer some of the challenges facing materials for gas-separating membranes.<sup>12</sup> Pore size tailorability combined with tunable sorption behavior provides promising avenues for applications of MOFs as membranes for gas separation applications. Synthesis conditions are less energy intensive as compared to zeolites. For instance, most MOFs do not require high-temperature pressure conditions for their fabrication and can be synthesized using click chemistry. Also, unlike zeolites, structure-directing agents are not required; therefore, a subsequent calcination step is not necessary. Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, are of particular interest for gas separation applications mainly due to their ultramicropores in the scale of small gas molecules as well as their remarkable thermal and chemical stability.<sup>13</sup>



**Figure 3.** Publications per year containing the phrase: (■) “metal organic framework” and (▲) “metal organic framework” and “thin film”. Data obtained from Sci-Finder. Data points in red indicate values up until July 25th, 2011.

The focus of current MOF research for the most part has been the discovery and characterization of new MOF structures. As illustrated in Figure 3, the number of publications discussing metal–organic frameworks has increased significantly recently. Despite this rising interest, the number of reports of MOF thin films is quite small, orders of magnitude fewer (see Figure 3).<sup>6f,14</sup> Still fewer in number are the reports of MOF membranes for gas separation,<sup>15</sup> the first MOF membranes having been published in 2009.<sup>15b,c</sup>

This scarcity of reports can perhaps be attributed to the challenges involved in fabricating thin films of MOF materials such as poor stability and/or poor binding to substrates among others.<sup>16</sup> In particular, various MOFs have been noted for their poor interaction with native substrates such as Au,<sup>14b</sup> silica,<sup>14c</sup> and  $\alpha$ -alumina,<sup>14k,15j,15m</sup> necessitating a linking agent to attach these MOFs to supports for film fabrication.

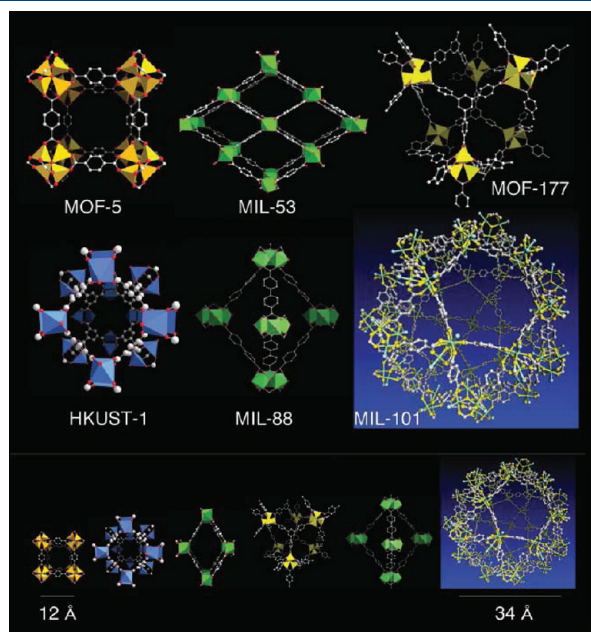
In this review, we will first give a brief introduction to the structure and chemistry of metal–organic frameworks followed by the current techniques for the preparation of polycrystalline MOF membranes. We will then summarize and discuss the performance of current MOF membranes. We will also present our perspectives on the future development of MOF membranes. Given the scope of this review, we will limit our discussion to polycrystalline membranes typically on inorganic supports for gas separation applications, though a brief discussion on mixed matrix membranes with MOFs is presented. Although a single-crystal MOF membrane has been reported,<sup>15l</sup> the comparatively low gas flux and difficulty in fabricating large single crystals make these impractical for practical applications. Those who are interested in the synthesis, structures, and applications of MOFs and MOF thin films are encouraged to read several excellent extensive review articles.<sup>6f,11c,17</sup>

## 2. METAL–ORGANIC FRAMEWORKS (MOFS): STRUCTURES, CHEMISTRY, AND STABILITY

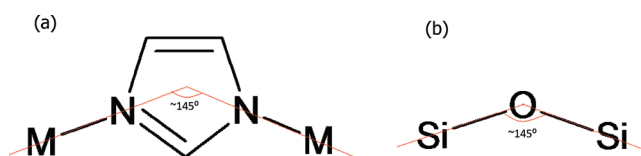
Metal–organic frameworks have attracted research interest as noteworthy porous materials for over a decade.<sup>11</sup> MOFs are comprised of metal nodes and organic linkers connected by coordination covalent bonds with a typical pore size ranging from ultramicroscale to mesoscale. Chemical functionalization of the organic linkers in the structures of MOFs affords facile control over pore size and chemical/physical properties, making MOFs attractive materials for overcoming the limitations of not only current membrane materials but also conventional membrane system design/integration and operation.<sup>18</sup>

In this section, we discuss the structures, chemistry, and stability of metal–organic frameworks. This discussion is relevant to the later discussions on the synthesis of MOF membranes.

**2.1. MOF Structures.** Thousands of metal–organic framework structures have been reported to date, exhibiting properties



**Figure 4.** Various reported MOF structures. Structures are arranged according to effective pore size along the bottom. Reproduced with permission from ref 11c, Copyright Royal Society of Chemistry, 2008.



**Figure 5.** The bridging angles in metal ZIFs (a) and zeolites (b).

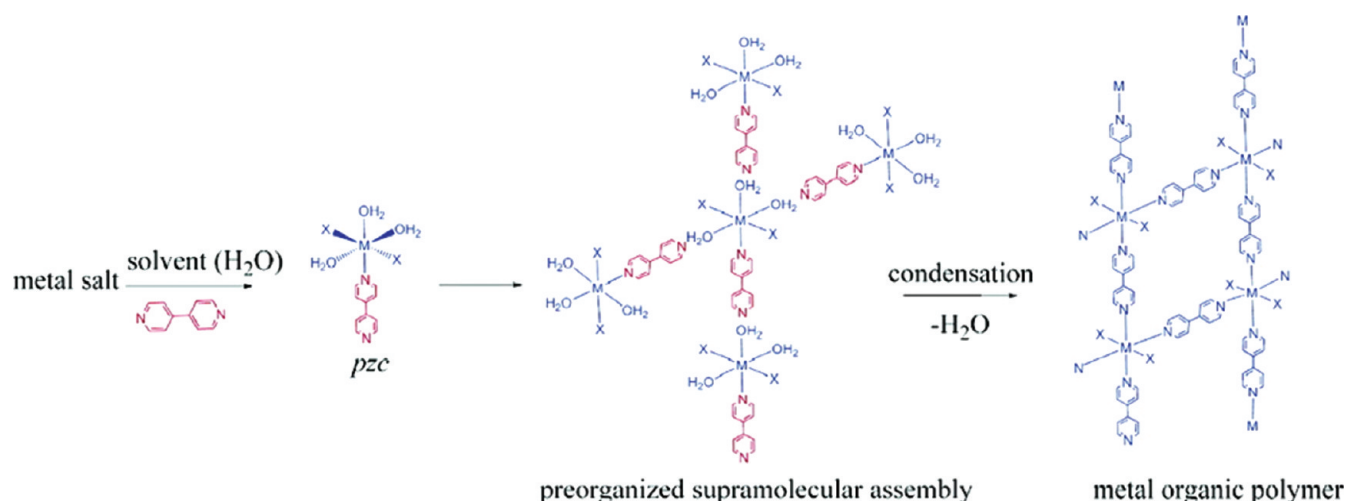
useful for gas separation,<sup>17b</sup> gas storage,<sup>19</sup> chemical sensors,<sup>14g</sup> and optical devices.<sup>14q</sup> Figure 4 illustrates some of the MOF structures that are most extensively studied, including two prototypical MOFs used in pioneering MOF membrane reports (MOF-5<sup>15c</sup> and HKUST-1<sup>15d</sup>). There are several excellent review articles<sup>8c,12c,14</sup> on the MOF structures (and chemistry) for those who are interested about the chemistry and structure of MOFs.

An important subclass of metal–organic frameworks, especially when considering gas separation applications, is zeolitic imidazolate frameworks (ZIFs).<sup>13b</sup> These materials, first reported in 2006 by Park et al.<sup>13a</sup> and expanded upon significantly in later reports,<sup>11d,20</sup> are remarkable for their exceptional thermal and chemical stability. The thermal/chemical stability of ZIFs in combination with their small pores (generally less than 5 Å) make ZIFs particularly promising candidates for membrane-based gas separation applications. ZIFs consist of metal nodes (usually zinc or cobalt) connected to imidazolate linkers and exhibit zeolite-like structures, perhaps due to the metal–linker–metal bond angle of  $\sim 145^\circ$  (close to the Si–O–Si angle found in many zeolites),<sup>13a</sup> as shown in Figure 5. However, unlike zeolites, which possess rather well-defined pores, ZIFs (like many other MOFs) exhibit framework flexibility on gas adsorption. This framework flexibility has been demonstrated by experimentation and simulations for ZIF-8.<sup>21</sup> It is noteworthy that, to date, more ZIFs have been investigated for gas separation membranes than any other kind of MOF.<sup>15a,e,f,h,i,k,n</sup>

**2.2. Mechanisms of MOF Formation and Chemistry.** One attractive attribute of MOFs is the ease with which they can be synthesized, the so-called “click-chemistry.” Approaches to the design and synthesis of these materials have been discussed in detail elsewhere.<sup>22</sup> Although the chemical steps leading to MOF formation are still debatable, there are two generally understood explanations (mechanisms). One explanation involves the formation of building blocks of molecules called secondary building units (SBUs) that in turn come together to form coherent structures.<sup>14c,22c,22d</sup> Not much evidence of this synthesis route is available, though there is one report that gives X-ray absorption extended fine structure (EXAFS) evidence of intact trimeric iron oxide SBUs during the crystallization of MIL-89.<sup>23</sup>


The second explanation does not include SBUs, but rather hydrolysis or condensation reactions between dissolved metal salts and organic ligands in solution (see Figure 6).<sup>24</sup> This explanation states that metal salts dissolve in solution and form point of zero charge (pzc) molecules. These metal complexes at their isoelectric points organize into supramolecular assemblies which then undergo condensation/hydrolysis to form crystalline structures.

Irrespective of the mechanisms, however, the bonding between the metal and organic linker in the final MOF structure (irrespective of the mechanism) is coordination bonding, which is kinetically weaker (i.e., more labile) than covalent or covalent/ionic bonding seen in zeolites. This



**Figure 6.** Proposed scheme of MOF crystal formation in solution through formation of point of zero charge (pzc) molecules and hydrolysis/condensation reactions with dissolved metal salts. Reproduced with permission from ref 24a, Copyright American Chemical Society, 2006.

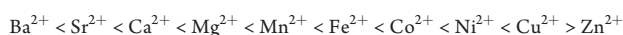
**Table 1.** Examples of Hard and Soft Acids and Bases (Reproduced with Permission from ref 30; Copyright Wiley, 2007)

	Hard	Soft	Borderline
<b>Acids</b>	H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Mn <sup>2+</sup> , Al <sup>3+</sup> , Cr <sup>3+</sup> , Co <sup>3+</sup> , Fe <sup>3+</sup>	Cu <sup>+</sup> , Ag <sup>+</sup> , Au <sup>+</sup> , Hg <sup>+</sup> , Pd <sup>2+</sup> , Cd <sup>2+</sup> , Pt <sup>2+</sup> , Hg <sup>2+</sup> , Pt <sup>4+</sup> , Te <sup>4+</sup>	Fe <sup>2+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup> , Sn <sup>2+</sup> , Sb <sup>2+</sup> , Bi <sup>3+</sup> , NO <sup>+</sup> , SO <sub>2</sub> , R <sub>3</sub> C <sup>+</sup> , C <sub>6</sub> H <sub>5</sub> <sup>+</sup>
	Si <sup>4+</sup> , Ti <sup>4+</sup> , Zr <sup>4+</sup> , Sn <sup>4+</sup> , Hf <sup>4+</sup> , BF <sub>3</sub> , AlH <sub>3</sub> , Al(Me) <sub>3</sub> , SO <sub>3</sub> , RSO <sub>2</sub> <sup>+</sup> , RPO <sub>2</sub> <sup>+</sup> , HF, HCl	RS <sup>+</sup> , I <sup>+</sup> , Br <sup>+</sup> , I <sub>2</sub> , Br <sub>2</sub> , O, Cl, Br, I	
<b>Bases</b>	H <sub>2</sub> O, OH <sup>-</sup> , F <sup>-</sup> , Cl <sup>-</sup> , RO <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , ClO <sub>4</sub> <sup>-</sup> , SO <sub>2</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> , ROH, RO, ROR, RCOR, RCOO <sup>-</sup> , NH <sub>3</sub> , RNH <sub>2</sub> , NH <sub>2</sub> NH <sub>2</sub>	R <sub>2</sub> S, RSH, RS <sup>-</sup> , I <sup>-</sup> , SCN <sup>-</sup> , CN <sup>-</sup> , I <sup>-</sup> , R <sup>-</sup> , H <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>2</sub> <sup>2-</sup> , N <sub>2</sub> , PhNH <sub>2</sub> , pyridine
		CH <sub>2</sub> =CH <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> CO, NO	 Imidazole

coordination bonding is likely the major factor contributing to many of the challenges associated with the fabrication of MOF membranes.

**2.3. Stability of Coordination Bonds in MOFs.** As mentioned above, coordination bonds between metal nodes and organic ligands are one of the major features of MOF structures. Coordinate covalent bonds involve the sharing of a pair of electrons, both donated from a Lewis base (organic linkers in MOFs) to a Lewis acid (metal nodes in MOFs). These special covalent bonds are thermodynamically as stable as other covalent bonds but are not kinetically as stable (i.e., they can be replaced or substituted with other ligands or species such as water). Complexes featuring coordination bonds between a metal and an organic ligand have been widely studied.<sup>25</sup> Although we will not attempt to give a complete overview of the nature of metal–organic coordination bonds, it is instructive to consider a few points that will help us to understand the stability or instability of MOF structures.

The well-known Irving–Williams series (listed below) describes the relative stability of metal–organic octahedral complexes in terms of metal ions regardless (generally) of ligands.<sup>26</sup>



There are a few explanations for this trend such as the decreasing ionic radius from Ba<sup>2+</sup> to Zn<sup>2+</sup> and the increasing crystal field stabilization energy (CFSE) from Mn(II) to Ni(II). Although copper does not fit the CFSE trend, it is generally accepted that distorted octahedral Cu(II) complexes are stabilized by the Jahn–Teller effect.<sup>25</sup> The Jahn–Teller theorem states that any nonlinear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy.<sup>27</sup> The Irving–Williams series may give some insight into the stability trends of MOFs in general based on the stability of their octahedral complexes, but it is helpful for our purposes to discuss in particular those MOFs that have been developed as membranes. Collectively, these MOFs feature only a few particular coordinate covalent bonds: Zn–O (IRMOF-1), Cu–O (HKUST-1), Al–O (MIL-53), and Zn–N (ZIF series). Of these, IRMOF-1 is the least stable since it will readily change phase to a nonporous structure in ambient humidity via water substitution of the carboxylic groups.<sup>28</sup> Apart from Al–O based MIL-53, the ZIF series are likely the most stable of these MOFs. In fact, many ZIFs (ZIF-8,<sup>13a</sup> ZIF-11,<sup>13a</sup> and ZIF-69<sup>15i</sup>) have been observed to maintain their crystal structure even in boiling solvents such as benzene and water.

To gain insight into the relative stabilities of these compounds, it is instructive to consider the hard or soft character of the cations and anions as first classified by Pearson in 1963.<sup>29</sup> Hard or soft character is determined by polarizabilities of species which in turn depends on their charge density.<sup>27</sup>  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  are both classified as intermediate acids (borderline between hard and soft). Ligands with carboxylate groups (such as acetate) are considered hard bases, whereas imidazole is an intermediate base (see Table 1).<sup>30</sup> Pearson's rule states that hard acids prefer bonding to hard bases and soft acids prefer bonding to soft bases. Consequently, it makes sense that ZIFs are more stable MOFs than the aforementioned MOFs (except MIL-53) used for membranes since the cation and anion have the same character (intermediate).

### 3. CRITERIA FOR MOFS FOR MEMBRANE-BASED GAS SEPARATIONS

For membrane-based gas separations, both the solubility and the diffusivity of the mixture components contribute to the separation factor. While the solubility of a gas molecule is governed by the thermodynamic affinity of the molecule on the membrane surface, its diffusivity is governed by the relative size of molecules with respect to the size of the framework pores. In principle, strongly adsorbing and faster diffusing species lead to higher separation factors. The solubility and/or diffusivity can be varied by the presence of side groups on the organic linkers. These side groups not only are responsible for altering the pore size but can also change the thermodynamic interaction or sorption behavior to achieve the desired separation.

For solubility-based separations, separations of molecules are based on the difference in the solubilities of gases. In this case, the framework pores are larger than the size of molecules of interest. The solubility of one component can be selectively enhanced by controlling surface properties. For example, it has been shown that by replacing carbon with nitrogen in imidazolates, one can tune the hydrophilicity of ZIFs and also affinity for  $\text{CO}_2$ , thereby increasing  $\text{CO}_2$  solubility.<sup>31</sup> Not only the ligands but also the functional groups (e.g., the CHO side groups for ZIF-90 and SIM-1 were postsynthetically modified with ethanolamine and dodecylamine respectively)<sup>32</sup> provide variable pore volume and interaction based on their radii and hydrophilic and hydrophobic character. Thus, the thermodynamic (and kinetic behaviors) can be varied for improved membrane performance.<sup>32a</sup>

In the case of molecular size-based separations, the kinetic diameters of the molecules to be separated determine the pore size of MOFs suitable for separation of the molecules.<sup>12b</sup> MOFs whose pore sizes lie in the desired range can be chosen accordingly. Framework interpenetration can also lead to the reduced pores for kinetic separations.<sup>33</sup> It is important to note here that molecules with a kinetic diameter greater than the pore size can pass through the membrane due to framework flexibility. Duren and co-workers<sup>21</sup> have shown by molecular simulation and experimental results that the structure of ZIF-8 can be modified by gas adsorption, thereby increasing the porosity. This phenomenon is akin to the swing effect seen in the case of imidazolate linkers at very high pressures (14 700 bar).<sup>34</sup> At a lower partial pressure of  $\text{N}_2$ , gas adsorption is in agreement with the ZIF-8 structure under ambient conditions; however, at higher partial pressures, the high uptake is due to the swing effect of imidazolate linkers.<sup>21</sup> As a result, some of these membranes may not exhibit

a sharp drop in permeance for molecules with a kinetic diameter greater than the pore size. Nijem and co-workers<sup>35</sup> have demonstrated that for a flexible MOF,  $\text{Zn}_2(\text{bpdc})_2(\text{bpee})$  (bpdc = 4,40-biphenyl dicarboxylate and bpee = 1,2-bis(4-pyridyl) ethylene), the  $\text{CO}_2$ -framework (guest-host) interaction leads to the twisting of one of its ligands made possible by bpee pillars. This is responsible for gate opening phenomenon and enhanced uptake of  $\text{CO}_2$  over  $\text{N}_2$ .

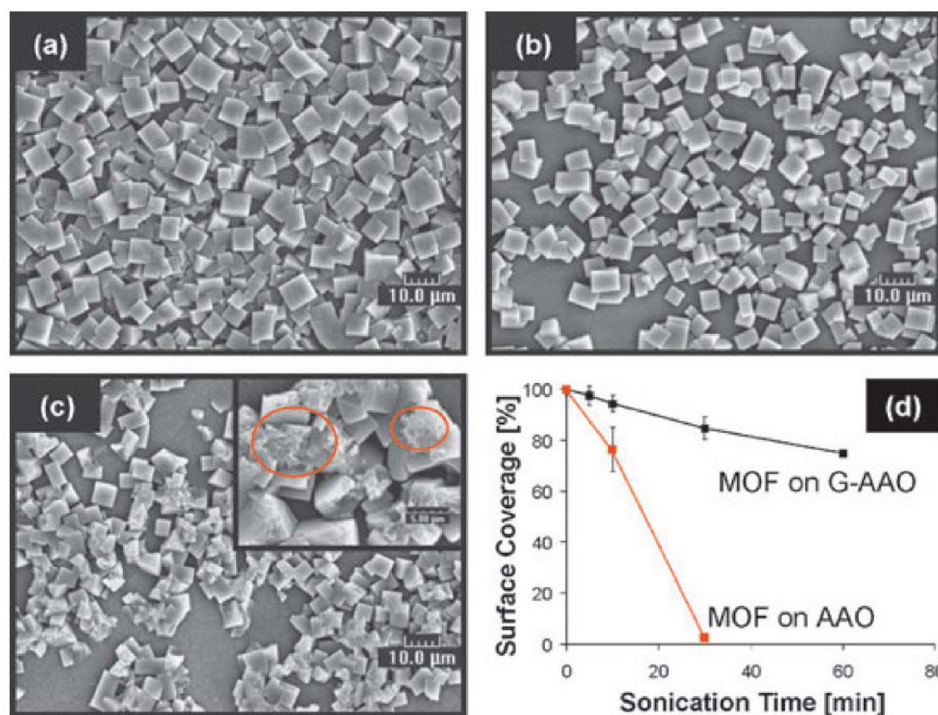
Other important factors to be considered are as follows:

1. Ease of fabrication: While zeolites typically require high temperature—pressure conditions for synthesis, most MOFs require lower activation energy for their synthesis. Room temperature fabrication of HKUST-1, ZIF-8, MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0 has been reported.<sup>11e,36</sup> This enhances the robustness of membrane fabrication in a shorter time with milder conditions.
2. Ease of activation: A large variety of MOFs can be synthesized using water and alcohol as a solvent.<sup>36b,37</sup> As a result, activation of such MOF membranes does not require time- and energy-consuming steps such as calcination and solvent exchange.
3. Active metal centers: Unsaturated metal sites facilitate electrostatic interaction with the guest molecules; Li and co-workers<sup>38</sup> demonstrated 100% oxidation of CO oxidation to  $\text{CO}_2$  using  $\text{Cu}(\text{mip})$  (mip = 5-methylisophthalate). The remarkable catalytic activity was attributed to the high density of active Cu sites.<sup>38</sup>
4. Gate opening or breathing effect: Several MOFs show a gate opening effect due to adsorbent—adsorbate interactions.<sup>39</sup> The breathing effect is determined by threshold pressures which are different for different gas molecules, thereby making them exciting for gas separation applications, especially olefin/paraffin separation.<sup>40</sup> Controlling the partial pressure of species to the desired threshold value might be challenging.

### 4. CHALLENGES SPECIFIC TO POLYCRYSTALLINE MOF MEMBRANES

Successful fabrication of polycrystalline metal—organic framework membranes of sufficient quality for gas separation is a challenging task mainly due to the unfavorable heterogeneous nucleation and the relative weakness of the coordination bonds. For instance, various MOFs have been noted for their poor interaction with native substrates such as Au,<sup>14b</sup> silica,<sup>14c</sup> and  $\alpha$ -alumina.<sup>14k,15j,15m</sup> The relative weakness of the coordination bond (as discussed in the previous section) is of particular challenge. The labile nature of the coordination bond in the MOF lattice leads to numerous complexities for MOF membrane fabrication (discussed in the following sections). Other nanoporous inorganic materials that have been studied for gas-separating membranes (e.g., zeolites) do not have to contend with these same challenges.<sup>41</sup>

It is perhaps self-evident that not all MOFs will present the same issues when incorporated into polycrystalline membranes for gas separation. However, a general understanding of the challenges encountered for some prototypical MOFs that have already been reported as polycrystalline membranes will help to mitigate and overcome similar challenges in the future. The common challenges facing polycrystalline MOF membranes can be broken down into the following categories: (1) poor membrane—substrate bonding, (2) poor membrane



**Figure 7.** SEM images of IRMOF-1 films on graphite coated AAO treated under sonication for (a) 0 min, (b) 10 min, and (c) 60 min. Section d shows the results of a sonication time-dependent surface coverage study comparing IRMOF-1 on bare AAO to IRMOF-1 on graphite-coated AAO. Reproduced with permission from ref 14i, Copyright Royal Society of Chemistry, 2008.

stability, and (3) macroscopic crack formation during membrane fabrication or activation.

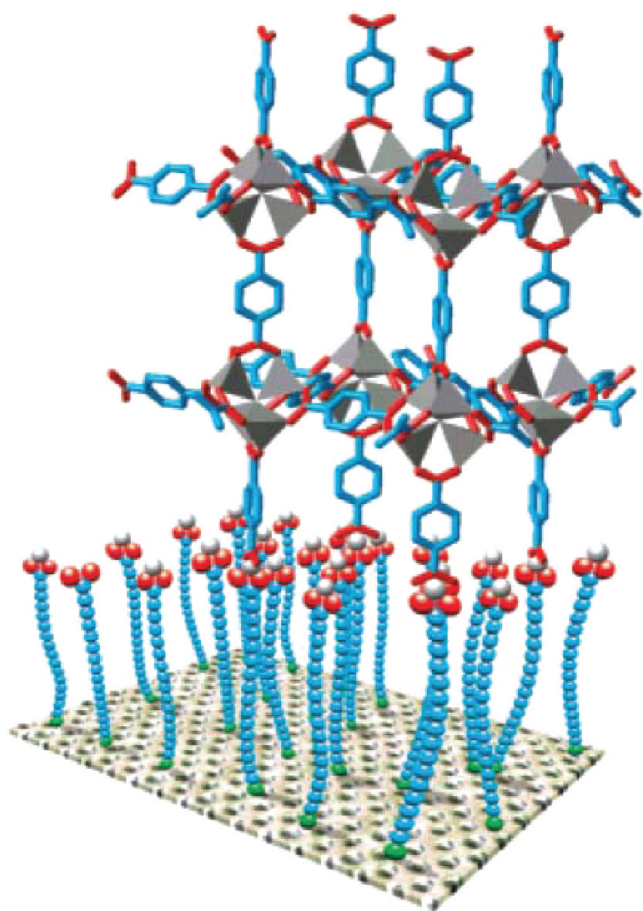
**4.1. Poor Substrate Bonding.** Various MOFs have been noted for their lack of sufficient interfacial interaction with native supports for membrane fabrication.<sup>15b,f,j,k,m</sup> IRMOF-1, for example, was found to easily detach when synthesized on anodized aluminum oxide (AAO) supports.<sup>14i</sup> As illustrated in Figure 7, films of IRMOF-1 grown on AAO easily break off under sonication. However, IRMOF-1 films on graphite coated AAO were much more strongly bound (~80% coverage remained after an hour of sonication). Although investigations of MOF film attachment are not abundant, this study illustrates the utility of linking agents for MOF film fabrication on porous supports. Some reported techniques used to improve MOF crystal adhesion to porous supports for membrane fabrication include the use of polymer binders,<sup>15f,m</sup> and graphite coatings,<sup>15b</sup> which enhance secondary bonding like H-bonding or van der Waals interactions, whereas silane tethers (Figure 8),<sup>14b,15k,15o</sup> and support modification with the precursor chemicals of the MOF of interest<sup>15j,n</sup> enhance the covalent attachment. The covalent attachment of the ligand to the substrate can also occur during *in situ* growth.<sup>42</sup> This last technique is notable as it requires no more chemicals than are already necessary for MOF growth.

**4.2. Poor Stability (Under Ambient Conditions).** Many MOFs (in particular MOFs based on Zn–O coordination bonds) exhibit poor stability. For instance, IRMOF-1 has been noted for its instability in contact with ambient humidity due to the exchange reaction of carboxylates with water.<sup>14m,28,43</sup> Although initial MOF membrane reports have not reported any investigation of this matter, it is nonetheless a crucial issue to be addressed before MOF membranes for gas separation can be industrially applied.

Postsynthetic modification of metal–organic frameworks has been studied to improve their stability. Nguyen and Cohen<sup>43</sup> showed that modification of the IRMOF-3 structure with long alkyl chains showed hydrophobic behavior, thereby improving stability against moisture. We have recently investigated IRMOF-3 membranes for application to CO<sub>2</sub> separation.<sup>44</sup> IRMOF-3 is a natural choice for this application as the amine functionalized benzenedicarboxylate linkers increase the pore affinity for CO<sub>2</sub>.<sup>45</sup> Pore functionalization of this MOF has also been demonstrated,<sup>46</sup> implying that membranes of this material would be useful as chemically tunable membranes. To stabilize these membranes, we have found it necessary to first coat the membranes, immediately after activation, with an amphiphilic surfactant (Span-80 in this case). It was found that this coating dramatically increased the material longevity, preventing ambient moisture from attacking the MOF structure<sup>44</sup> (Figure 9).

The ligand used for membrane fabrication itself can be modified to improve stability. Li and co-workers<sup>47</sup> have demonstrated for carboxylate-based bridging MOF with a bipyridine pillar linker that the presence of hydrophobic groups adjacent to the coordinating nitrogen atom of the bipyridine protects the metal ions and leads to enhanced moisture resistance.

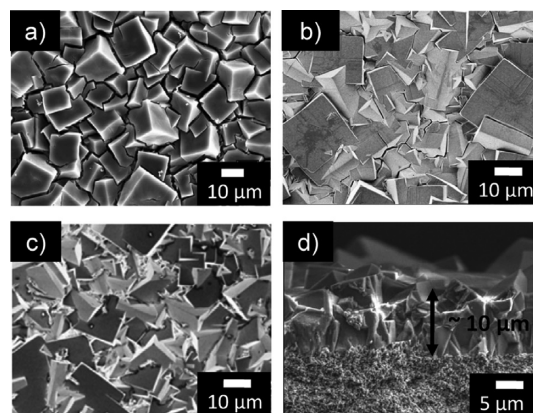
**4.3. Crack Formation during Fabrication.** Macroscopic or microscopic cracks in polycrystalline films can form for a number of reasons and will likely ruin a membrane's performance for gas separation.<sup>7a</sup> Crystalline materials such as zeolites are hard but tend to crack rather than deform under stress. MOFs, also being crystalline, are mechanically brittle. Consequently, when using MOFs for polycrystalline gas-separating membranes, methods used for the prevention of cracks is a subject of importance.



**Figure 8.** The concept of possible anchoring of a typical MOF-5 building unit to a carboxylic acid-terminated SAM. Reproduced with permission from ref 14b, Copyright American Chemical Society, 2005.

Cracks in MOF membranes have been observed to form due to thermal stresses induced while cooling membranes after synthesis at elevated temperature.<sup>15j</sup> HKUST-1,<sup>15j</sup> ZIF-69,<sup>15i</sup> and IRMOF-1<sup>15b,c</sup> membranes were all reported to require slow (natural) cooling after synthesis rather than quenching (as is common after synthesis of zeolite membranes). The effect of cooling rate on HKUST-1 membranes is quite dramatic, as seen in Figure 10. The reasons for crack formation in films that were rapidly cooled can perhaps be explained by the mismatch in thermal expansion between the MOF film and porous supports. Although no MOF membrane report to date has given specific evidence of this (by measuring and comparing thermal expansion coefficients of film and support), several reports have mentioned natural cooling for long times as part of the membrane synthesis (sometimes for as long as 30 h).<sup>15b,c,i,j</sup>

Drying of MOF membranes after synthesis can also result in crack formation. Capillary stresses in drying films are caused by surface tension at the solid/liquid interface in film pores during drying and by vapor-pressure differences at the liquid–gas interface in different film pores.<sup>48</sup> The vapor pressure at the liquid/gas interface is inversely proportional to the radius of curvature of the surface. Thus, as the film dries and the drying front of the liquid moves into the film pores, any nonuniformity in the pore structure (such as grain boundaries or film defects) will lead to asymmetric stress in the film due to the differences in vapor pressure in adjacent pores. One method we have found for reducing



**Figure 9.** SEM images of IRMOF-3 membranes after drying (a) without surfactant (b) with a triblock copolymer, P-123, and (c) Span 80. The cross-sectional view (d) is from the membrane dried in the presence of Span 80. Reproduced with permission from ref 44, Copyright American Chemical Society, 2011.

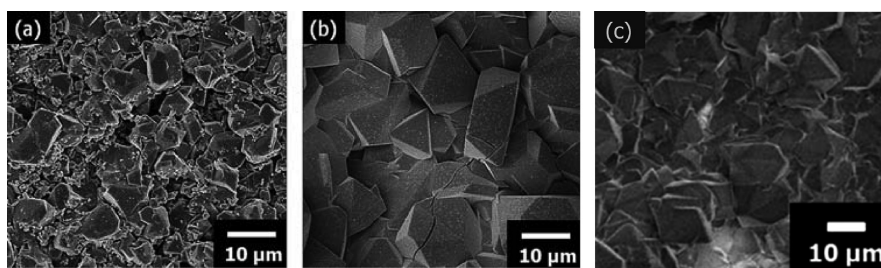
capillary stresses in MOF membranes is decreasing the drying rate (drying in nearly saturated conditions), as shown in Figure 10c.<sup>15j</sup> Another method we have found for decreasing capillary stress is introducing a surfactant to the film surface during the drying stage.<sup>44</sup> A surfactant serves to decrease solid/liquid surface tension and thereby decrease capillary stress.<sup>48</sup>

## 5. MOF MEMBRANE FABRICATION TECHNIQUES

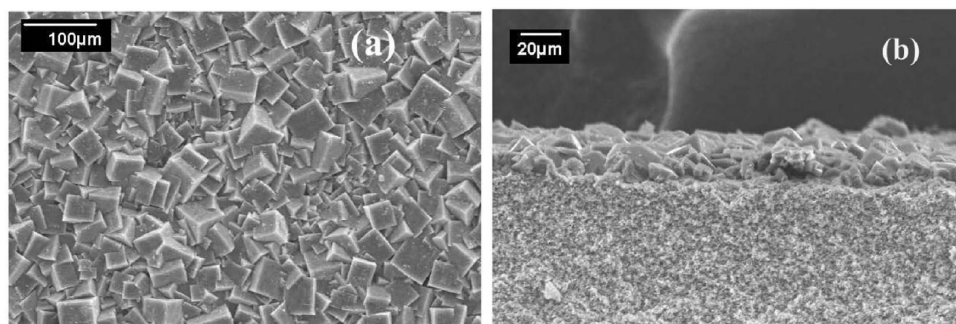
The first MOF membranes were reported in 2009 by the Lai and Jeong groups.<sup>15b,c</sup> These were polycrystalline IRMOF-1 membranes and exhibited Knudsen diffusion. Although Knudsen selectivity is unsurprising considering the large pore size of IRMOF-1 (14.5 Å),<sup>15b</sup> these reports demonstrated the feasibility of fabricating MOF membranes for gas separation. The absence of macroscopic cracks in both of these reports was demonstrated by pressure-dependent gas permeation measurements. Polycrystalline membranes of few MOFs have been reported, such as IRMOF-1,<sup>15b,c</sup> IRMOF-3,<sup>44</sup> HKUST-1,<sup>15d,h,j</sup> MCMO, <sup>15m</sup> ZIF-7,<sup>15f,g</sup> ZIF-8,<sup>15e,n</sup> ZIF-22,<sup>15k</sup> ZIF-69,<sup>15i</sup> ZIF-90,<sup>15o</sup> MIL-53,<sup>49</sup> SIM-1,<sup>50</sup> and MIL-47<sup>51</sup> (on polymer surface).

In general, fabrication of thin films of crystalline framework materials follows one of two approaches: *in situ* growth and secondary or seeded growth.<sup>6c</sup> *In situ* growth here refers to a film fabrication method in which the substrate is immersed in the growth solution without any crystals previously attached to the surface; nucleation, growth, and intergrowth of crystals on the substrate all happen during the same fabrication step. Secondary or seeded growth refers to film growth from preattached seed crystals. Although not as simple as *in situ* growth, secondary growth has been noted to allow better control over the microstructure as well as reduced dependence on the nature of supports in polycrystalline films.<sup>52</sup>

There have been reported many different MOF film synthesis techniques<sup>6f,17a</sup> including chemical modification of the support surfaces with self-assembled monolayers (SAMs).<sup>14b–d,f</sup> Though not discussed here, those who are interested in MOF film synthesis should direct their attention to recent review articles.<sup>6f,17a</sup> It is worth noting here that the requirements of MOF membranes are much more demanding than those of MOF films. Therefore, it is much more challenging to prepare MOF membranes than



**Figure 10.** SEM images of HKUST-1 membranes we reported which illustrate the difference in (a) rapid cooling, (b) slower cooling, and (c) slow cooling and slow drying under nearly saturated conditions of films after synthesis. Reproduced with permission from ref 15j, Copyright Royal Society of Chemistry, 2010.

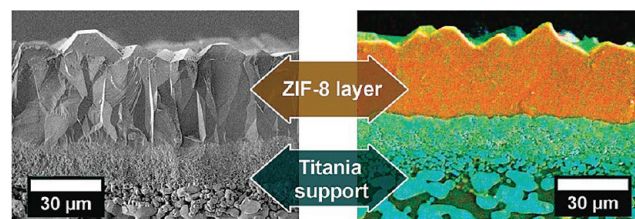


**Figure 11.** SEM images of MOF-5 membrane: (a) top view, (b) cross section. Reproduced with permission from ref 15c, Copyright Elsevier, 2009.

MOF films. MOF membranes require crystals to be well-intergrown so as to minimize nonselective gas transport through grain boundary defects. Also, the presence of pinhole defects, intracrystalline and intercrystalline cracks (even submicrometer-scale cracks), can significantly mar the gas separation performance of the membrane. Stability in harsh environments as well as the consistency of performance for long periods of operation would be some of the other requirements that become critical from the point of view of the commercial application of MOF membranes. MOF films (generally for sensor applications) do not need to fulfill these requirements.

**5.1. In Situ growth.** **5.1.1. In Situ Growth on Unmodified Supports.** As mentioned above, fabrication of membranes of metal–organic frameworks is complicated by the fact that there is usually no strong interfacial bonding between MOFs and the native substrates of interest (which for MOF membranes are typically  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub>). Consequently, not many MOF membranes have been reported that were synthesized without some kind of pretreatment of the porous support. Liu and co-workers were able to grow membranes of IRMOF-1<sup>15c</sup> (Figure 11) and ZIF-69<sup>15i</sup> on  $\alpha$ -alumina without substrate modification. Bux et al.<sup>15e</sup> grew membranes of ZIF-8 on bare titania using microwave irradiation (Figure 12). The nature of the bonding of their membranes with the substrate is not discussed. For MOFs based on ligands with carboxylic acid groups, however, it is very likely to form covalent bonds between the carboxyl groups of ligands and the surface hydroxyl groups of alumina supports.<sup>42a</sup>

**5.1.2. In Situ Growth on Modified Supports.** Support modification, as mentioned previously, is an effective strategy for improving heterogeneous nucleation of MOFs for membrane fabrication. Caro and co-workers have reported ZIF-22,<sup>15k</sup> ZIF-8,<sup>15k</sup> ZIF-7,<sup>15k</sup> and ZIF-90<sup>15o</sup> membranes on alumina

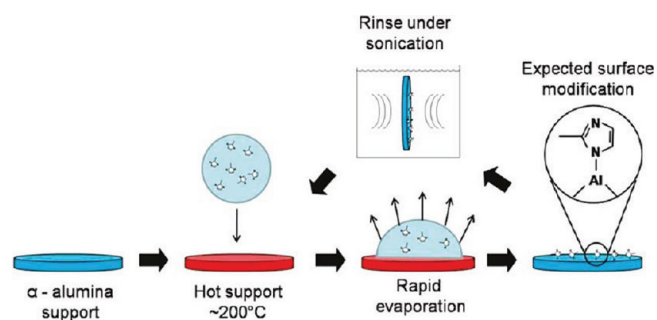


**Figure 12.** (left) SEM image of the cross section of a simply broken ZIF-8 membrane. (right) EDXS mapping of the sawn and polished ZIF-8 membrane (color code: orange, Zn; cyan, Ti). Reproduced with permission from ref 15e, Copyright American Chemical Society, 2009.

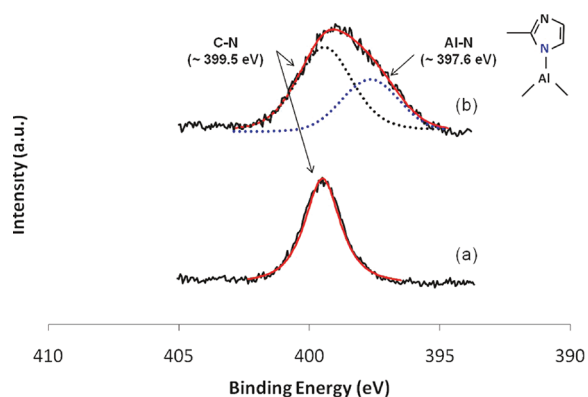
supports modified with 3-aminopropyltriethoxysilane (APTES) as a covalent linker between ZIF crystals and alumina supports, thereby promoting heterogeneous nucleation and growth. Thus, this technique provides a fairly general route to fabricating ZIF membranes on porous ceramic supports.

We have recently reported a silane-free route for substrate modification that yields well-attached polycrystalline MOF membranes.<sup>15n</sup> This method, demonstrated for ZIF-8/-7 membranes, is based on the covalent linkage of imidazole ligands to supports via an Al–N bond.<sup>15n</sup> As illustrated in Figure 13, supports were thermally modified by rapid evaporation of a solution of the organic linker (2-methylimidazole in methanol for ZIF-8 or benzimidazole in methanol for ZIF-7) on the surface of hot  $\alpha$ -alumina ( $\sim 200$  °C). The solvent evaporates quickly, leaving organic linkers covalently attached to the  $\alpha$ -alumina surface, as evidenced by N 1s XPS data, as can be seen Figure 14. The XPS data also confirm that a high temperature ( $\sim 200$  °C) is necessary for covalent bonding between the organic linker and the surface, as supports modified at room temperature did not

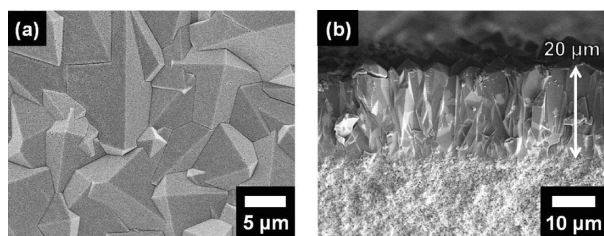




**Figure 13.** Illustration of the substrate modification process. Reproduced with permission from ref 15n, Copyright American Chemical Society, 2010.



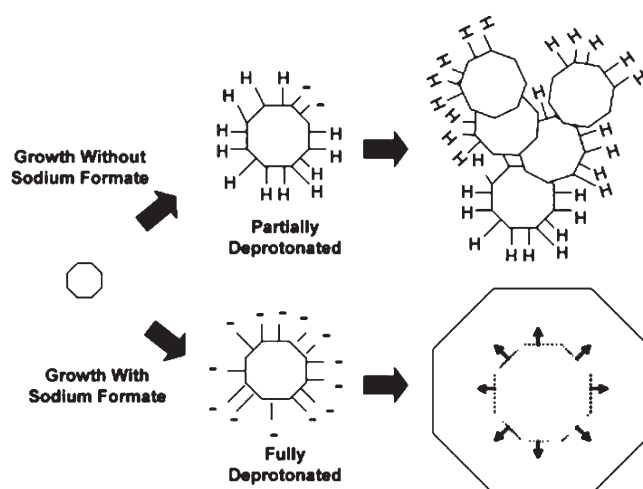
**Figure 14.** N 1s XPS spectra of  $\alpha$ -alumina supports modified with 2-methylimidazole (a) at 25 °C and (b) at 200 °C (bottom). Reproduced with permission from ref 15n, Copyright American Chemical Society, 2010.



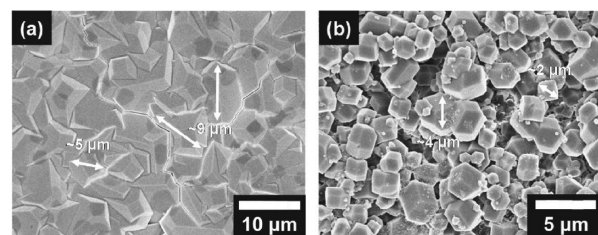
**Figure 15.** (a) Top-down and (b) side-view SEM images of ZIF-8 membranes fabricated using thermal deposition of imidazolate linkers on porous supports. Reproduced with permission from ref 15n, Copyright American Chemical Society, 2010.

have any XPS peaks characteristic of Al–N bonding. Solvothermal growth of supports modified in this way was found to yield ZIF-8 membranes half as thick (see Figure 15) as those reported previously.<sup>15e</sup> These membranes exhibit preferential permeation of small gas molecules with selectivities far in excess of Knudsen selectivity. It is interesting to note though that, unlike molecular sieving observed in zeolite membranes, ZIF membranes have not been observed to exhibit sharp permeance cutoffs. This is understood to be a result of the flexible nature of organic ligands in the ZIF structure.<sup>21</sup>

The role of sodium formate (HCOONa) as deprotonator has been found to be critical for the growth of well-intergrown films on supports modified by thermal deposition (Figure 16).<sup>15n</sup> We



**Figure 16.** Illustration of the possible role of HCOONa in ZIF-8 growth. Reproduced with permission from ref 15n, Copyright American Chemical Society, 2010.



**Figure 17.** ZIF-8 films after secondary growth (a) with sodium formate and (b) without sodium formate. Note that these films were regrown from poorly intergrown films. Reproduced with permission from ref 15n, Copyright American Chemical Society, 2010.

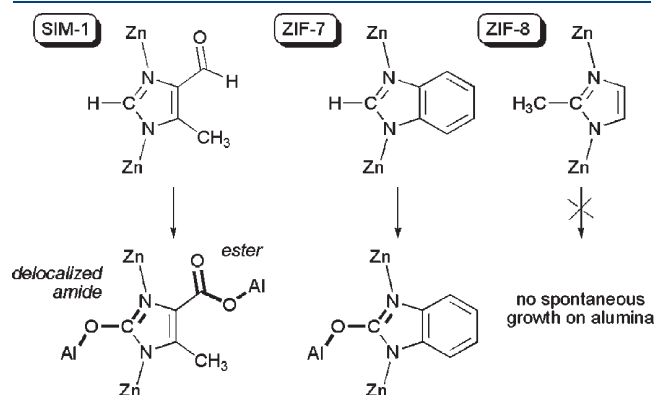
have shown that in the absence of HCOONa the ligand is partially protonated, and this results in a microstructure that is poorly intergrown.<sup>15n</sup> As shown by Wiebcke and co-workers,<sup>53</sup> neutral *m*-Im acts as a capping agent for ZIF-8 crystal growth. The deprotonation was confirmed by the increase in pH of the solution on the addition of sodium formate. When poorly intergrown films were regrown using sodium formate, well intergrown films were obtained (Figure 17).<sup>15n</sup>

Farrusseng and co-workers<sup>42b</sup> postulated the presence of direct attachment of imidazolate to alumina in the case of SIM-1 and ZIF-7, as shown in Figure 18.

**5.1.3. In Situ Growth Using Secondary Metal Source.** Some groups have used alternate metal sources to anchor MOF films.<sup>14e,15d</sup> As mentioned above, MOF synthesis involves coordination bonding between organic and inorganic moieties in solution creating the hybrid organic–inorganic framework. In this approach, the support structure for the membrane itself is the same metal in the framework of the MOF of interest. Guo et al.<sup>15d</sup> reported an HKUST-1 membrane grown on an oxidized copper mesh (Figure 19). It should be noted that this membrane is essentially free-standing and is likely to have problems with mechanical stability for practical applications.

**5.2. Secondary (Seeded) Growth.** Secondary growth is a film growth approach commonly used for zeolite membranes.<sup>52b,c,54</sup> This method involves first seeding the support with seed crystals

of the material of interest followed by hydrothermal or solvothermal growth. Secondary growth decouples the nucleation and growth steps for polycrystalline membrane fabrication.<sup>6e</sup> This allows for better control over film microstructure (density of grain boundaries, film thickness, orientation, etc.) by controlling the relevant properties of the seed crystal layer such as seed crystal size, thickness, and orientation.<sup>55</sup> By having preattached seed crystals to the support, secondary growth also allows film growth to be somewhat substrate independent. For zeolite membranes, seed attachment is not an issue. Simple calcination of seed crystals on the surface of porous supports leads to a condensation reaction between surface hydroxyl groups, and the zeolite seeds become covalently bound. For MOF membranes, this approach is not viable as MOFs cannot withstand high

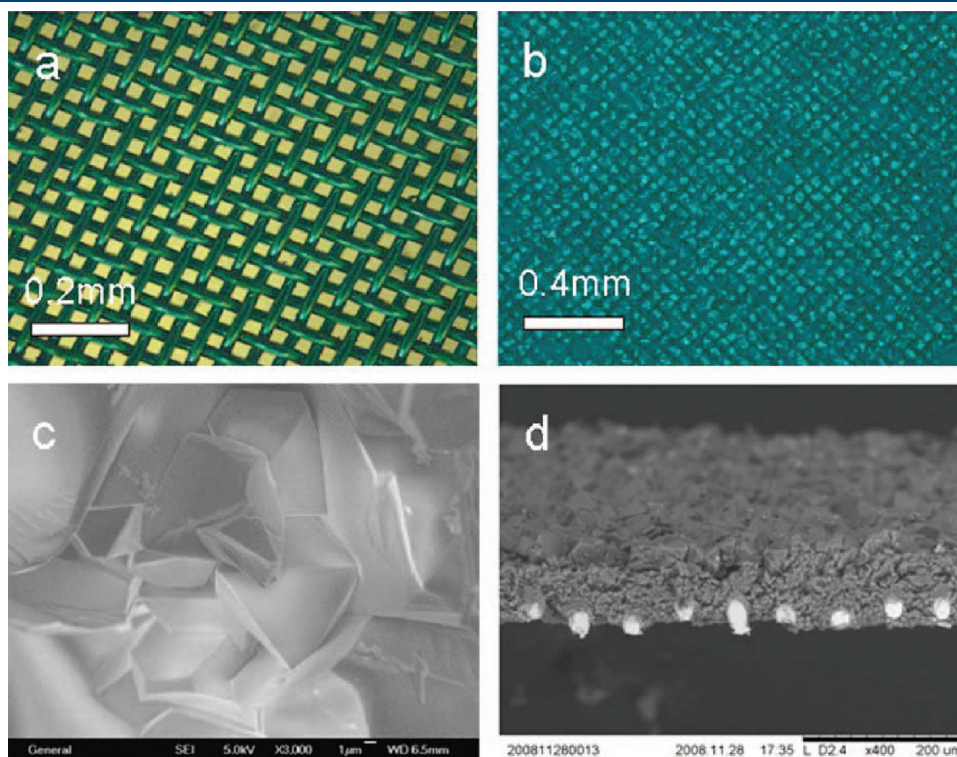


**Figure 18.** Postulated anchoring method of imidazolate based MOFs on alumina support. Reproduced with permission from ref 42b, Copyright Royal Society of Chemistry, 2010.

temperatures. Manual deposition (i.e., rubbing seed crystals on a support) and subsequent heat treatment for zeolite seed crystals is a simple method for attaching crystal seeds to a substrate,<sup>56</sup> but the reports of MOF membranes seeded in this way generally required the use of a polymer binder to attach seed crystals to the support.

**5.2.1. Synthesis of MOF Nanocrystals.** It has been shown in zeolite membranes that when using the secondary growth, nano-sized seed crystals are much preferred to prepare zeolite membranes with controlled microstructures (such as thickness).<sup>55</sup> Therefore, the synthesis of submicrometer sized MOF seed crystals with a narrow size distribution is desirable to form MOF membranes with controllable thickness. There have been reports on the synthesis of nanosized MOFs using various methods ranging from conventional solvothermal methods<sup>15a</sup> to microwave assisted solvothermal synthesis,<sup>57</sup> sonochemical methods,<sup>58</sup> and nonsolvent induced crystallization.<sup>59</sup> MOFs whose nanocrystals have been synthesized include ZIFs,<sup>15a,36b,53,59,60</sup> HKUST-1,<sup>61</sup> IRMOFs,<sup>14b,57,62</sup> MOCP-L and MOCP-H,<sup>63</sup> Cu-4,4'-bipyridine-hexafluorosilicate (Cu-BPY-HFS),<sup>64</sup> and Cu(4,4'-hexafluoroisopropylidenebis-benzoate)<sub>1.5</sub> (Cu\_hfipbb).<sup>58</sup> These nanoparticles can also be used for the fabrication of mixed matrix membranes to provide higher interfacial area and thinner selective skin layers. Further morphology control of these nanocrystals (e.g., plates vs cubes) can allow for the fabrication of preferentially oriented polycrystalline MOF membranes, which might exhibit enhanced separation performance if MOFs of interest are anisotropic in gas transport.

**5.2.2. Secondary Growth—Supports with Physically Attached Seeds.** Ranjan and Tsapatsis<sup>15m</sup> reported a membrane of a microporous MOF using secondary growth in 2009 (see Figure 20).

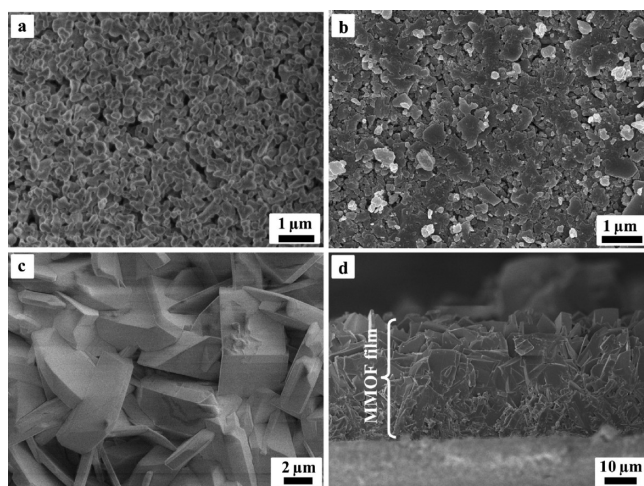


**Figure 19.** Optic micrographs of the (a) copper net and (b) net-supported Cu<sub>3</sub>(BTC)<sub>2</sub> membrane; SEM image of (c) the surface and (d) cross-section of the membrane. Reproduced with permission from ref 15d, Copyright American Chemical Society, 2009.

The seeds were deposited by manually rubbing the crystals onto PEI coated  $\alpha$ -alumina. According to the report, *in situ* growth did not yield membrane quality films. Their results showed *b*-out-of-plane orientation in their membrane, demonstrated using the crystallographic preferential orientation (CPO) indexing method and pole figure analysis. Although the seeds used for secondary growth were randomly oriented, the investigators attributed the membrane orientation to faster crystal growth in the *b* direction. The effective pore size of this MOF is 3.2–3.5 Å.<sup>65</sup>

Li et al.<sup>15f</sup> also used this approach to synthesize membranes of ZIF-7. Poor interaction between seed crystals and the substrate surface necessitated the use of a polymer binder. Although the use of a polymer binder attached seed crystals to the support surface, the seed crystals are not directly attached to the substrate. This means that seed attachment strength is only as good as the polymer attachment strength, and one would expect that membranes fabricated in this way are only physically attached to the support surface. Venna et al.<sup>15h</sup> reported a ZIF-8 tubular membrane obtained by secondary growth of ZIF-8 crystals seeded by rubbing. No polymer binder was used. The membranes thus obtained were fairly thin, 5–9  $\mu\text{m}$ .

**5.2.3. Secondary Growth—Supports with Chemically Attached Seeds.** We recently reported a novel secondary growth technique for MOF membranes which circumvents the problem of MOF crystal thermal instability and does not require foreign binders. This technique, termed thermal seeding, was demonstrated for HKUST-1 membranes.<sup>15j</sup> Thermal seeding consists of dropping an HKUST-1 crystal seed solution onto hot (200 °C) porous  $\alpha$ -alumina supports followed by rinsing under gentle



**Figure 20.** (a) Bare  $\alpha$ -alumina support, (b) seeded support, (c) top-down image of MMOF membrane, (d) side view of MMOF membrane. Reproduced with permission from ref 15m, Copyright American Chemical Society, 2009.

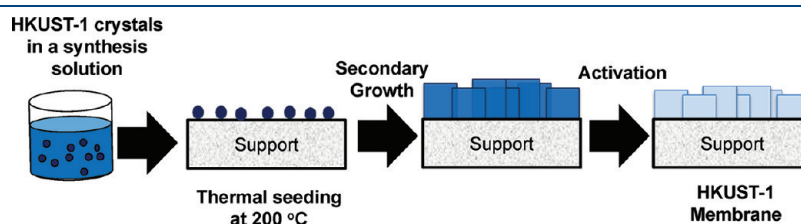
sonication (see Figure 21). This process is repeated to ensure sufficient coating of seed crystals. Solvothermal growth of supports seeded in this way results in continuous, crack-free, well intergrown membranes of HKUST-1. The separation performance of these membranes is comparable to those previously reported by Guo et al.<sup>15d,j</sup> It was observed that HKUST-1 seed crystals alone in solution during thermal seeding do not remain attached after sonication. Only when seeded in the presence of HKUST-1 precursor chemicals do the seed crystals adhere to the support. This indicates that crystals of HKUST-1 do not interact attractively with porous  $\alpha$ -alumina, and there is the need for linking chemicals. This method for MOF crystal seeding has the potential to be applied to other MOFs.

Lee and co-workers<sup>49</sup> showed that this seeding can be carried during *in situ* growth as well (Figure 22). They first carried out *in situ* growth to generate seed crystals attached to the substrate. This seeded support was further used for secondary growth to generate well intergrown films of MIL-53. This technique is called reactive seeding.

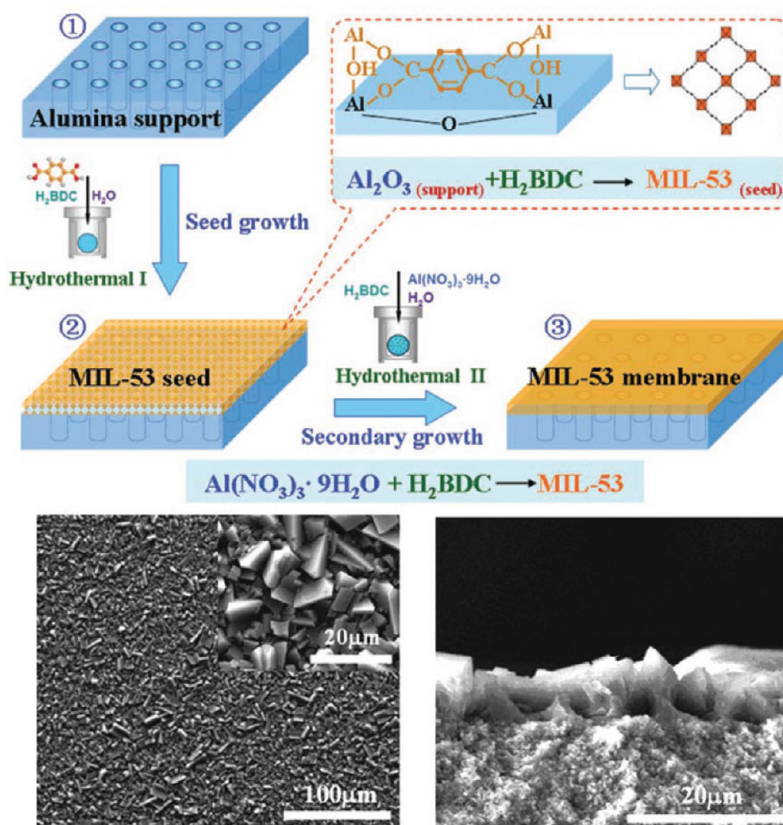
In one of the earliest MOF membrane reports,<sup>14i,15b</sup> our group reported a membrane of IRMOF-1 produced by secondary growth using a seed layer that was deposited using microwave-induced thermal deposition (MITD). Fast microwave seeding resulted in a dense, randomly oriented seed layer on  $\alpha$ -alumina thinly coated with graphite. This was immersed in MOF-5 growth solution and produced well intergrown MOF-5 membranes. A thicker graphite layer was also used for MITD and resulted in oriented MOF-5 crystals attached to the surface (see Figure 23). When this oriented seed layer was grown solvothermally, it produced dense, highly oriented MOF-5 films. Unfortunately, the mechanical instability of these films (readily peeling off) made gas permeation measurement impossible.

Li et al.<sup>15a</sup> recently reported oriented ZIF-7 membranes fabricated on porous  $\alpha$ -alumina. Supports were seeded with ZIF-7 nanocrystals followed by secondary growth. The orientation sharpening observed in this report is explained according to the Van der Drift growth model (also referred to as *evolutionary selection*).<sup>66</sup> This model states that crystals with fast-growing facets oriented vertically with respect to the support eventually overgrow crystals of other orientations during synthesis, yielding a preferentially oriented film. Oriented ZIF-7 and ZIF-8 membranes have been reported<sup>15a,67</sup> (Figure 24). Oriented ZIF-8 membranes have a relatively higher  $\text{H}_2/\text{CH}_4$  separation factor.

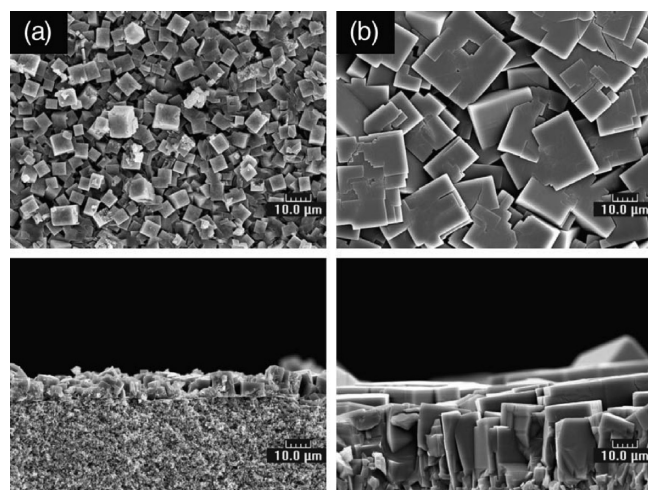
**5.5. Other Techniques for Membrane Fabrication and Modification.** **5.5.1. Liquid Phase Epitaxy (LPE).** Liquid phase epitaxy or stepwise layer by layer involves alternately immersing the substrate into metal and ligand solutions.<sup>68</sup> This technique is typically used to synthesize MOF thin films; however, it has the potential to be applied for fabrication of thin membranes. Typically, the films are a few nanometers thick. Shekhah et al.<sup>68</sup> have demonstrated heteroepitaxial growth of  $[\text{Zn}_2(\text{ndc})_2]$



**Figure 21.** Illustration of HKUST-1 membrane fabrication using thermal seeding and secondary growth. Reproduced with permission from ref 15j, Copyright Royal Society of Chemistry, 2010.



**Figure 22.** Schematic diagram of preparation of the MIL-53 membrane on alumina support via the RS method (above). SEM images of MIL-53 membrane surface and cross-section (below). Reproduced with permission from ref 49, Copyright Royal Society of Chemistry, 2011.



**Figure 23.** SEM images of the oriented IRMOF-1 seed layer (a) and the oriented membrane after secondary growth (b). Reproduced with permission from ref 15b, Copyright Elsevier, 2009.

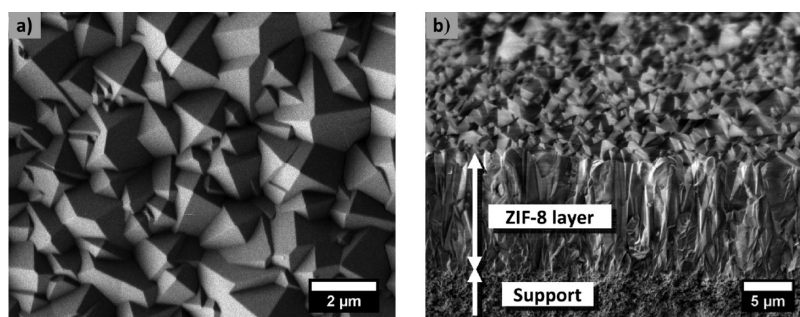
$(\text{dabco})_n$  on  $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$  ( $\text{ndc}$  = 1,4-naphthalene dicarboxylate and  $\text{dabco}$  = 1,4-diazabicyclo(2.2.2)octane) using LPE to give rise to perfectly oriented hybrid MOF thin films. These oriented thin films are exciting for chemical sensor and gas separation applications. Nan et al.<sup>69</sup> showed that a similar approach (step by step procedure) can be used to prepare seeded supports of HKUST-1. These seeded supports under optimum

hydrothermal secondary growth conditions yielded continuous and well-intergrown HKUST-1 membranes.

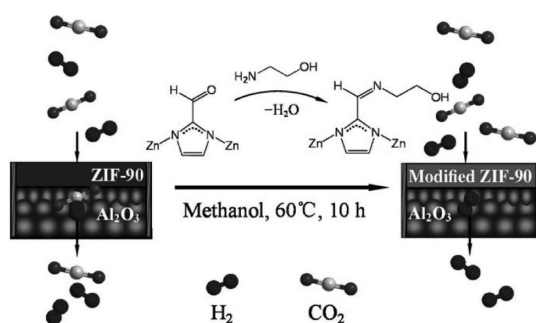
Recently, Betard et al.<sup>70</sup> reported  $\text{Cu}_2(\text{BME-bdc})_2(\text{dabco})$  and  $\text{Cu}_2(\text{ndc})_2(\text{dabco})$  ( $\text{dabco}$  = 1,4-diazabicyclo(2.2.2)octane,  $\text{ndc}$  = 1,4-naphthalenedicarboxylate, 2,5-bis(2-methoxyethoxy)-1,4-benzene-dicarboxylate = BME-bdc) MOF membranes using step by step liquid phase deposition. Here, separation was carried out by a MOF layer formed inside the macroporous support. Although the pumps were computer-controlled, the synthesis time was fairly long ( $\sim 2$  days). Scaleup of such a technique for commercial applications could be difficult. Using a spray-based method<sup>71</sup> for LPE (demonstrated for HKUST-1 SURMOF), deposition time was significantly reduced. It should be noted here that LPE provides for fabrication of thin films (submicrometer regime) with controllable thickness. Thickness is governed by the number of cycles, which can be easily tuned.

**5.5.2. Postsynthetic Modification.** Side groups having functionality can be further subjected to postsynthetic modification after the fabrication of membranes. This has been shown for IRMOF-3,<sup>44</sup> ZIF-90<sup>32a</sup> (Figure 25), and SIM-1<sup>32b</sup> membranes. Amine functionalization of SIM-1 gives SIM-2, which shows catalytic activity and enhanced  $\text{CO}_2/\text{N}_2$  separation.<sup>32b</sup>

**5.6. MOF Films on Polymer Supports.** Inorganic supports such as alumina and titania are generally expensive as compared to organic supports. So far, most of the MOF films and membranes have been grown on these rather expensive oxide supports. Due to their inorganic/organic hybrid nature, MOFs have the potential to be fabricated on polymer substrates.<sup>51,72</sup>



**Figure 24.** (a) SEM top view of the well-intergrown ZIF-8 layer after 2 h of secondary growth. (b) SEM top down view on the corresponding cross-section of the broken membrane. Reproduced with permission from ref 67, Copyright American Chemical Society, 2011.

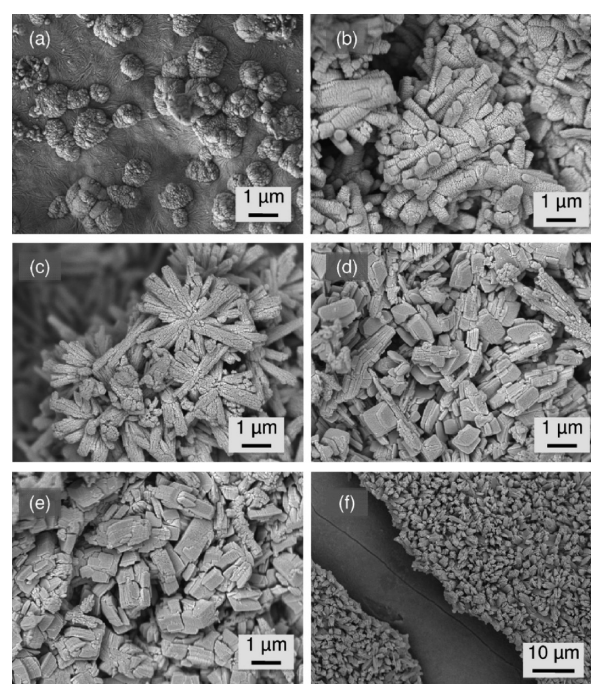


**Figure 25.** Covalent postfunctionalization of a ZIF-90 molecular sieve membrane by imine condensation with ethanolamine to enhance  $\text{H}_2/\text{CO}_2$  selectivity. Reproduced with permission from ref 32a, Copyright Wiley, 2011.

Centrone et al.<sup>51</sup> reported for the first time the fabrication of MOF material on a polymer substrate using fast microwave irradiation (Figure 26). *In situ* functionalization of nitrile from a PAN substrate to carboxylic acid groups leads to the MIL-47 growth on the polymer surface. Yao et al.<sup>72</sup> demonstrated the growth of a continuous and compact ZIF-8 membrane on a nylon membrane using the contra-diffusion method (Figure 27). These membranes use polymers as supports. In this regard, they are different from mixed matrix membranes, in which the MOF particles are dispersed in a polymer matrix.

In either case, the adhesion of MOF to the polymer surface is necessary. The control of the MOF/polymer interface is relatively easier in general due to the increased affinity of organic linkers to the polymer surface. Further, postsynthetic modification of MOFs can allow modulation of the surface properties of MOFs.<sup>73</sup> In the case of MMM with ZIF-90,<sup>59</sup> no interface modification was required. For MMMs of ZIF-7 in PBI,<sup>74</sup> a subnano interphase structure was formed between ZIF-7 and PBI which acted as an extension of ZIF-7 frameworks, thereby providing strong interfacial interactions.

**5.7. Mixed-Matrix Membranes with MOFs.** Mixed matrix membranes (MMM) with MOFs are a new class of membranes which combine the advantages of polymers and MOFs. In general, MMMs with zeolites face difficulties which include expensive synthesis of defect-free crystals with long preparation times and a limited range of zeolite structures with a discontinuous pore size and little chemical tailorability and a poor polymer zeolite interface. Synthesis of MOFs with various physical/chemical properties is relatively easier than that of zeolites, and the MOF/polymer interface can be controlled by varying the affinity of organic



**Figure 26.** SEM images of a polyacrylonitrile substrate prepared initially as an electrospun nanofiber mat, coated with MIL-47 material as a function of time: (a) 5 s, (b) 30 s, (c) 3 min, (d) 6 min, and (e) 10 min. (f) MIL-47-coated grooved PAN. Reproduced with permission from ref 51, Copyright American Chemical Society, 2010.

linkers to the polymer matrix. Also, the surface of MOFs can be modified by functionalization for favorable interaction with the polymer.<sup>73</sup> MOFs, in general, offer greater pore volumes and weigh less than zeolites. Thus, for a given mass loading, a MMM with MOF will affect the membrane behavior significantly greater than MMM with a zeolite. MMMs with MOFs that have been reported include Cu-BPY-HFS (Cu-4,40-bipyridine hexafluorosilicate) in Matrimid;<sup>64</sup> HKUST-1 in poly(sulfone);<sup>75</sup> MOF-5 in Matrimid;<sup>62b</sup> Cu-TPA (terephthalic acid) in poly(vinyl acetate);<sup>72</sup> ZIF-90 in 6FDA-DAM<sup>59</sup> (6FDA: 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride and DAM: diaminomesitylene); ZIF-7 in polybenzimidazole (PBI);<sup>74</sup>  $\text{Cu}_3(\text{BTC})_2$ , ZIF-8, and MIL-53 (Al) in Matrimid;<sup>76</sup> ZIF-8 in Matrimid;<sup>77</sup> HKUST-1 in polyimide hollow fiber mixed matrix membrane;<sup>78</sup> HKUST-1 in Matrimid;<sup>79</sup> and HKUST-1, MIL-53, MIL-47, and ZIF-8 in PDMS.<sup>80</sup> In particular, the ZIF-7/PBI nanocomposite<sup>74</sup>

showed remarkably higher ideal  $H_2/CO_2$  permselectivity, as compared to pure PBI membranes and pure polycrystalline ZIF-7 membranes. The enhanced selectivity was attributed to the strong interfacial interactions between ZIF-7 and the polymer, which reduced nonselective pathways for gas transport. Thus mixed matrix membranes (MMMs) with MOFs provide potential

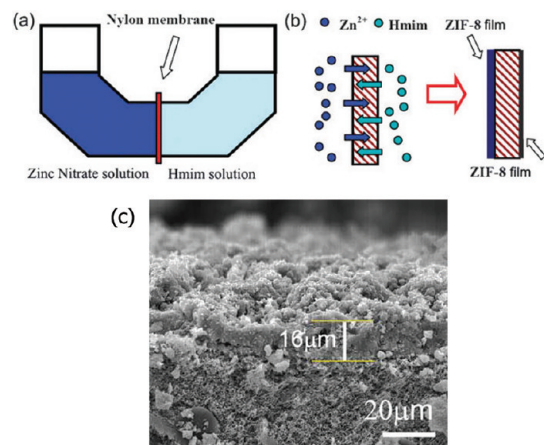
alternatives as enhanced gas separation membranes. Some of these membranes might still face challenges of plasticization and poor thermal and chemical stability that limit polymeric membranes.

## 6. GAS SEPARATION PERFORMANCE OF MOF MEMBRANES

Single gas permeation properties of reported MOF membranes are summarized in Table 2. Two reported MOFs exhibit ideal selectivity values that are consistent with Knudsen diffusion (MOF-5 (Figure 28) and ZIF-69).<sup>15b,c,i</sup>

HKUST-1 membranes exhibit lower  $H_2/CH_4$  separation than expected.<sup>15d</sup> The authors speculated that this was due to the slowly diffusing and strongly sorbing methane blocking the fast diffusing and slowly sorbing hydrogen. Gas permeation results for the microporous MOF (MMOF) investigated by Ranjan and Tsapatsis<sup>15m</sup> showed an ideal selectivity of 23 for  $H_2/N_2$ . Low fluxes were also reported for this membrane and ascribed to the randomly oriented seed layer impeding gas diffusion. Membranes of ZIF-7, ZIF-8 (Figure 29), and ZIF-22 exhibit molecular sieving, preferentially allowing higher permeation of small gases over larger molecules.<sup>15e,f,k</sup>

ZIF-8 has a reported an aperture diameter of  $3.4 \text{ \AA}$ .<sup>11d,13a</sup> This aperture diameter leads one to expect that ZIF-8 membranes would be capable of good hydrogen/methane separation. Binary mixture permeation data confirms this expectation; the membrane's  $H_2/CH_4$  separation factor at room temperature and pressure was 11.2. As pointed out by the author, however, the membrane's hydrogen flux is about half that obtained by zeolite

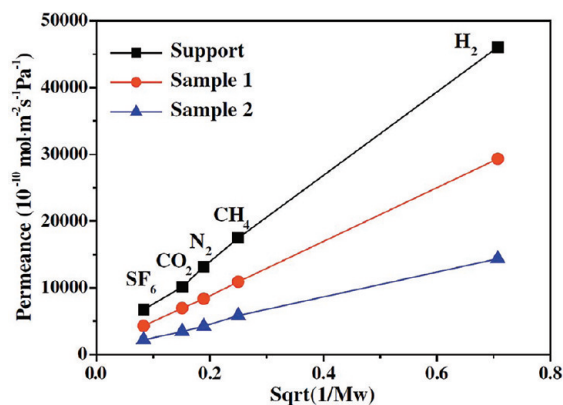


**Figure 27.** (a) Diffusion cell for ZIF-8 film preparation, (b) the schematic formation of ZIF-8 films on both sides of the nylon support via contra-diffusion of  $Zn^{2+}$  and Hmim through the pores of the nylon support, and (c) SEM image of the cross section of the ZIF-8 film. Reproduced with permission from ref 72, Copyright Royal Society of Chemistry, 2011.

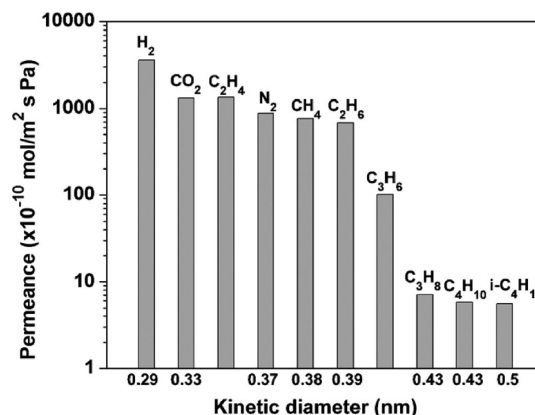
**Table 2. Summary of Single Gas Permeances of MOF Membranes<sup>a</sup>**

MOF	ref	$T$ ( $^{\circ}C$ )	$d_a$ (nm)	$d_m$ ( $\mu m$ )	reported permeances at $\sim 1 \text{ atm}$ [ $10^{-8} (\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$ ]									
					$H_2$	$CH_4$	$N_2$	CO	$O_2$	$CO_2$	$SF_6$	$C_2H_4$	$C_2H_6$	
MOF-5	15b	25	1.4	40	80	39	30			25				
MOF-5	15e	25	1.4	25	285	103.3	80			66.7	41.7			
MOF-5	15e	25	1.4	85	131.7	56.7	40			33.3	21.7			
ZIF-7	15g	220	0.29	1.5	4.55	0.31	0.22			0.35				
*ZIF-7	15g	220	0.29	1.5	-	0.33	0.25			0.31				
ZIF-7	15f	200	0.29	1.5	7.40	1.18	1.10			1.10				
*ZIF-7	15f	200	0.29	1.5		1.35	1.03			1.19				
ZIF-8	15h	20	0.34	5		472				2430				
ZIF-8	15h	20	0.34	9		242				1690				
*ZIF-8	84	25	0.34	25								1.8	0.65	
ZIF-8	15n	25	0.34	20	17.3	1.33	1.49		5.22	4.45				
ZIF-8	81	25	0.34	2.5	36.0	7.8	9.0			14.0		14.0	6.90	
ZIF-8	15e	25	0.34	40	6.04	0.48	0.52		1.04	1.33				
ziF-22	15k	50	0.29	40	20.2	3.02	2.84		2.8	2.38				
ZIF-69	15i	25	0.44	50	6.5	1.85		1.1			0.5			
MMOF	15m	25	0.32	20	1.6		0.35			0.35				
MMOF	15m	190	0.32	20	0.2		0.01			0.04				
HKUST-1	15d	25	0.9	60	125.3	16.1				27.7				
HKUST-1	69	25	0.9	25	74.8	25.7	20.3			14.8				
HKUST-1	15j	25	0.9	25	200	80	50			50				
HKUST-1	15j	190	0.9	25	110	20	15							
SIM-1	50	25	0.34	25	8.2					3.5				
ZIF-90**	32a	200		20	21.0	1.08	1.2S			1.34				
ZIF-90	15o	200	0.35	20	25.0	1.57	1.9S			3.48				

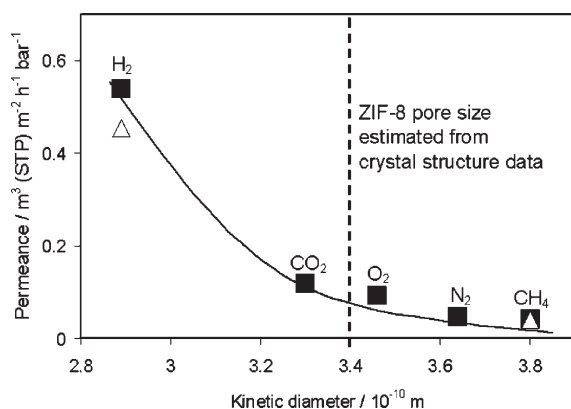
<sup>a</sup>\* = Equimolar binary gas measurement with 50% hydrogen, \*\* = ZIF-90 after post-synthetically modification with ethanolamine.



**Figure 28.** Single-component gas permeation results through the  $\alpha$ -alumina support (square), sample 1 (circle), and sample 2 (triangle) under 800 Torr. Reproduced with permission from ref 15c, Copyright Elsevier, 2009.



**Figure 30.** Single gas permeances measured on an as-synthesized ZIF-8 membrane using the Wicke–Kallenbach technique. Reproduced with permission from ref 81, Copyright Royal Society of Chemistry, 2011.

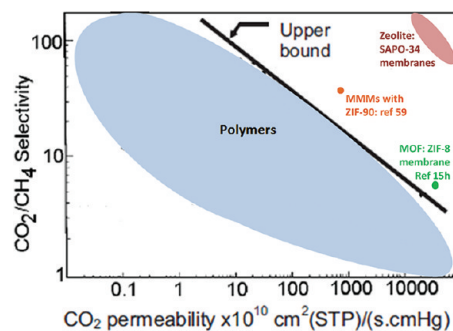


**Figure 29.** Single (squares) and mixed (triangles) gas permeances for a ZIF-8 membrane vs kinetic diameters. Reproduced with permission from ref 15e, Copyright American Chemical Society, 2009.

membranes with similar selectivity. This was attributed to the fact that the membrane is quite thick ( $\sim 40 \mu\text{m}$ ). The ZIF-8 tubular membrane reported by Venna and Carreon<sup>15h</sup> with a thickness of  $5\text{--}9 \mu\text{m}$  exhibits a CO<sub>2</sub> permeance of  $\sim 2.4 \times 10^{-5} \text{ mol/m}^2 \text{ s Pa}$  with CO<sub>2</sub>/CH<sub>4</sub> selectivities ranging from 4 to 7.

Recently, Pan and Lai<sup>81</sup> reported an excellent ZIF-8 membrane by secondary growth in aqueous solution near room temperature (greener route). Single gas permeances are shown in Figure 30. High selectivities were obtained for C<sub>2</sub>/C<sub>3</sub> hydrocarbon separation (for mixtures, ethane/propane  $\sim 80$ , ethylene/propylene  $\sim 10$ , and ethylene/propane  $\sim 167$ ). Also, the membranes obtained were much thinner ( $2.5 \mu\text{m}$ ) than previously reported membranes.<sup>15c</sup> Correspondingly, the permeances were 4 times higher. The authors reported a higher H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> separation factor than previous membranes. The superior separation performance was attributed to enhanced membrane microstructure (reduced grain boundary defects), which was possibly due to their novel aqueous recipe.

As stated earlier, the sharp permeance cut-offs have not been observed for ZIF membranes,<sup>15c</sup> mainly due to the flexible nature of the framework.<sup>21</sup> This is in contrast to the zeolite membranes that in general exhibit substantial reduction (orders of magnitude) in permeance for molecules with a kinetic diameter greater than



**Figure 31.** Comparison of different types of membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. This figure has been modified from the original figure. Reproduced with permission from ref 99, Copyright Wiley, 2006.

the pore size of zeolites.<sup>82</sup> However, most MOFs including ZIFs allow molecules whose kinetic diameters are greater than their pore sizes to pass through (see Figure 29) without substantial hindrance (i.e., the permeance does not decrease sharply for molecules greater than the pore size). This suggests that one has to select MOFs with a much smaller pore size than the molecules of interest for membrane applications.

Postsynthetic modification of ZIF-90 reduces the pore size due to the presence of an imine group and leads to significant enhancement in molecular sieving.<sup>32a</sup> Huang and Caro<sup>32a</sup> reported a significant selectivity enhancement for ZIF-90 without a significant permeance drop. They also attribute higher selectivity to reduced pore aperture and improved grain boundary structure due to the elimination of intercrystalline defects. However, Aguado et al.<sup>32b</sup> reported a decrease in CO<sub>2</sub> permeation flux for SIM-1 after post synthetic modification, which was attributed to the reduced capacity of modified MOF (SIM-2). Surface modification could result in pore blocking at the surface and hinder molecular transport at the pore entrance/mouth, which could reduce the available area for gas transport, thereby decreasing the flux and permeance. Thus, the extent of modification needs to be optimized to achieve selectivity enhancement without significantly affecting the permeance.

H<sub>2</sub>/CO<sub>2</sub> selectivity is increased from 7.3 to 62.5. Postsynthetic modification of SIM-1 with dodecylamine to give imine groups (the new phase is called SIM-2) shows better CO<sub>2</sub>/N<sub>2</sub> separation

under moist conditions.<sup>32b</sup> For moisture-sensitive MOFs like IRMOF-3, surfactant assisted drying significantly reduces fracture and crack formation.<sup>44</sup> This leads to enhanced gas permeation performance. Postsynthetic modification has also been demonstrated for IRMOF-3, which enables tuning the performance for CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> separation.<sup>44</sup>

On the basis of single component diffusion rate measurement, Li and co-workers<sup>83</sup> demonstrated the probability of kinetic separation of propane/propene using ZIF materials in powder form. Gucuyener et al.<sup>40</sup> showed that ZIF-7 can be used for ethane/ethylene separation with selective adsorption of the paraffin due to the gate-opening effect. Caro's group<sup>84</sup> showed, in the case of the ZIF-8 membrane, for an equimolar mixture, a modest selectivity of 2.8 of ethene over ethane (at 1 bar and room temperature). Using simulations, they explained that the faster diffusing ethene surpasses the more strongly adsorbing ethane, and hence the membrane is selective for olefin and not the paraffin.

Despite the progress made over the past several years, MOF membranes are still relatively new, thereby having substantial potential for improvement. Nevertheless, it is informative to compare MOF membranes with different types of membranes. Figure 31 presents the CO<sub>2</sub>/CH<sub>4</sub> separation performance of ZIF-8 membranes compared with those of other membranes, showing relatively high CO<sub>2</sub> permeability though the CO<sub>2</sub>/CH<sub>4</sub> selectivity is relatively low.

## 7. CONCLUSIONS AND PERSPECTIVES

In conclusion, metal–organic frameworks (MOFs) offer unprecedented opportunities for membrane-based gas separations (e.g., olefin/paraffin separations) due to their facile control over pore size and functionality. Thermally and chemically stable zeolitic–imidazolate frameworks (ZIFs) are of particular interest as membrane materials.

Current MOF membrane fabrication techniques do involve several issues mainly due to the unfavorable heterogeneous nucleation on support surfaces and the coordination chemistry of MOFs. Several strategies aimed at addressing these issues have been discussed.

A large variety of exciting MOFs have been reported in the literature, which when prepared as membranes might have potential applications for commercially relevant separations. On the basis of diverse MOF structures reported, many new MOF membranes are still to be reported.

It is also important to note that all of the research on MOF membranes for gas separation to date has been approached with a view to application similar to that of zeolite membranes. However, it would be exciting to see the many unique properties of metal–organic frameworks be applied to gas separating membranes.

In this vein, this review will close with a few suggestions for possible research directions for MOF membranes. There are many more MOFs with exciting properties than listed here, but these examples serve at least to illustrate the potential for impact in this new and largely unexplored area of research. Future research directions should also involve carrying out detailed investigations discussing important topics such as microstructure control, grain boundaries, and defect/crack removal.

**7.1. MOF Membranes with Controllable Selectivity.** There is also room for the application of MOFs with other interesting properties for membrane separations. Ma et al.<sup>85</sup> have reported

four different MOFs that exhibit temperature tunable molecular gates. These MOFs, termed mesh-adjustable molecular sieves (MAMS), have a controllable uptake of gases, discriminating between gases based on molecular size. This size discrimination was shown to be controlled by the temperature of the material. Controllable gas uptake has been reported before for titanosilicate zeolites, but these materials have not been reported for gas separating membranes.<sup>86</sup> If these materials could be applied as membranes with controllable selectivity, this could yield high resolution membrane separation of any gases with different kinetic diameters.

**7.2. MOF Membranes with Enantioselective Pores.** Another interesting group of MOFs are those with enantioselective pores such as POST-1.<sup>87</sup> Different MOFs exhibiting pores with handedness have been reported, but none have been explored for membranes or thin films. Enantioselective catalysis is one application of these MOFs, but this has only been explored for powders.<sup>88</sup> MOF membranes with chiral channels would enable high resolution separation of racemic mixtures, providing an alternative to methods such as chiral column chromatography. In addition, enantioselective MOF membranes could also be used as membrane reactors for chiral synthesis (i.e., chemical reaction happens in the pores yielding products with both chiralities, but only one chirality can diffuse out of the pores).

**7.3. MOF Membranes with Readily Functionalized Pores.** One of the most often referred to strengths of metal–organic frameworks is their chemical functionality. In theory, a MOF with functionalizable pores can have its pore size controllably adjusted by functionalization with different sized molecules.<sup>14m,89</sup> This property would be useful for separation flexibility and control. Functionalization of a MOF membrane could also be used to change its properties such as making it hydrophobic instead of hydrophilic or increasing the solubility of CO<sub>2</sub> in the membrane by adding amines to the framework. This has been demonstrated by several groups.<sup>32,44</sup> Also, a membrane with functionalizable pores could potentially be useful for catalytic and enantioselective membrane applications.

**7.4. Anionic Frameworks for Gas Separation and Catalysis.** The gas sorption/diffusion properties of MOFs can be tuned by incorporating cations inside the pores of MOFs. Yang et al.<sup>90</sup> showed that for a parent anionic framework, built using indium(III) centers and tetracarboxylic acid ligands, the porosity and heat of adsorption for H<sub>2</sub> can be modified by post synthetic ion exchange using an appropriately sized cation. Also, unlike postsynthetic modification demonstrated for ZIF-90<sup>32a</sup> and SIM-1,<sup>32b</sup> this modification seems to be reversible in nature. An et al.<sup>91</sup> have synthesized a zinc-adenine-based bio-MOF-1 (Zn<sub>8</sub>(ad)<sub>4</sub>(BPDC)<sub>6</sub>O·2Me<sub>2</sub>NH<sub>2</sub>), which also has an anionic framework. The pore size and adsorption property of bio-MOF-1 was altered by exchanging diammonium cations (present in as-synthesized sample) with ammonium cations of different sizes, resulting in the enhanced CO<sub>2</sub> uptake.<sup>92</sup> As seen in aluminosilicate zeolites, the cations can be varied, and gas adsorption/diffusion properties can be altered, which gives an additional handle to finely tune the separation properties of membranes. The metal cations can also act as sites for catalysis, potentially resulting in MOF membrane reactors.

**7.5. External Surface Barriers in MOFs.** In a simple description of molecular diffusion in a nanoporous material, the external boundaries of the material are simple terminations of the pores enabling the adsorption and desorption of gas molecules.<sup>93</sup> Contrary to this simple picture, Karger and co-workers<sup>94</sup> have



showed, using sorption rate measurements on Zn(tbip) (H2tbip = 5-tertbutylisophthalic acid) crystals, that surface resistances or barriers exist for sorption due to many pore entrances being blocked and very few pores being open. If this external pore blockage is general in MOFs, it is critical to open external pore mouths to minimize this barrier and to improve flux through MOF membranes. If understood and controlled, the surface barriers in MOFs may serve as a “selective filter” for gas separations.<sup>93</sup>

**7.6. Grain Boundaries of MOF Membranes.** The microstructure (size of grains and their orientation, thickness, grain boundary structure, and location of active films) of polycrystalline MOF membranes can affect their performances as well as their durabilities. The microstructure of MOF membranes may not be similar to that of zeolite membranes. It is, therefore, of critical importance to characterize the microstructure (grain boundary defects in particular) of MOF membranes perhaps by applying well-known techniques used in zeolite membrane research such as He/SF<sub>6</sub> permeation and fluorescence confocal optical microscopy (FCOM) techniques.<sup>95</sup>

**7.7. Designing Ligands, MOFs, and Their Membranes Based on Desired Separations.** Currently, membrane fabrication is pursued from MOFs that show interesting behavior in powder form. Some of these materials may not perform well, when fabricated as membranes, because kinetics (diffusion of species) plays a major role in the case of membranes. However, we could work backward, i.e., systematically design MOF materials (even design the ligands) for membranes based on end application.<sup>18a,96</sup> Also, since a large variety of MOFs have already been reported in the literature, potential candidates for the targeted separation could be identified using computational studies.<sup>97</sup> In particular, the sorption and diffusion measurements which govern the membrane selectivities could be used to selectively filter out the best MOFs. This approach would save a lot of time on investigating different MOF membranes for their gas separation performance.

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## ACKNOWLEDGMENT

H.-K.J. acknowledges the financial supports from the National Science Foundation (CBET-0930079), the Department of Energy Advanced Research Project Agency-Energy (DE-AR0000073) and the Artie McFerrin Department of Chemical Engineering at Texas A&M University and Texas Engineering Experiment Station through a new faculty startup. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund (PRF-48884-DNIS) for partial support of this research.

## REFERENCES

(1) Council, N. R. *Separation Technologies for the Industries of the Future*. National Academy Press: Washington, DC, 1998.  
(2) Baker, R. W. Future directions of membrane gas separation technology. *Ind. Eng. Chem. Res.* **2002**, *41* (6), 1393–1411.  
(3) Robeson, L. M. Correlation of Separation Factor versus Permeability for Polymeric Membranes. *J. Membr. Sci.* **1991**, *62* (2), 165–185.

(4) Robeson, L. M. The upper bound revisited. *J. Membr. Sci.* **2008**, *320* (1–2), 390–400.

(5) Burns, R. L.; Koros, W. J. Defining the challenges for C3H6/C3H8 separation using polymeric membranes. *J. Membr. Sci.* **2003**, *211* (2), 299–309.

(6) (a) Matsukata, M.; Kikuchi, E. Zeolitic membranes: Synthesis, properties, and prospects. *Bull. Chem. Soc. Jpn.* **1997**, *70* (10), 2341–2356. (b) Lin, Y. S.; Kumakiri, I.; Nair, B. N.; Alsyouri, H. Microporous inorganic membranes. *Sep. Purif. Methods* **2002**, *31* (2), 229–379. (c) Caro, J.; Noack, M. Zeolite membranes - Recent developments and progress. *Microporous Mesoporous Mater.* **2008**, *115* (3), 215–233. (d) Caro, J.; Noack, M.; Kolsch, P.; Schafer, R. Zeolite membranes - state of their development and perspective. *Microporous Mesoporous Mater.* **2000**, *38* (1), 3–24. (e) Gavalas, G. R. Zeolite Membranes for Gas and Liquid Separations. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Y., Pinnau, I., Freeman, B. D., Eds.; John Wiley & Sons, Ltd.: New York, 2006; pp 307–336. (f) Zacher, D.; Shekhan, O.; Woll, C.; Fischer, R. A. Thin films of metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1418–1429.

(7) (a) Choi, J.; Jeong, H.; Snyder, M.; Stoeger, J.; Masel, R.; Tsapatsis, M. Grain Boundary Defect Elimination in a Zeolite Membrane by Rapid Thermal Processing. *Science* **2009**, *325* (5940), 590. (b) Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. Microstructural Optimization of a Zeolite Membrane for Organic Vapor Separation. *Science* **2003**, *300* (5618), 456–460. (c) Poshusta, J. C.; Tuan, V. A.; Pape, E. A.; Noble, R. D.; Falconer, J. L. Separation of light gas mixtures using SAPO-34 membranes. *AIChE J.* **2000**, *46* (4), 779–789.

(8) Caro, J.; Noack, M. Zeolite Membranes - Status and Prospective. In *Advances in Nanoporous Materials*; Stefan, E., Ed.; Elsevier: New York, 2010; Vol. 1, pp 1–96.

(9) Mahajan, R.; Vu, D. Q.; Koros, W. J. Mixed matrix membrane materials: An answer to the challenges faced by membrane based gas separations today? *J. Chin. Inst. Chem. Eng.* **2002**, *33* (1), 77–86.

(10) Moore, T. T.; Koros, W. J. Non-ideal effects in organic-inorganic materials for gas separation membranes. *J. Mol. Struct.* **2005**, *739* (1–3), 87–98.

(11) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keefe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science* **2002**, *295* (5554), 469–472. (b) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keefe, M.; Yaghi, O. M. Hydrogen storage in microporous metal-organic frameworks. *Science* **2003**, *300* (5622), 1127–1129. (c) Ferey, G. Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **2008**, *37* (1), 191–214. (d) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O’Keefe, M.; Yaghi, O. M. High-throughput synthesis of zeolitic imidazolate frameworks and application to CO<sub>2</sub> capture. *Science* **2008**, *319* (5865), 939–943. (e) Zhuang, J. L.; Ceglarek, D.; Pethuraj, S.; Terfort, A. Rapid Room-Temperature Synthesis of Metal-Organic Framework HKUST-1 Crystals in Bulk and as Oriented and Patterned Thin Films. *Adv. Funct. Mater.* **2011**, *21* (8), 1442–1447.

(12) (a) Sholl, D. S.; Watanabe, T.; Keskin, S.; Nair, S. Computational identification of a metal organic framework for high selectivity membrane-based CO<sub>2</sub>/CH<sub>4</sub> separations: Cu(hfipbb)(H<sub>2</sub>hfipbb)(0.5). *Phys. Chem. Chem. Phys.* **2009**, *11* (48), 11389–11394. (b) Sholl, D. S.; Haldoupis, E.; Nair, S. Efficient Calculation of Diffusion Limitations in Metal Organic Framework Materials: A Tool for Identifying Materials for Kinetic Separations. *J. Am. Chem. Soc.* **2010**, *132* (21), 7528–7539. (c) Keskin, S.; van Heest, T. M.; Sholl, D. S. Can Metal–Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations? *ChemSusChem* **2010**, *3* (8), 879–891.

(13) (a) Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O’Keefe, M.; Yaghi, O. M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103* (27), 10186–10191. (b) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O’Keefe, M.; Yaghi, O. M. Synthesis, Structure, and Carbon Dioxide Capture

Properties of Zeolitic Imidazolate Frameworks. *Acc. Chem. Res.* **2009**, *43* (1), 58–67.

(14) (a) Arnold, M.; Kortunov, P.; Jones, D. J.; Nedellec, Y.; Karger, J.; Caro, J. Oriented crystallisation on supports and anisotropic mass transport of the metal-organic framework manganese formate. *Eur. J. Inorg. Chem.* **2007**, *1*, 60–64. (b) Hermes, S.; Schroder, F.; Chelmoski, R.; Woll, C.; Fischer, R. A. Selective nucleation and growth of metal-organic open framework thin films on patterned COOH/CF<sub>3</sub>-terminated self-assembled monolayers on Au(111). *J. Am. Chem. Soc.* **2005**, *127* (40), 13744–13745. (c) Hermes, S.; Zacher, D.; Baunemann, A.; Woll, C.; Fischer, R. A. Selective growth and MOCVD loading of small single crystals of MOF-5 at alumina and silica surfaces modified with organic self-assembled monolayers. *Chem. Mater.* **2007**, *19* (9), 2168–2173. (d) Biemmi, E.; Scherb, C.; Bein, T. Oriented growth of the metal organic framework Cu-3(BTC)(2)(H<sub>2</sub>O)(3)center dot xH(2)O tunable with functionalized self-assembled monolayers. *J. Am. Chem. Soc.* **2007**, *129* (26), 8054–8055. (e) Zou, X. Q.; Zhu, G. S.; Hewitt, I. J.; Sun, F. X.; Qiu, S. L. Synthesis of a metal-organic framework film by direct conversion technique for VOCs sensing. *Dalton Trans.* **2009**, *16*, 3009–x3013. (f) Zacher, D.; Baunemann, A.; Hermes, S.; Fischer, R. A. Deposition of microcrystalline [Cu-3(btc)(2)] and [Zn-2(bdc)(2)-(dabco)] at alumina and silica surfaces modified with patterned self assembled organic monolayers: evidence of surface selective and oriented growth. *J. Mater. Chem.* **2007**, *17* (27), 2785–2792. (g) Allendorf, M. D.; Houk, R. J. T.; Andruszkiewicz, L.; Talin, A. A.; Pikarsky, J.; Choudhury, A.; Gall, K. A.; Hesketh, P. J. Stress-induced Chemical Detection Using Flexible Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2008**, *130* (44), 14404–. (h) Biemmi, E.; Darga, A.; Stock, N.; Bein, T. Direct growth of Cu-3(BTC)(2)(H<sub>2</sub>O)(3)center dot xH(2)O thin films on modified QCM-gold electrodes - Water sorption isotherms. *Microporous Mesoporous Mater.* **2008**, *114* (1–3), 380–386. (i) Yoo, Y.; Jeong, H. K. Rapid fabrication of metal organic framework thin films using microwave-induced thermal deposition. *Chem. Commun.* **2008**, *21*, 2441–2443. (j) Shekhah, C.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; Woll, C. Step-by-step route for the synthesis of metal-organic frameworks. *J. Am. Chem. Soc.* **2007**, *129* (49), 15118–15119. (k) Gascon, J.; Aguado, S.; Kapteijn, F. Manufacture of dense coatings of Cu-3(BTC)(2) (HKUST-1) on alpha-alumina. *Microporous Mesoporous Mater.* **2008**, *113* (1–3), 132–138. (l) Ameloot, R.; Pandey, L.; Van der Auweraer, M.; Alaerts, L.; Sels, B. F.; De Vos, D. E. Patterned film growth of metal-organic frameworks based on galvanic displacement. *Chem. Commun.* **2010**, *46* (21), 3735–3737. (m) Yoo, Y.; Jeong, H. K. Hetero-epitaxial Growth of Isorecticular Metal-Organic Frameworks and Their Hybrid Films. *Cryst. Growth Des.* **2010**, *10* (3), 1283–1288. (n) Scherb, C.; Schodel, A.; Bein, T. Directing the structure of metal-organic frameworks by oriented surface growth on an organic monolayer. *Angew. Chem., Int. Ed.* **2008**, *47* (31), 5777–5779. (o) Zou, X. Q.; Zhu, G. S.; Zhang, F.; Guo, M. Y.; Qiu, S. L. Facile fabrication of metal-organic framework films promoted by colloidal seeds on various substrates. *CrystEngComm* **2010**, *12* (2), 352–354. (p) Horcajada, P.; Serre, C.; Grosso, D.; Boissiere, C.; Perruchas, S.; Sanchez, C.; Ferey, G. Colloidal Route for Preparing Optical Thin Films of Nanoporous Metal-Organic Frameworks. *Adv. Mater.* **2009**, *21* (19), 1931–1935. (q) Patricia, H.; Christian, S.; David, G.; Cedric, B. E.; Sandrine, P.; Clement, S.; Ferey, G. Colloidal Route for Preparing Optical Thin Films of Nanoporous Metal-Organic Frameworks. *Adv. Mater.* **2009**, *21* (19), 1931–1935. (r) Lu, G.; Hupp, J. T. Metal-Organic Frameworks as Sensors: A ZIF-8 Fabry-Perot Device as a Selective Sensor for Chemical Vapors and Gases. *J. Am. Chem. Soc.* **2010**, *132* (23), 7832–7833. (15) (a) Li, Y.-S.; Bux, H. G.; Feldhoff, A.; Li, G.-L.; Yang, W. S.; Caro, J. Controllable Synthesis of Metal-Organic Frameworks: From MOF Nanorods to Oriented MOF Membranes. *Adv. Mater.* **2010**, [Online] DOI: 10.1002/adma.201000857. (b) Yoo, Y.; Lai, Z. P.; Jeong, H. K. Fabrication of MOF-5 membranes using microwave-induced rapid seeding and solvothermal secondary growth. *Microporous Mesoporous Mater.* **2009**, *123* (1–3), 100–106. (c) Liu, Y. Y.; Ng, Z. F.; Khan, E. A.; Jeong, H. K.; Ching, C. B.; Lai, Z. P. Synthesis of

continuous MOF-5 membranes on porous alpha-alumina substrates. *Microporous Mesoporous Mater.* **2009**, *118* (1–3), 296–301. (d) Guo, H.; Zhu, G.; Hewitt, I. J.; Qiu, S. “Twin Copper Source” Growth of Metal-organic Framework Membrane: Cu<sub>3</sub>(BTC)<sub>2</sub> with High Permeability and Selectivity for Recycling H<sub>2</sub>. *J. Am. Chem. Soc.* **2009**, *131* (5), 1646–1647. (e) Bux, H.; Liang, F. Y.; Li, Y. S.; Cravillon, J.; Wiebcke, M.; Caro, J. Zeolitic Imidazolate Framework Membrane with Molecular Sieving Properties by Microwave-Assisted Solvothermal Synthesis. *J. Am. Chem. Soc.* **2009**, *131* (44), 16000–16001. (f) Li, Y. S.; Liang, F. Y.; Bux, H.; Feldhoff, A.; Yang, W. S.; Caro, J. Molecular Sieve Membrane: Supported Metal-Organic Framework with High Hydrogen Selectivity. *Angew. Chem., Int. Ed.* **2010**, *49* (3), 548–551. (g) Li, Y. S.; Liang, F. Y.; Bux, H. G.; Yang, W. S.; Caro, J. Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation. *J. Membr. Sci.* **2010**, *354* (1–2), 48–54. (h) Venna, S. R.; Carreon, M. A. Highly Permeable Zeolite Imidazolate Framework-8 Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation. *J. Am. Chem. Soc.* **2010**, *132* (1), 76–78. (i) Liu, Y.; Hu, E.; Khan, E. A.; Lai, Z. Synthesis and characterization of ZIF-69 membranes and separation for CO<sub>2</sub>/CO mixture. *J. Membr. Sci.* **2010**, *353* (1–2), 36–40. (j) Guerrero, V. V.; Yoo, Y.; McCarthy, M. C.; Jeong, H. K. HKUST-1 Membranes on Porous Supports using Secondary Growth. *J. Mater. Chem.* **2010**, *20*, 3938–3943. (k) Huang, A.; Bux, H.; Steinbach, F.; Caro, J. Molecular-Sieve Membrane with Hydrogen Permselectivity: ZIF-22 in LTA Topology Prepared with 3-Aminopropyltriethoxysilane as Covalent Linker. *Angew. Chem., Int. Ed.* **2010**, *49* (29), 4958–4961. (l) Takamizawa, S.; Takasaki, Y.; Miyake, R. Single-Crystal Membrane for Anisotropic and Efficient Gas Permeation. *J. Am. Chem. Soc.* **2010**, *132* (9), 2862–2863. (m) Ranjan, R.; Tsapatsis, M. Microporous Metal Organic Framework Membrane on Porous Support Using the Seeded Growth Method. *Chem. Mater.* **2009**, *21* (20), 4920–4924. (n) McCarthy, M. C.; Guerrero, V. V.; Barnett, G.; Jeong, H. K. Synthesis of Zeolitic Imidazolate Framework Films and Membranes with Controlled Microstructure. *Langmuir* **2010**, *26* (18), 14636–14641. (o) Huang, A.; Dou, W.; Caro, J. Steam-stable zeolitic imidazolate framework ZIF-90 membrane with hydrogen selectivity through covalent functionalization. *J. Am. Chem. Soc.* **2010**, *132* (44), 15562–15564. (p) Hu, Y.; Dong, X.; Nan, J.; Jin, W.; Ren, X.; Xu, N.; Lee, Y. M. Metal-organic framework membranes fabricated via reactive seeding. *Chem. Commun.* **2011**, *47*, 737–739.

(16) Mitzi, D. B. Thin-film deposition of organic-inorganic hybrid materials. *Chem. Mater.* **2001**, *13* (10), 3283–3298.

(17) (a) Shekhah, O.; Liu, J.; Fischer, R. A.; Woll, C. MOF thin films: existing and future applications Part of the themed issue on hybrid materials. *Chem. Soc. Rev.* **2011**, *40* (2), 1081–1106. (b) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1477–1504. (c) Czaja, A. U.; Trukhan, N.; Muller, U. Industrial applications of metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1284–1293. (d) Long, J. R.; Yaghi, O. M. The pervasive chemistry of metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1213–1214. (e) Carne, A.; Carbonell, C.; Imaz, I.; Maspocho, D. Nanoscale metal-organic materials. *Chem. Soc. Rev.* **2011**, *40* (1), 291–305. (f) Kitagawa, S.; Kitaura, R.; Noro, S.-i. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43* (18), 2334–2375. (g) Jian Rong, L.; Yuguang, M.; M, C. M.; Julian, S.; Jiamei, Y.; Hae Kwon, J.; Perla, B. B.; Hong Cai, Z. Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks. *Coord. Chem. Rev.* **2011**, *255* (15–16), 1791–1823.

(18) (a) Haldoupis, E.; Nair, S.; Sholl, D. S. Efficient Calculation of Diffusion Limitations in Metal Organic Framework Materials: A Tool for Identifying Materials for Kinetic Separations. *J. Am. Chem. Soc.* **2010**, *132* (21), 7528–7539. (b) Zacher, D.; Liu, J. N.; Huber, K.; Fischer, R. A. Nanocrystals of [Cu-3(btc)(2)] (HKUST-1): a combined time-resolved light scattering and scanning electron microscopy study. *Chem. Commun.* **2009**, *9*, 1031–1033.

(19) Murray, L. J.; Dinca, M.; Long, J. R. Hydrogen storage in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1294–1314.

- (20) Hayashi, H.; Cote, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. Zeolite imidazolate frameworks. *Nat. Mater.* **2007**, *6* (7), 501–506.
- (21) Fairen-Jimenez, D.; Moggach, S. A.; Wharmby, M. T.; Wright, P. A.; Parsons, S.; Düren, T. Opening the Gate: Framework Flexibility in ZIF-8 Explored by Experiments and Simulations. *J. Am. Chem. Soc.* **2011**, *133* (23), 8900–8902.
- (22) (a) Yaghi, O.; O'Keeffe, M.; Ockwig, N.; Chae, H.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. *Nature* **2003**, *423* (6941), 705–714. (b) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. Modular chemistry: Secondary building units as a basis for the design of highly porous and robust metal-organic carboxylate frameworks. *Acc. Chem. Res.* **2001**, *34* (4), 319–330. (c) Yaghi, O. M.; Li, H. L. Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels. *J. Am. Chem. Soc.* **1995**, *117* (41), 10401–10402. (d) Rowsell, J. L. C.; Yaghi, O. M. Metal-organic frameworks: a new class of porous materials. *Microporous Mesoporous Mater.* **2004**, *73* (1–2), 3–14. (e) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. Design and Synthesis of Metal-Organic Frameworks Using Metal-Organic Polyhedra as Supermolecular Building Blocks. *Chem. Soc. Rev.* **2009**, *38*, 1400–1417.
- (23) Surble, S.; Millange, F.; Serre, C.; Férey, G.; Walton, R. I. *Chem. Commun.* **2006**, 1518–1520.
- (24) (a) Ramanan, A.; Whittingham, M. S. How Molecules Turn into Solids: the Case of Self-Assembled Metal-Organic Frameworks. *Cryst. Growth Des.* **2006**, *6* (11), 2419–2421. (b) Michaelides, A.; Skoulik, S. Crystallographic Evidence for Ionic Molecular Building Blocks in the Assembly of a Two Dimensional Metal-Organic Framework. *Cryst. Growth Des.* **2009**, *9* (12), 4998–5002.
- (25) Gispert, J. R. *Coordination Chemistry*; Wiley-VCH: New York, 2008.
- (26) Irving, H. M. N. H.; Williams, R. J. P. The stability of transition-metal complexes. *J. Chem. Soc.* **1953**, 3192–3210.
- (27) Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*; Pearson Prentice Hall: Upper Saddle River, NJ, 2008.
- (28) (a) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn<sub>4</sub>O(1,4-benzenedicarboxylate)<sub>3</sub> (MOF-5). *J. Am. Chem. Soc.* **2007**, *129*, 14176–14177. (b) Wu, T.; Shen, L.; Luebbers, M.; Hu, C.; Chen, Q.; Ni, Z.; Masel, R. I. Enhancing the stability of metal-organic frameworks in humid air by incorporating water repellent functional groups. *Chem. Commun.* **2010**, *46*, 6120–6122.
- (29) Pearson, R. J. Hard Acids and Soft Bases. *J. Am. Chem. Soc.* **1963**, *85* (22), 3533–3539.
- (30) Thomas, G. *Medicinal Chemistry: An Introduction*, 2nd edition; Wiley: New York, 2007.
- (31) Zhang, J.-P.; Zhu, A.-X.; Lin, R.-B.; Qi, X.-L.; Chen, X.-M. Pore Surface Tailored SOD-Type Metal-Organic Zeolites. *Adv. Mater.* **2011**, *23* (10), 1268–1271.
- (32) (a) Huang, A.; Caro, J. Covalent Post-Functionalization of Zeolitic Imidazolate Framework ZIF-90 Membrane for Enhanced Hydrogen Selectivity. *Angew. Chem., Int. Ed.* **2011**, *50* (21), 4979–4982. (b) Aguado, S.; Canivet, J.; Farrusseng, D. Engineering structured MOF at nano and macroscales for catalysis and separation. *J. Mater. Chem.* **2011**, *21* (21), 7582–7588.
- (33) Yaghi, O. M. Metal-organic Frameworks: A tale of two entanglements. *Nat. Mater.* **2007**, *6* (2), 92–93.
- (34) Moggach, S. A.; Bennett, T. D.; Cheetham, A. K. The Effect of Pressure on ZIF-8: Increasing Pore Size with Pressure and the Formation of a High-Pressure Phase at 1.47 GPa. *Angew. Chem., Int. Ed.* **2009**, *48* (38), 7087–7089.
- (35) Nijem, N.; Thissen, P.; Yao, Y.; Longo, R. C.; Roodenko, K.; Wu, H.; Zhao, Y.; Cho, K.; Li, J.; Langreth, D. C.; Chabal, Y. J. Understanding the Preferential Adsorption of CO<sub>2</sub> over N<sub>2</sub> in a Flexible Metal–Organic Framework. *J. Am. Chem. Soc.* **2011**.
- (36) (a) Tranchemontagne, D. J.; Hunt, J. R.; Yaghi, O. M. Room temperature synthesis of metal-organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0. *Tetrahedron* **2008**, *64* (36), 8553–8557. (b) Pan, Y.; Liu, Y.; Zeng, G.; Zhao, L.; Lai, Z. Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system. *Chem. Commun.* **2011**, *47* (7), 2071–2073.
- (37) Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. A chemically functionalizable nanoporous material [Cu-3(TMA)(2)(H<sub>2</sub>O)(3)](n). *Science* **1999**, *283* (5405), 1148–1150.
- (38) Zhao, Y.; Padmanabhan, M.; Gong, Q.; Tsumori, N.; Xu, Q.; Li, J. CO catalytic oxidation by a metal organic framework containing high density of reactive copper sites. *Chem. Commun.* **2011**, *47* (22), 6377–6379.
- (39) Aguado, S.; Bergeret, G.; Titus, M. P.; Moizan, V.; Nieto-Draghi, C.; Bats, N.; Farrusseng, D. Guest-induced gate-opening of a zeolite imidazolate framework. *New J. Chem.* **2011**, *35* (3), 546–550.
- (40) Gücüyener, C.; van den Bergh, J.; Gascon, J.; Kapteijn, F. Ethane/Ethene Separation Turned on Its Head: Selective Ethane Adsorption on the Metal–Organic Framework ZIF-7 through a Gate-Opening Mechanism. *J. Am. Chem. Soc.* **2010**, *132* (50), 17704–17706.
- (41) *Fundamentals of Inorganic Membrane Science and Technology*; Elsevier: New York, 1996; Vol. 4.
- (42) (a) Bertazzo, S.; Rezwani, K. Control of  $\alpha$ -Alumina Surface Charge with Carboxylic Acids. *Langmuir* **2009**, *26* (5), 3364–3371. (b) Aguado, S.; Canivet, J.; Farrusseng, D. Facile shaping of an imidazolate-based MOF on ceramic beads for adsorption and catalytic applications. *Chem. Commun.* **2010**, *46* (42), 7999–8001.
- (43) Nguyen, J. G.; Cohen, S. M. Moisture-Resistant and Superhydrophobic Metal-Organic Frameworks Obtained via Postsynthetic Modification. *J. Am. Chem. Soc.* **2010**, *132*, 4560–4561.
- (44) Yoo, Y.; Varela-Guerrero, V.; Jeong, H.-K. Isoreticular Metal–Organic Frameworks and Their Membranes with Enhanced Crack Resistance and Moisture Stability by Surfactant-Assisted Drying. *Langmuir* **2011**, *27* (6), 2652–2657.
- (45) Millward, A. R.; Yaghi, O. M. Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *J. Am. Chem. Soc.* **2005**, *127* (51), 17998–17999.
- (46) Wang, Z.; Cohen, S. M. Postsynthetic Covalent Modification of a Neutral Metal-Organic Framework. *J. Am. Chem. Soc.* **2007**, *129* (41), 12368–12369.
- (47) Ma, D.; Li, Y.; Li, Z. Tuning the moisture stability of metal-organic frameworks by incorporating hydrophobic functional groups at different positions of ligands. *Chem. Commun.* **2011**, *47* (26), 7377–7379.
- (48) Brinker, C. J.; Scherer, G. W. *Sol-gel science: the physics and chemistry of sol-gel processing*; Academic Press, Inc.: New York, 1990.
- (49) Hu, Y.; Dong, X.; Nan, J.; Jin, W.; Ren, X.; Xu, N.; Lee, Y. M. Metal-organic framework membranes fabricated via reactive seeding. *Chem. Commun.* **2011**, *47* (2), 737–739.
- (50) Aguado, S.; Nicolas, C.-H.; Moizan-Basle, V.; Nieto, C.; Amrouche, H.; Bats, N.; Audebrand, N.; Farrusseng, D. Facile synthesis of an ultramicroporous MOF tubular membrane with selectivity towards CO<sub>2</sub>. *New J. Chem.* **2011**, *35* (1), 41–44.
- (51) Centrone, A.; Yang, Y.; Speakman, S.; Bromberg, L.; Rutledge, G. C.; Hatton, T. A. Growth of Metal–Organic Frameworks on Polymer Surfaces. *J. Am. Chem. Soc.* **2010**, *132* (44), 15687–15691.
- (52) (a) Lovallo, M. C.; Gouzinis, A.; Tsapatsis, M. Synthesis and characterization of oriented MFI membranes prepared by secondary growth. *Aiche J.* **1998**, *44* (8), 1903–1913. (b) Lai, Z. P.; Tsapatsis, M.; Nicolich, J. R. Siliceous ZSM-5 membranes by secondary growth of b-oriented seed layers. *Adv. Funct. Mater.* **2004**, *14* (7), 716–729. (c) Lee, I.; Buday, J. L.; Jeong, H. K. mu-Tiles and mortar approach: A simple technique for the facile fabrication of continuous b-oriented MFI silicalite-1 thin films. *Microporous Mesoporous Mater.* **2009**, *122* (1–3), 288–293.
- (53) Cravillon, J.; Munzer, S.; Lohmeier, S. J.; Feldhoff, A.; Huber, K.; Wiebeck, M. Rapid Room-Temperature Synthesis and Characterization of Nanocrystals of a Prototypical Zeolitic Imidazolate Framework. *Chem. Mater.* **2009**, *21* (8), 1410–1412.
- (54) Lai, Z. P.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. Microstructural optimization of a zeolite membrane for organic vapor separation. *Science* **2003**, *300* (5618), 456–460.

- (55) Snyder, M. A.; Tsapatsis, M. Hierarchical nanomanufacturing: From shaped zeolite nanoparticles to high-performance separation membranes. *Angew. Chem., Int. Ed.* **2007**, *46* (40), 7560–7573.
- (56) Lee, J. S.; Kim, J. H.; Lee, Y. J.; Jeong, N. C.; Yoon, K. B. Manual assembly of microcrystal monolayers on substrates. *Angew. Chem., Int. Ed.* **2007**, *46* (17), 3087–3090.
- (57) Ni, Z.; Masel, R. I. Rapid Production of Metal–Organic Frameworks via Microwave-Assisted Solvothermal Synthesis. *J. Am. Chem. Soc.* **2006**, *128* (38), 12394–12395.
- (58) Carson, C. G.; Brown, A. J.; Sholl, D. S.; Nair, S. Sonochemical Synthesis and Characterization of Submicrometer Crystals of the Metal–Organic Framework Cu<sub>3</sub>(hfpbb)(H<sub>2</sub>hfpbb)<sub>0.5</sub>. *Cryst. Growth Des.* **2011**, *11* (10), 4505–4510.
- (59) Bae, T.-H.; Lee, J. S.; Qiu, W.; Koros, W. J.; Jones, C. W.; Nair, S.; High-Performance Gas-Separation, A Membrane Containing Submicrometer-Sized Metal–Organic Framework Crystals. *Angew. Chem., Int. Ed.* **2010**, *49* (51), 9863–9866.
- (60) Nune, S. K.; Thallapally, P. K.; Dohnalkova, A.; Wang, C.; Liu, J.; Exarhos, G. J. Synthesis and properties of nano zeolitic imidazolate frameworks. *Chem. Commun.* **2010**, *46* (27), 4878–4880.
- (61) (a) Li, Z.-Q.; Qiu, L.-G.; Xu, T.; Wu, Y.; Wang, W.; Wu, Z.-Y.; Jiang, X. Ultrasonic synthesis of the microporous metal–organic framework Cu<sub>3</sub>(BTC)<sub>2</sub> at ambient temperature and pressure: An efficient and environmentally friendly method. *Mater. Lett.* **2009**, *63* (1), 78–80. (b) Biemmi, E.; Scherb, C.; Bein, T. Oriented Growth of the Metal Organic Framework Cu<sub>3</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>·xH<sub>2</sub>O Tunable with Functionalized Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2007**, *129* (26), 8054–8055.
- (62) (a) Ma, M.; Zacher, D.; Zhang, X.; Fischer, R. A.; Metzler-Nolte, N. A Method for the Preparation of Highly Porous, Nanosized Crystals of Isorecticular Metal–Organic Frameworks. *Cryst. Growth Des.* **2010**, *11* (1), 185–189. (b) Perez, E. V.; Balkus, K. J., Jr.; Ferraris, J. P.; Musselman, I. H. Mixed-matrix membranes containing MOF-5 for gas separations. *J. Membr. Sci.* **2009**, *328* (1–2), 165–173.
- (63) Huang, L.; Wang, H.; Chen, J.; Wang, Z.; Sun, J.; Zhao, D.; Yan, Y. Synthesis, morphology control, and properties of porous metal–organic coordination polymers. *Microporous Mesoporous Mater.* **2003**, *58* (2), 105–114.
- (64) Zhang, Y.; Musselman, I. H.; Ferraris, J. P.; Balkus, K. J., Jr. Gas permeability properties of Matrimid membranes containing the metal-organic framework Cu–BPY–HFS. *J. Membr. Sci.* **2008**, *313* (1–2), 170–181.
- (65) (a) Pan, L.; Sander, M. B.; Huang, X. Y.; Li, J.; Smith, M.; Bittner, E.; Bockrath, B.; Johnson, J. K. Microporous metal organic materials: Promising candidates as sorbents for hydrogen storage. *J. Am. Chem. Soc.* **2004**, *126* (5), 1308–1309. (b) Pan, L.; Olson, D. H.; Ciemmolonski, L. R.; Heddy, R.; Li, J. Separation of hydrocarbons with a microporous metal-organic framework. *Angew. Chem., Int. Ed.* **2006**, *45* (4), 616–619.
- (66) Van der Drift, A. Evolutionary Selection, A Principle Governing Growth Orientation in Vapour-Deposited Layers. *Philips Res. Rep.* **1967**, *22*, 267–288.
- (67) Bux, H.; Feldhoff, A.; Cravillon, J.; Wiebcke, M.; Li, Y.-S.; Caro, J. Oriented Zeolitic Imidazolate Framework-8 Membrane with Sharp H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>Molecular Sieve Separation. *Chem. Mater.* **2011**, *23* (8), 2262–2269.
- (68) Shekha, O.; Hirai, K.; Wang, H.; Uehara, H.; Kondo, M.; Diring, S.; Zacher, D.; Fischer, R. A.; Sakata, O.; Kitagawa, S.; Furukawa, S.; Woll, C. MOF-on-MOF heteroepitaxy: perfectly oriented [Zn<sub>2</sub>(ndc)<sub>2</sub>(dabco)]<sub>n</sub> grown on [Cu<sub>2</sub>(ndc)<sub>2</sub>(dabco)]<sub>n</sub> thin films. *Dalton Trans.* **2011**, *40* (18), 4954–4958.
- (69) Nan, J.; Dong, X.; Wang, W.; Jin, W.; Xu, N. Step-by-Step Seeding Procedure for Preparing HKUST-1 Membrane on Porous  $\alpha$ -Alumina Support. *Langmuir* **2011**, *27* (8), 4309–4312.
- (70) Bétard, A.; Bux, H.; Henke, S.; Zacher, D.; Caro, J.; Fischer, R. A. Fabrication of a CO<sub>2</sub>-selective membrane by stepwise liquid-phase deposition of an alkylether functionalized pillared-layered metal-organic framework [Cu<sub>2</sub>L<sub>2</sub>P]<sub>n</sub> on a macroporous support. *Microporous Mesoporous Mater.* **2012**, *150* (0), 76–82.
- (71) Arslan, H. K.; Shekha, O.; Wohlgemuth, J.; Franzreb, M.; Fischer, R. A.; Wöll, C. High-Throughput Fabrication of Uniform and Homogenous MOF Coatings. *Adv. Funct. Mater.* **2011**.
- (72) Yao, J.; Dong, D.; Li, D.; He, L.; Xu, G.; Wang, H. Contradiffusion synthesis of ZIF-8 films on a polymer substrate. *Chem. Commun.* **2011**, *47* (9), 2559–2561.
- (73) Wang, Z.; Cohen, S. M. Postsynthetic modification of metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1315–1329.
- (74) Yang, T.; Xiao, Y.; Chung, T.-S. Poly-/metal-benzimidazole nano-composite membranes for hydrogen purification. *Energy Environ. Sci.* **2011**, *4* (10), 4171–4180.
- (75) Car, A.; Stropnik, C.; Peinemann, K.-V. Hybrid membrane materials with different metal–organic frameworks (MOFs) for gas separation. *Desalination* **2006**, *200* (1–3), 424–426.
- (76) Basu, S.; Cano-Odena, A.; Vankelecom, I. F. J. MOF-containing mixed-matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> binary gas mixture separations. *Sep. Purif. Technol.* **2011**, *81* (1), 31–40.
- (77) Ordoñez, M. J. C.; Balkus, K. J., Jr.; Ferraris, J. P.; Musselman, I. H. Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes. *J. Membr. Sci.* **2010**, *361* (1–2), 28–37.
- (78) Hu, J.; Cai, H.; Ren, H.; Wei, Y.; Xu, Z.; Liu, H.; Hu, Y. Mixed-Matrix Membrane Hollow Fibers of Cu<sub>3</sub>(BTC)<sub>2</sub> MOF and Polyimide for Gas Separation and Adsorption. *Ind. Eng. Chem. Res.* **2010**, *49* (24), 12605–12612.
- (79) Basu, S.; Cano-Odena, A.; Vankelecom, I. F. J. Asymmetric Matrimid/[Cu<sub>3</sub>(BTC)<sub>2</sub>] mixed-matrix membranes for gas separations. *J. Membr. Sci.* **2010**, *362* (1–2), 478–487.
- (80) Basu, S.; Maes, M.; Cano-Odena, A.; Alaerts, L.; De Vos, D. E.; Vankelecom, I. F. J. Solvent resistant nanofiltration (SRNF) membranes based on metal-organic frameworks. *J. Membr. Sci.* **2009**, *344* (1–2), 190–198.
- (81) Pan, Y.; Lai, Z. Sharp separation of C<sub>2</sub>/C<sub>3</sub> hydrocarbon mixtures by zeolitic imidazolate framework-8 (ZIF-8) membranes synthesized in aqueous solutions. *Chem. Commun.* **2011**, *47* (37), 10275–10277.
- (82) Caro, J.; Noack, M., Chapter 1 - Zeolite Membranes – Status and Prospective. In *Advances in Nanoporous Materials*; Stefan, E., Ed.; Elsevier: New York, 2010; Vol. 1, pp 1–96.
- (83) Li, K. H.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H. W.; Zeng, H. P.; Li, J. Zeolitic Imidazolate Frameworks for Kinetic Separation of Propane and Propene. *J. Am. Chem. Soc.* **2009**, *131* (30), 10368–10369.
- (84) Bux, H.; Chmelik, C.; Krishna, R.; Caro, J. Ethene/ethane separation by the MOF membrane ZIF-8: Molecular correlation of permeation, adsorption, diffusion. *J. Membr. Sci.* **2011**, *369* (1–2), 284–289.
- (85) (a) Ma, S. Q.; Sun, D. F.; Wang, X. S.; Zhou, H. C. A mesh-adjustable molecular sieve for general use in gas separation. *Angew. Chem., Int. Ed.* **2007**, *46* (14), 2458–2462. (b) Ma, S. Q.; Sun, D. F.; Yuan, D. Q.; Wang, X. S.; Zhou, H. C. Preparation and Gas Adsorption Studies of Three Mesh-Adjustable Molecular Sieves with a Common Structure. *J. Am. Chem. Soc.* **2009**, *131* (18), 6445–6451.
- (86) Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacobinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules. *Nature* **2001**, *412* (6848), 720–724.
- (87) Ma, L. Q.; Abney, C.; Lin, W. B. Enantioselective catalysis with homochiral metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1248–1256.
- (88) (a) Li, J. R.; Tao, Y.; Yu, Q.; Bu, X. H.; Sakamoto, H.; Kitagawa, S. Selective gas adsorption and unique structural topology of a highly stable guest-free zeolite-type MOF material with N-rich chiral open channels. *Chem.—Eur. J.* **2008**, *14* (9), 2771–2776. (b) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. B. Homochiral porous metal-organic framework for highly enantioselective heterogeneous asymmetric catalysis. *J. Am. Chem. Soc.* **2005**, *127* (25), 8940–8941.
- (89) Tanabe, K. K.; Wang, Z. Q.; Cohen, S. M. Systematic functionalization of a metal-organic framework via a postsynthetic modification approach. *J. Am. Chem. Soc.* **2008**, *130* (26), 8508–8517.

(90) Yang, S.; Lin, X.; Blake, A. J.; Walker, G. S.; Hubberstey, P.; Champness, N. R.; Schröder, M. Cation-induced kinetic trapping and enhanced hydrogen adsorption in a modulated anionic metal–organic framework. *Nat. Chem.* **2009**, *1* (6), 487–493.

(91) An, J.; Geib, S. J.; Rosi, N. L. Cation-Triggered Drug Release from a Porous Zinc–Adeninate Metal–Organic Framework. *J. Am. Chem. Soc.* **2009**, *131* (24), 8376–8377.

(92) An, J.; Rosi, N. L. Tuning MOF CO<sub>2</sub> Adsorption Properties via Cation Exchange. *J. Am. Chem. Soc.* **2010**, *132* (16), 5578–5579.

(93) Sholl, D. S. Metal-organic frameworks: A porous maze. *Nat. Chem.* **2011**, *3* (6), 429–430.

(94) Hibbe, F.; Chmelik, C.; Heinke, L.; Pramanik, S.; Li, J.; Ruthven, D. M.; Tzoulaki, D.; Kärger, J. R. The Nature of Surface Barriers on Nanoporous Solids Explored by Microimaging of Transient Guest Distributions. *J. Am. Chem. Soc.* **2011**, *133* (9), 2804–2807.

(95) (a) Bonilla, G.; Tsapatsis, M.; Vlachos, D. G.; Xomeritakis, G. Fluorescence confocal microscopy imaging of the grain boundary structure of zeolite MFI membranes made by secondary (seeded) growth. *J. Membr. Sci.* **2001**, *182* (1–2), 103–109. (b) Snyder, M. A.; Lai, Z.; Tsapatsis, M.; Vlachos, D. G. Combining simultaneous reflectance and fluorescence imaging with SEM for conclusive identification of polycrystalline features of MFI membranes. *Microporous Mesoporous Mater.* **2004**, *76* (1–3), 29–33. (c) Snyder, M. A.; Vlachos, D. G. Nanopatterned standards for improving the quantitative capability of laser scanning confocal microscopy for materials characterization. *Microporous Mesoporous Mater.* **2007**, *102* (1–3), 101–110.

(96) Keskin, S.; Sholl, D. S. Assessment of a Metal–Organic Framework Membrane for Gas Separations Using Atomically Detailed Calculations: CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>Mixtures in MOF-5. *Ind. Eng. Chem. Res.* **2008**, *48* (2), 914–922.

(97) Watanabe, T.; Keskin, S.; Nair, S.; Sholl, D. S. Computational identification of a metal organic framework for high selectivity membrane-based CO<sub>2</sub>/CH<sub>4</sub> separations: Cu(hfipbb)(H<sub>2</sub>hfipbb)<sub>0.5</sub>. *Phys. Chem. Chem. Phys.* **2009**, *11* (48), 11389–11394.

(98) McLeary, E. E.; Jansen, J. C.; Kapteijn, F. Zeolite based films, membranes and membrane reactors: Progress and prospects. *Microporous Mesoporous Mater.* **2006**, *90* (1–3), 198–220.

(99) Li, S.; Falconer, J. L.; Noble, R. D. Improved SAPO-34 Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separations. *Adv. Mater.* **2006**, *18* (19), 2601–2603.