

Mixed-Matrix Membranes

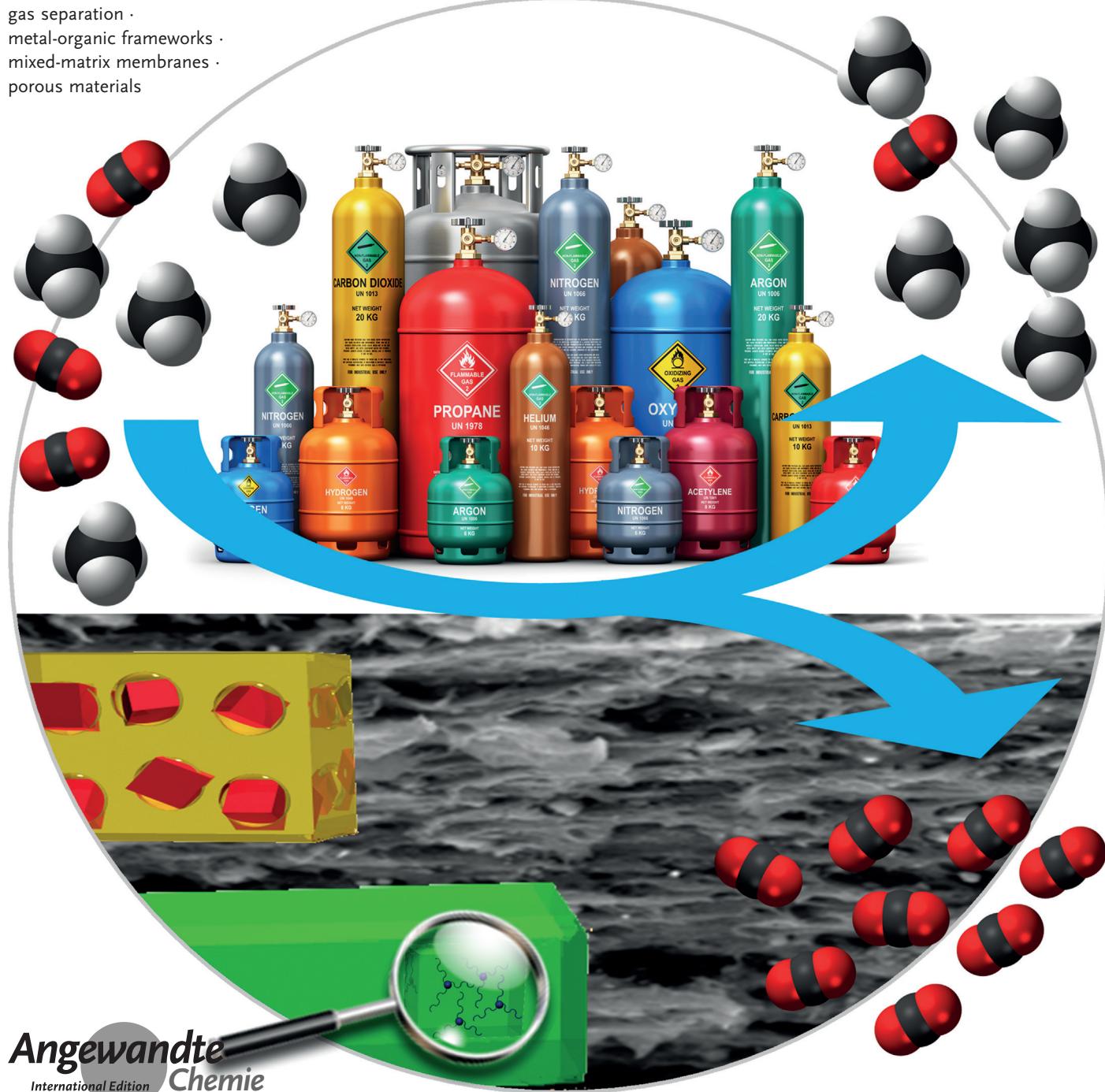
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Mixed-Matrix Membranes

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Research into extended porous materials such as metal-organic frameworks (MOFs) and porous organic frameworks (POFs), as well as the analogous metal-organic polyhedra (MOPs) and porous organic cages (POCs), has blossomed over the last decade. Given their chemical and structural variability and notable porosity, MOFs have been proposed as adsorbents for industrial gas separations and also as promising filler components for high-performance mixed-matrix membranes (MMMs). Research in this area has focused on enhancing the chemical compatibility of the MOF and polymer phases by judiciously functionalizing the organic linkers of the MOF, modifying the MOF surface chemistry, and, more recently, exploring how particle size, morphology, and distribution enhance separation performance. Other filler materials, including POFs, MOPs, and POCs, are also being explored as additives for MMMs and have shown remarkable anti-aging performance and excellent chemical compatibility with commercially available polymers. This Review briefly outlines the state-of-the-art in MOF-MMM fabrication, and the more recent use of POFs and molecular additives.

1. Introduction

Membrane processes are highly advantageous for the chemical industry by allowing energy to be saved during the separation of mixtures commonly encountered during production.^[1] Energy savings of up to 50% of the production costs can be achieved by applying membrane technology.^[1a,b] The membrane processes used in industry include natural gas sweetening (CO_2 removal), hydrogen isolation and recovery (i.e. in cracking processes), and oxygen (medical devices) and nitrogen enrichment from air (as a protecting atmosphere for oxygen-sensitive compounds).^[2] Membrane processes such as vapor recovery systems,^[3] monomer recovery units (e.g. ethylene/ N_2 or propylene/ N_2 separation),^[4] the dehydration of organic solvents, and the removal of larger molecules from organic solvents^[5] have a fast-growing market potential. At

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present, organic polymers are mostly used in the preparation of commercially applied membranes, as they are cheap to produce and easy to process compared with inorganic materials.

Although polymeric membranes have been used in industry for gas separation since the 1980s, they face challenges because of their compromise between gas permeability and selectivity. The well-known Robeson plot (log permeability versus log selectivity), states that as permeability increases, the selectivity of the membranes decreases—the so-called upper bound of membrane performance (Figure 1).^[6] Enormous, ongoing efforts are being undertaken to meet this challenge through the development of new polymeric materials^[7] and membranes of materials such as zeolites,^[8] metal-organic frameworks (MOFs),^[9] carbon molecular sieves,^[10] carbon nanotubes,^[11] and graphenes.^[12]

Permeability and selectivity (“permselectivity”) are the most important membrane parameters that determine the economics of separation processes.^[13] Lower selectivity necessitates more complex, higher cost operations because of multistep processing, while the permeability correlates with the productivity of the membrane and, therefore, determines the area or the number of membrane modules required. Both factors affect the capital expenditure of the process. For example, precombustion separation of H_2/CO_2 ,

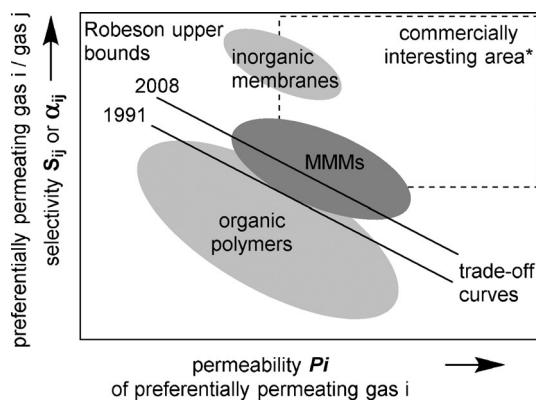


Figure 1. Schematic representation of the relationship between permeability and selectivity, with the 1991 and 2008 Robeson upper bounds shown. * The distance or position of the commercially interesting area relative to the upper bound can vary depending on the separation problem.

oxy-combustion O₂/N₂ separation, and natural gas treatments require highly permeable membranes for large-volume gas-feed streams. Pure MOF membranes, like inorganic zeolite membranes, have very good permselectivity characteristics.^[6,14] The challenges are, however, to develop manufacturing methods that would eventually allow for the reliable preparation of membranes (especially in the case of zeolites and other molecular sieves) and also to maintain the integrity of such membranes during operation (avoid cracks or pin-holes which would result in the loss of separation performance).^[15]

1.1. Mixed-Matrix Membranes

Mixed-matrix membranes (MMMs) are composite membranes made by combining an inorganic or inorganic-organic hybrid material in the form of micro- or nanoparticles (the discrete or dispersed phase; additive or filler) and a polymer matrix (the continuous phase; Scheme 1).^[16] By using two materials with different transport properties, such membranes have the potential to combine synergistically the easy

processability of polymers and the superior gas-separation performance of porous filler materials. MMMs may provide separation properties which can be above the Robeson upper bound^[6] by overcoming the trade-off between the selectivity and permeability that is typical for pure polymer membranes.

Different types of inorganic additives—impermeable and permeable ones—have been used as filler materials.^[16f,j-r,17] In particular, improvements in gas-permeation performance would be expected if nanostructured, highly porous additives such as zeolites or MOFs were used. Since a MMM is the dispersion of filler particles in a polymeric matrix, the properties of both the polymer and filler affect the separation performance.^[16f,j-r] The chemical structure, surface chemistry, particle size distribution, and aspect ratio are other important factors of a filler material.

1.2. Zeolites and MOF Additives—Advantages and Challenges

MOFs offer various advantages over zeolites and are, therefore, promising additives for MMMs.^[18] MOFs are chemically mutable, highly porous materials prepared from the combination of metal ions or metal-oxido clusters and organic ligands. In comparison with purely inorganic zeolites, the chemical diversity of MOF structures can be used to facilitate strong interactions with the polymer bulk material. This is achieved through judicious choice of ligands with appropriate chemical functionalities (Scheme 1a), which allows the formation of micropores between the inorganic and organic phases that cause loss of selectivity, to be reduced.^[16i-r] Furthermore, the chemical mutability of the MOF scaffold can be utilized to provide enhanced adsorption of a particular chemical species and to facilitate improved separation performance. The limited chemical complexity of



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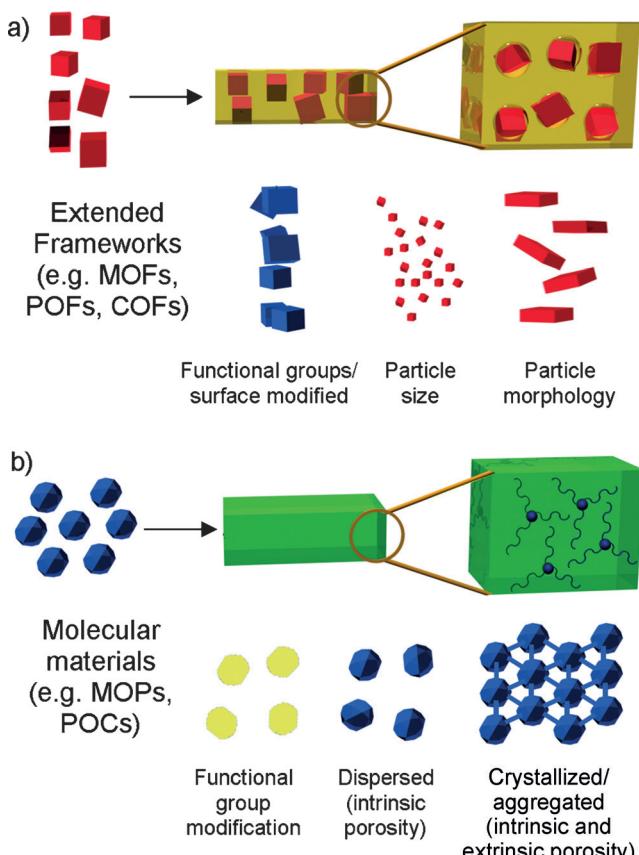
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Scheme 1. Schematic representations of the structure of mixed-matrix membranes containing a) an extended framework or b) molecular additives (fillers). A selection of parameters is shown for the extended frameworks with different possible components for the filler materials, particle sizes, and shapes. For molecular materials, the intimate blending of the continuous and filler phase is indicated by a change in the membrane color and a lack of apparent particles. Similarly, some of the possible permutations for molecular fillers are shown: external functional groups and full dispersion or the possibility of crystallites forming in the polymer phase.

zeolites does not provide the level of tunability displayed by MOFs. In addition to the incorporation of chemical functionality through judicious choice of starting material, MOFs can also be modified post-synthesis (post-synthetic modification, as discussed later) to enhance the separation performance or facilitate stronger polymer-additive interactions. MOFs are not only tunable in terms of their chemical groups, but also their pore volumes, pore shapes, and surface areas, thus enabling them to contribute to either the permeability or selectivity of the MMM.^[19] Many MOFs display considerably higher surface areas and larger pore volumes than zeolites, and can often display performance characteristics commensurate with the polymer matrix.

Despite these significant advantages, the hydrothermal stability of MOFs is a key, but often overlooked, factor for their potential applications in separation. Moisture is a major concern in industrial gas separations, and it is not economically feasible to use completely dry feed-gas streams. Although in some cases synergy between the two MMM

components results in an improved stability of the MOF and polymer,^[20] hydrolytically stable MOF materials are preferred as additives for the preparation of MMMs where a realistic technical application is envisioned.^[21,22] Another challenge includes the scale-up of commercially useful MOF additives to facilitate the formation of the desired membrane modules; this has recently been a research focus.^[23] Zeolites, in comparison, are commercially available materials with a long history of use in industry as a result of their ready availability as well as hydrothermal and chemical stability.

1.3. Alternative Additives

Although MOF fillers have attracted considerable attention, alternative crystalline and noncrystalline organic porous materials, such as covalent organic frameworks (COFs),^[24] and a broad range of porous organic polymers^[25] have also been explored very recently. In contrast to MOFs, these additives, which can be broadly referred to as porous organic frameworks (POFs), have entirely organic extended frameworks with either crystalline (e.g. COFs)^[26] or amorphous structures (e.g. porous aromatic frameworks, PAFs).^[27] The distinct advantages of POFs are their organic structures, which display excellent chemical compatibility with the organic polymer phase, and the chemical stability conferred by irreversible covalent bonding, particularly for materials such as PAFs and polymers of intrinsic microporosity (PIMs). Selected COFs also have chemically robust structures as a consequence of chemical modifications post-synthesis.^[28]

The majority of the MMM additives examined are extended solids which possess strong directional bonding and open architectures with interconnected pores. However, the use of molecular porous additives such as shape-persistent porous organic cage molecules (POCs)^[29] and metal-organic polyhedra (MOPs)^[30] has recently garnered attention (Scheme 1b).^[31] POCs are discrete organic molecules, often formed by a dynamic chemistry approach, that possess a defined cage-like structure that envelops an intrinsic void volume, whereas MOPs are metal-organic variants. Organic cages and MOPs with a range of cage geometries can be procured through judicious control of the molecular precursors. Their highly convergent bonding provides excellent stability and a recent advance of POC chemistry has included all-C–C-bonded variants.^[32] These materials afford ultrahigh porosities common to extended solids, but retain their molecular identity. This allows them to be readily solubilized and in turn to be processed into composite materials.^[24,25] Chemical compatibility between the filler and polymer can facilitate homogeneous dispersion of the MOP or POC within the continuous phase of a MMM. This can be exploited as many POC and MOP series can be prepared with an identical cage topology but diverse exterior functionality. Similar to their extended porous analogues such as MOFs and COFs, discrete porous materials can also be carefully tuned to achieve exceptional performance in gas separations.

1.4. Overview and Scope

This Review outlines the state-of-the-art in the fabrication of MOF-MMMs, examining how the chemical functionality of both the porous filler additive and organic chemical matrix combine to produce high-performance MMMs. Newer aspects of MOF-MMMs, particularly the role of MOF particle size, distribution, and importantly morphology will also be examined, as will the role of the MOF surface and post-synthetic modification. New composites with higher filler compositions or greater integration (e.g. so-called polyMOFs) between a crystalline MOF and the organic polymer component will also be discussed.

Additional sections of the Review will assess the use of porous organic frameworks and molecular additives. Materials such as COFs, POCs, and MOPs provide potentially greater chemical compatibility with the organic polymer of a MMM than do MOF fillers. Finally, future challenges in the field will be considered, with a view to developing applications for these bespoke composites. To assist the reader, some general considerations of membrane performance and a glossary of polymer and selected filler structures are given in the Supporting Information.

2. Emerging Directions

2.1. MOF Inclusion—Significant Strategies

The identification of MOFs as excellent fillers with great potential because of their high porosity, tunable pore networks, and chemical variability of their structures^[33c] has led to MOF-MMMs being intensively investigated.^[16c, 18a, 33] These properties provide opportunities to enhance the performance or avoid defects at the polymer/particle interface, which result in loss of separation performance. Although most current studies of MOF-based MMMs are fundamental in nature, directed toward understanding the interactions and processes which occur at the phase interface, they will ultimately assist the development of materials for industrial application. Emerging aspects of MMM fabrication will be examined in the following sections, with a focus on recent, significant developments concerning MOFs (linker functionalization, surface modification, and post-synthetically modified MOFs, polyMOFs) as well as the choice of the polymer continuous phase. An overview of newer aspects of particle size and shape control in the fabrication of MOF-MMMs is also provided. Overall, these examples will demonstrate how separation performance can be advanced through the incorporation of compositionally and morphologically designed MOF additives.

2.1.1. Organic Linkers with Functional Groups

Depending on the type of gas separation, MOFs which have polar functional groups on their linkers can give rise to several different improvements in the performance of the MOF-MMM.^[34] The interactions of the quadrupolar gas CO₂ with the linkers in MOFs can be enhanced by introducing

NH₂ and SO₃H groups in chemically stable MOFs such as MIL-125(Ti)-NH₂^[35] and MIL-101(Cr)-SO₃H.^[36] Amine-functionalized linkers are a common focus because of their preferential adsorption of the weakly acidic CO₂. DFT also predicts that polar functional groups such as OH, NO₂, and NH₂ would be advantageous for the separation of polar gases.^[37] A second way in which the functionality of the organic linker can be utilized is to achieve better compatibility with the polymer matrix and to enhance the morphology of the polymer/particle interface. Potential hydrogen bonding in MMMs between the polymer backbone and functional groups on the surface of the MOF filler particle can lead to increased compatibility and improvements, as seen in the gas separation properties of MMMs based on the amine-containing MOFs UiO-66-NH₂, MOF-199-NH₂,^[16b] MIL-53(Al)-NH₂,^[16a,r,36] and MIL-101(Al)-NH₂.^[38]

Detrimental performance can also be encountered when a titanium-based and amine-functionalized MIL-125(Ti)-NH₂ (Ti₈O₈(OH)₄(NH₂-bdc)₆) (NH₂-bdc = 2-amino-1,4-benzenedicarboxylate)^[35] was investigated as a filler in MMMs for the separation of CO₂/CH₄ gas mixtures. With polysulfone (PSF) as the polymer matrix, the selectivity dropped from 27 for neat PSF membranes to 6 at high filler loadings (30 wt %), together with enhanced permeability from 7 to 37 Barrer as a result of nonselective voids arising from poor polymer-filler adhesion.^[39] However, MIL-125-NH₂ MMMs with Matrimid (30 wt % loading) gave significantly improved separation results, leading to a 550% increase in selectivity combined with 35% higher CO₂ permeability compared to the PSF-based MMMs previously reported. Compared to pure Matrimid films (CO₂ permeability: 6 Barrer, CO₂/CH₄ selectivity: 30), the separation properties were enhanced for the MMMs with 30 wt % loading (CO₂ permeability: 50 Barrer, CO₂/CH₄ selectivity: 37).^[40] Covalent bonding between the polyimide and the filler as a result of the linker amine group was postulated, although not demonstrated, as the main reason for the better performance of the membrane.^[41]

The presence of sulfonic acid groups in the polymer or MOF filler materials can also be effective for increasing the separation performance of the membrane.^[38a, 42] The combination of a sulfonated derivative of MIL-101(Cr)^[36] and sulfonated poly(ether ether ketone) (SPEEK) in a MMM was originally used as a proton-exchange membrane with improved proton conductivity for fuel cells.^[43] These films also showed significant gain in CO₂/CH₄ gas selectivity compared with those loaded with unmodified MIL-101(Cr) fillers. The highest ideal selectivity for CO₂/CH₄ was 50 (at a CO₂ permeability of 2064 Barrer) with a 40 wt % MIL101-(Cr)-SO₃H loading in a humidified environment; in comparison, the pure SPEEK membrane had an ideal selectivity of 30 (at a CO₂ permeability of 540 Barrer; Figure 2). The sulfonic acid groups from both the polymer matrix and sulfonated MOF may construct facilitated transport pathways for CO₂ and, thereby, improve CO₂ solubility and hence selectivity.^[44]

2.1.2. Pre- and Post-Synthetic MOF Modifications

There are many strategies to overcome defective membrane morphology or to influence the selectivity and perme-

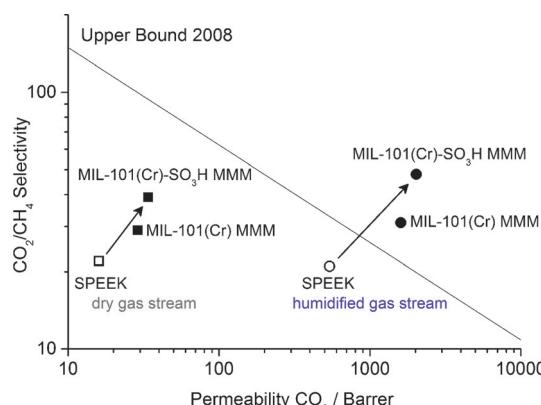


Figure 2. Example of a high-performing MMM from MIL-101(Cr)-SO₃H/SPEEK with a 40 wt% filler loading that exceeds the Robeson upper bound for CO₂/CH₄ separations compared to the pure polymer SPEEK and nonfunctionalized MIL-101(Cr) MMM. Permselectivity data obtained from Ref. [44] (Data measured and calculated from figures).

ability of particular MOF fillers in MMMs.^[16h,33a] For the modification of MOF synthesis, a distinction is drawn between in situ modulation during formation of the MOF crystallites and post-synthetic modification (PSM, see below). Modulation of the MOFs is a technique through which the internal MOF structure, as well as the crystal size, particle morphology, and outer-surface functionalities, can be controlled by using, for example, monodentate ligands during the synthesis of the material.^[45] The modulators compete with conventional multidentate ligands for coordination to the metal cations, thereby allowing the surface of the particles to be better tuned for a desired application.^[46]

Modulation approaches were used during the synthesis of UiO-66 [Zr₆O₄(OH)₄(bdc)₆]^[47] (bdc = 1,4-benzenedicarboxylate) and UiO-66-NH₂ [Zr₆O₄(OH)₄(NH₂-bdc)₆]^[46a] to increase the affinity of the fillers for the Matrimid matrix and reduce leaks along the crystal-membrane interface.^[48] Benzoic acid (BA) or 4-aminobenzoic acid (ABA) was added to the MOF synthesis as a modulator in a 50:1 molar ratio relative to the linker to study the impact of amine groups in the modulator. The amine groups on the outer surface of the MOF can interact with the imide groups of polyimides, as confirmed by ATR-FTIR spectroscopic analysis of MMMs with high loadings of amino-MOF fillers. The membranes were tested for their performance in the separation of CO₂/CH₄ mixes. The results showed that the combination of the amine-functionalized modulator and linker in UiO-66-NH₂-ABA gave the best performance among the MMMs with different filler/modulator combinations. The MMMs with 30 wt% filler loading (CO₂ permeability: 38 Barrer, CO₂/CH₄ selectivity: 48) were over 50% more selective and 540% more permeable than the reference Matrimid membrane (CO₂ permeability: 6 Barrer, CO₂/CH₄ selectivity: 31) as well as 30% and 140% more selective and permeable, respectively, than MMMs based on the reference UiO-66 (CO₂ permeability: 16 Barrer, CO₂/CH₄ selectivity: 36).^[48]

Neat ZIF-8^[49] membranes exhibit only moderate CO₂/CH₄ selectivities (kinetic diameter of CO₂ 3.3 Å; CH₄ 3.8 Å), much less than anticipated based on the pore aperture

(ca. 3.4 Å).^[14b,50] Thus, an in situ ionothermal synthesis method was used to incorporate a room-temperature ionic liquid (RTIL), for example, butylmethylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N], into the nanocages of ZIF-8. RTILs are ideal cavity occupants because of their negligible vapor pressure, high thermal stability, and good affinity to CO₂.^[51] The sorption of N₂ and CH₄ by IL@ZIF-8 was notably decreased as a result of the reduced pore volume. In contrast, the uptake of CO₂ was enhanced (especially in the low relative pressure region), which can be attributed to the good solubility of CO₂ in [bmim][Tf₂N]. Gas permeability measurements on an IL@ZIF-8 MMM made with PSF showed that the selectivities of CO₂/N₂ and CO₂/CH₄ were remarkably improved from 29 to 115 and from 19 to 34 compared to MMMs incorporating unmodified ZIF-8.^[52] Advantageously, MMMs prepared with the IL-incorporated filler showed excellent stability against plasticization at elevated pressure.

Post-synthetic modification (PSM) of MOFs is a widely investigated method to influence the stability, properties, and chemical environment within the material.^[53] PSM can also be used to control the properties and interaction of the fillers in MMMs. PSM of MOFs can be divided into several methodological categories; for details, readers are directed to reviews on the subject.^[53a] PSM in the context of MMMs allows the introduction of chemical moieties that interact well with the polymer matrix onto the surface of the MOF particles. The technique can also permit surface functionalization of MOF crystallites, while not altering the internal MOF structure.

Thin polymer coatings can be added to MOF particles by controlled polymerization of a suspension of the particles. Cao et al.^[54] coated a layer of polydopamine (PDA) on CAU-1-NH₂^[55] by using pH-dependent polymerization through the addition of dopamine hydrochloride to the dispersed particles. The coated particles showed enhanced interfacial properties when embedded into polymethylmethacrylate (PMMA) because of the adhesive PDA layer between the CAU-1-NH₂ particles and the polymer matrix. These films were characterized as oxygen-permeable layers for the air electrode of Li-air batteries working under real ambient atmosphere conditions. The films enhanced the stability of the Li-air cell by repelling CO₂ and moisture in the air. Gas permeability measurements indicate that the MMMs exhibit a high O₂ permeability (627 Barrer) and low CO₂ permeability (114 Barrer). Additionally, the ideal O₂/N₂ selectivity of 3 for the MMM with PDA-coated MOF was higher than that (selectivity: 2) without the coating, which facilitated O₂ enrichment from air.^[54]

PSM UiO-66-NH₂ has been studied as a filler, with the aim of improving the mechanical and gas separation properties of MMMs.^[56] Three different functionalities—polar (acidic), nonpolar (C10), or aromatic—were introduced systematically into UiO-66-NH₂ and the PSM derivatives were characterized as fillers in MMMs with Matrimid. Analysis revealed that the two larger reactants, phenylacetyl chloride and decanoyl chloride, do not diffuse inside the network and only react with the amine groups on the crystallite surface of the MOF. In contrast, succinic acid is smaller and could react with the internal amino groups. The

morphology of all the MMMs from Matrimid with the various modified UiO-66-NH₂ fillers showed good film formation as well as strong interaction between the polymer and the particles (scanning electron microscopy (SEM) images showed no observable cavity formation around the particles and no sieve-in cage morphology). The influence of the different functionalities on the membrane morphology was shown with CO₂/N₂ single gas permeation measurements. An increased selectivity and permeability confirmed a defect-free interface in the case of MMMs possessing 23 wt % filler. MMMs with the phenylacetyl-functionalized UiO-66-NH₂ showed the strongest increase (CO₂ permeability: 28 Barrer, CO₂/N₂ selectivity: 36), followed by the unmodified UiO-66-NH₂ (CO₂ permeability: 23 Barrer, CO₂/N₂ selectivity: 35), decanoyl-functionalized (CO₂ permeability: 22 Barrer, CO₂/N₂ selectivity: 27), and the succinic acid functionalized UiO-66-NH₂ (CO₂ permeability: 19 Barrer, CO₂/N₂ selectivity: 30). The favored interaction of MOF particles with NH₂ and phenylacetyl functionalities was explained by the presence of aromatic and imide groups in the polymer (Figure 3).

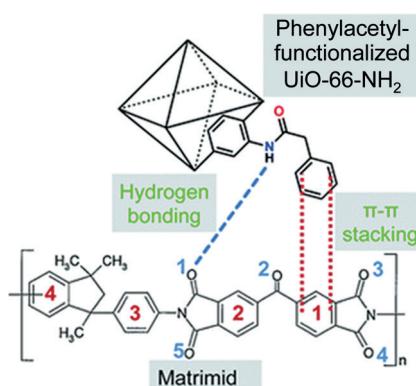


Figure 3. Scheme demonstrating the favorable interactions between the Matrimid polymer and phenylacetyl-functionalized UiO-66-NH₂ based on surface functionality. Figure adapted from Ref. [56] with permission. Copyright Royal Society of Chemistry, 2015.

2.1.3. Polymer-MOF Hybrids (polyMOFs)

A new subclass of porous materials, so-called polymer-MOF hybrids (polyMOFs),^[57] use organic polymers as an inherent component of the MOF structure. These harness not only the advantages of polymers, such as the facile fabrication of films, good processability, and chemical stability, but also the best traits of MOFs, including crystallinity, well-determined structures, and permanent porosity. Polymer-MOF hybrid materials can be understood in the context of the broader metallopolymer field, in which metal centers are linked to classic polymeric structures.^[58] These newly developed polymer-MOF hybrid materials could be used as neat membrane materials if their prototypical MOF structures possess high selectivity and porosity, and at the same time have the capability to form films with high mechanical stability similar to polymeric materials. This would obviate the challenges of traditional pure MOF membranes, but also

allow the generally high selectivity of the MOF material to be used without dilution in a polymer matrix.

There are several routes for the fabrication of polymer-MOF hybrid materials. PSM approaches to form polymer monoliths (MOF-to-polymer conversion) have been followed and resulted in the transformation of cubic MOF crystals into polymer gels by inner cross-linking of the organic linkers in the void space of the MOFs.^[59] For example, an azide-tagged MOF was prepared from a functionalized ligand and subjected to reaction with a tetraacetylene cross-linker to obtain a cross-linked MOF (CLM). In another post-synthetic approach, a Cu-based MOF with bifunctional linkers (2,5-divinylterephthalate) that could participate in radical polymerization was synthesized.^[60] The radical polymerization of isolated parallel chains and their cross-linking was performed by reaction with styrene or methyl methacrylate inside the pores of the MOF (host-guest cross-polymerization). Once the polymerization was completed, a cross-linked polymer could be obtained easily by selective dissolution of the MOF matrix.^[60] However, these strategies for polymerization within the pores of MOFs have not yet enabled the preparation of thin films for separation applications or allowed the resulting polyMOFs to reach the separation potential of their prototypical MOFs.

Stemming from an interest in the interface between MOFs and polymer materials, Zhang et al.^[57] have developed a strategy to transform 1D, nonporous, amorphous polymers into three-dimensional, highly porous, crystalline MOFs. This synthetic approach can be seen as a presynthetic modification of MOFs, since the ligands are polymerized before synthesis (Figure 4). IRMOF-1 (MOF-5) possesses a very high surface area ($S_{\text{BET}} \approx 3000 \text{ m}^2 \text{ g}^{-1}$)^[61] and selectively adsorbs CO₂ over CH₄.^[62] These characteristics make it interesting as a filler in MMMs for gas separation,^[63] but with the problem that it is labile in humid conditions. To overcome this, new polymer-MOF hybrid materials were synthesized from 2,2'-cross-linked bdc ligands^[64] and 2,5-connected bdc polymeric ligands (pbdc).^[57a] Depending on the length of the methylene spacers in the polymer backbone, networks with IRMOF structures could be obtained. The morphology of the polyMOFs obtained at low synthesis temperatures (80 °C) was also studied and revealed that morphologies ranging from spherical superstructures to crystalline films are obtained. The film morphology for two Zn-based polyMOFs was revealed to be an intergrown network of crystallites around 20 μm thick. Such films may be useful for small-molecule and gas

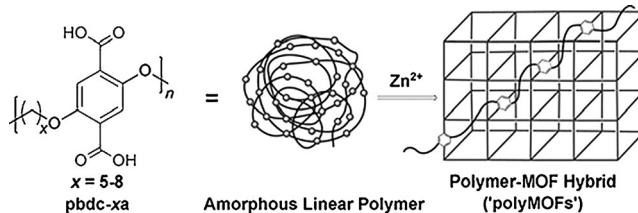


Figure 4. The synthesis of a polyMOF, isoreticular with MOF-5, from 2,5-connected bdc polymeric ligands with different lengths (x) of methylene spacers. Figure reproduced from Ref. [57a] with permission. Copyright John Wiley and Sons, 2015.

separations, but have not been characterized for this application.

The potential for the industrial application of the poly-MOFs derived from IRMOF-1 was also examined. Contact angle measurements showed increased hydrophobicity of the IRMOF-1 polyMOFs and better stability against exposure to air/humidity. Whereas MOF-5 loses crystallinity and gas adsorption properties, the Zn-based carboxylate polyMOFs remained stable. This enhanced stability can be rationalized by the increased hydrophobicity limiting access, such that water vapor cannot enter the MOF and hydrolyze the Zn-carboxylate bond. These results offer the tantalizing prospect of examining realistic technical application conditions whereby a humidified gas stream is used to test the separation performance of membranes. The polyMOFs derived from IRMOF-1 exhibit much smaller BET surface areas than IRMOF-1, but were found to take up more CO₂ because of the incorporation of polymer chains in the framework.^[65]

Other MOF prototypes can also be used for the synthesis of polyMOFs, including the UiO-66 topology.^[57b] Mixed-ligand MOF systems with bdc and ligands such as bpy = 4,4'-bipyridine and bpe = 1,2-bis(4-pyridyl)ethane are well-investigated.^[66] These MOF topologies were used as a design template to synthesize new polyMOFs from a polyether dicarboxylate ligand in combination with N-donor coligands. Again, the polyMOFs were found to form particles that were packed into uniform films. Experiments to determine the polymer to metal stoichiometry indicated that the polyMOFs may contain structural defects such that not all the bdc units from the polymer ligands are coordinated to the secondary bonding units (SBUs). This also includes the possibility that polymer ligands extend outside the crystal domain and serve as a binder on the surface of the MOF particles. The polyMOF hybrids exhibit relatively high CO₂ sorption but very low N₂ sorption, thus making them promising materials for CO₂/N₂ separation. In addition, the mixed-ligand poly-MOFs also demonstrate good stability to water or water vapor compared to the parent materials.^[57b]

2.1.4. Functionalized Polymers

The application of polymers grafted with functional groups as a continuous phase combined with suitable MOFs as the dispersed phase for MMMs is also expected to enhance the polymer-MOF interaction. Furthermore, the distribution of MOF particles could be improved and the intrinsic permeability of the polymer tuned. Grafting is a method wherein groups are covalently bonded (modified) onto the polymer chain.^[67] Combining MIL-53(Al)-NH₂ with 6FDA-ODA (6FDA = 4,4'-hexafluoroisopropylidene diphthalic anhydride, ODA = 4,4'-oxidianiline), a nonfunctional polyimide with very low gas permeation (CO₂ permeability: 14 Barrer, CO₂/CH₄ selectivity: 50), results in a MMM providing less than 15 Barrer for CO₂ permeability but an enhanced selectivity of 78, a noticeable particle agglomeration, and a weak polymer-MOF adhesion. The performance suggested that the MOF particles were agglomerating to form clusters rather than being dispersed homogeneously in the bulk polymer.^[16p] To confirm this behavior, a MIL-53(Al)-

NH₂/6FDA-DAM (DAM = diaminomesitylene) membrane was prepared, in which the MOF-NH₂ particles also aggregated into clusters with diameters of about 500 nm and their bare surface could be observed easily.^[68] In contrast to these 6FDA-ODA and 6FDA-DAM based MMMs, membranes prepared from 6FDA-DAM-HAB (1:1, where HAB = 3,3'-dihydroxy-4,4'-diaminobiphenyl) copolyimide (CO₂ permeability: 46 Barrer, CO₂/CH₄ selectivity: 34) and 10 wt % MIL-53(Al)-NH₂ showed a permeability/selectivity behavior approaching the 2008 Robeson upper bound (CO₂ permeability: 42 Barrer, CO₂/CH₄ selectivity: 78). Furthermore, the OH groups on the polymer appeared to play a critical role in improving the interaction between the MOF-NH₂ particles and the polymer matrix, thereby enhancing the particle dispersion as well as effectively eliminating interfacial voids.^[68]

2.1.5. Controlling MOF Particle Size and Morphology

In addition to changing the chemical properties of either the filler or the polymer, another powerful approach towards enhanced membrane performance consists of changing the morphological properties of the filler. It is indeed easy to envisage that issues such as particle aggregation, dispersion of the filler in the continuous polymer matrix, orientation of the porosity of the filler with respect to the membrane, and filler utilization in general will be greatly affected by the particle morphology. Such multiscale crystal engineering of MOFs has achieved significant recent attention and has been the subject of reviews.^[69,70]

Although still scarce, a few examples highlighting the importance of filler particle size and morphology have been published. Submicrometer ZIF-90 particles (0.81 ± 0.05 μm) in the polyimide 6FDA-DAM (15 wt %) gave a CO₂ permeability of 720 Barrer with a CO₂/CH₄ selectivity of 37 (mixed gas, 1:1 CO₂/CH₄ mixture). The small size was deemed crucial for the permeability, as ZIF-90 with 2.0 ± 0.6 μm sized particles in 6FDA-DAM (15 wt %) yielded a permeability of 590 Barrer with a selectivity of 34 (for a 1 μm MMM, the permeance was 720 and 590 GPU, respectively).^[71] To provide some context, these values can be compared to a CO₂ permeance of 100 GPU and selectivity of 15 for commercial CO₂/CH₄ membranes.^[71] Membranes with very high permeability and good selectivity, as encountered for these ZIF-90/6FDA-DAM MMMs, may be industrially attractive.^[72]

In a similar manner, ZIF-7 nanoparticles with sizes of around 30–35 nm were incorporated as a suspension into commercially available poly(amide-*b*-ethylene oxide) (Pebax 1657) and the MMM formed on a porous polyacrylonitrile (PAN) support with a PTMSP gutter layer (CO₂/CH₄ selectivity: 14, CO₂/N₂ selectivity: 34).^[73] The SEM data showed ideal blending between the two phases and no apparent voids or clusters. The separation performance of the composite membranes was investigated by single gas permeation experiments and analyzed for CO₂/N₂ and CO₂/CH₄ mixtures. Both the permeability (up to 145 Barrer from 72 Barrer) and gas selectivity (CO₂/N₂ up to 97 and CO₂/CH₄ up to 30) are increased at a low ZIF loading into Pebax 1657.

The first real consideration of particle morphology was reported by Rodenas et al.^[20a] These researchers identified that the ideal morphology of a MOF nanofiller would be a nanosheet form. As previously discussed by Konduri and Nair^[74] as well as Tsaptsis^[75] and co-workers, the use of 2D materials in MMMs offers several advantages, such as an almost full utilization of the filler and a better matching with the polymer matrix. Based upon this hypothesis, Cu(bdc) MOF lamellae (CuBDC) of micrometer lateral dimensions and nanometer thickness were prepared. These nanosheets were readily dispersed within a polyimide (PI) matrix at different filler loadings (2–12 wt %) by a solution processing method to give cast membranes with a thickness of 30–50 µm. The composites showed outstanding CO₂ separation performance from CO₂/CH₄ gas mixtures, with the separation selectivity for 8 wt % nanosheet-CuBDC@PI being 30–80% higher than for the pure polymer membrane and 75–800% higher than for the bulk-CuBDC@PI counterpart. Notably, the intrinsic sorption properties of bulk-type and nanosheet CuBDC precursors are similar and, thus, the difference in crystal morphology accounts for the difference in performance. Tomographic focused ion beam SEM provided evidence for better occupation of the membrane cross-section by the MOF nanosheets compared with isotropic crystals, and explains the improved separation efficiency (Figure 5). By

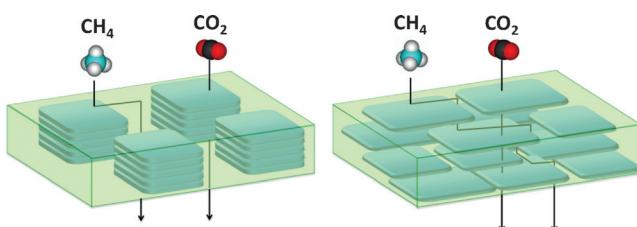


Figure 5. Representations of composite membranes containing bulk-type (left) and nanosheet (right) CuBDC MOF embedded in polyimide. The morphology and dispersion of the nanosheet form in the MMM enhances the separation performance.

using the same approach, Zhao and co-workers^[76] developed a method for the preparation of [Cu₂(ndc)₂(dabco)]_n in the morphologies of nanocubes and nanosheets, and observed an improved performance of the nanosheet-based MMMs with polybenzimidazole (PBI) and 20 wt % loading, with the overall H₂/CO₂ separation performance (H₂ permeability: 6 Barrer, H₂/CO₂ selectivity: 27) exceeding the 2008 polymer upper bound.

A systematic investigation of particle morphology was recently reported^[77] in which MMMs composed of MIL-53(Al)-NH₂ in three different morphologies—nanoparticles, nanorods, and microneedles—and Matrimid or 6FDA-DAM, at loadings between 5 and 20 wt %, were prepared. Matrimid membranes were tested for CO₂/CH₄ (1:1) separations at 3 bar and 298 K for 8 wt % MOF loading, where it was observed that the incorporation of MIL-53(Al)-NH₂ nanoparticles gave the largest improvement in performance compared to nanorods and microneedles. It was also noted that the best performing morphology of nanofiller (particles)

gave a more pronounced improvement in performance when incorporated into a highly permeable matrix (6FDA-DAM). The best performing membranes had a permeability of 660 Barrer, with a CO₂/CH₄ separation factor of 28, thus placing them close to the 2008 Robeson upper bound. Overall, these results demonstrate that tuning particle morphology is a very powerful approach to tune MMM performance.

2.2. Porous Organic Frameworks as Additives

The term porous organic framework (POF) includes a number of porous solids based only on organic constituents.^[78] POFs possess high surface areas, tunable pore sizes, and adjustable scaffolds. When the organic constituents are aromatic, the term porous aromatic framework (PAF) is adopted.^[27] In this section, the fabrication of MMMs from POFs, which has only recently been explored, will be outlined. These organic additives can be broadly categorized as having either crystalline (e.g. COFs) or amorphous (e.g. POPs) structures. PAFs, one of the classes of porous polymers, are 3D extended materials constructed by linking tetrahedral building units together through irreversible C–C coupling reactions.^[27] PAFs can exhibit unusually high porosity and narrow pore-size distributions for amorphous solids and, by virtue of their covalent backbone, are chemically robust. MMMs composed of PAFs and poly(1-trimethylsilyl-1-propyne) (PTMSP) were first explored by Lau et al.^[25a] PTMSP is a super-glassy polymer with excellent potential for gas separations, however, its practical use is limited by rapid aging, which leads to a significant decrease in its free volume (the CO₂ permeability of PTMSP decreases from 29796 Barrer to 8045 Barrer over one year). An unforeseen benefit of adding PAF particles to PTMSP was that physical aging was dramatically halted in the host polymer. Indeed, the CO₂ permeability decreased by only approximately 7% after 240 days, nearly sixfold less than pure PTMSP membranes. Solid-state NMR experiments indicate that the pore network of the PAF incorporates the pendant methyl groups of the PTMSP polymer and, as a result, “freezes” the polymer backbone in place (Figure 6). An important observation is that this mechanism is not general for nanoporous additives (such as MOFs), as the chemical compatibility of the additive and polymer appear to be essential. To this end, PAFs also modify the aging properties of PIMs,^[79] another class of glassy polymer that show promising separation properties. In this case, the PAFs give rise to selective aging in the MMM, where the H₂/N₂ selectivity increases approximately threefold after 400 days of aging. A feature of PAFs is that their pores can be routinely functionalized to tune adsorbent/adsorbate interactions. This chemistry was exploited by Lau et al., who showed that MMMs composed of PTMSP and a series of functionalized PAFs (-NH₂, -SO₃H, C₆₀, and Li₆C₆₀) showed a significant enhancement in permeability for industrially relevant gases (CH₄, CO₂, H₂, and N₂) compared to neat PAF MMMs.^[80] The best performing composite was found to be PTMSP/PAF-Li₆C₆₀, which showed both outstanding gas permeability and anti-aging properties. For example,

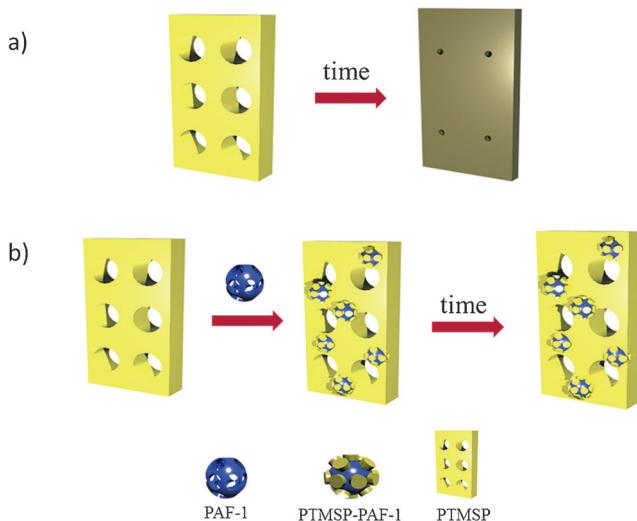


Figure 6. a) A schematic showing the pronounced physical aging that occurs in pure PTMSP membranes. b) Anchoring the PTMSP side chains to the PAF network to halt aging.

PTMSP/PAF-Li₆C₆₀ membranes showed an 85 % increase in CO₂ permeability compared to their PTMSP/PAF counterparts.

Based on the excellent anti-aging properties of PAFs, hyper-cross-linked polymers (HCPs) were also explored as MMM additives.^[81] A clear advantage that this class of materials offer is their facile synthesis relative to PAFs.^[82] To this end the aromatic-rich HCP α,α' -dichloro-*p*-xylene (*p*-DCX) was added to the glassy polymer PTMSP and the performance characteristics of the material examined. Indeed, *p*-DCX was found to be a more effective additive for decreasing physical aging than PAF materials, especially with respect to CO₂ permeability. For example, the CO₂ permeability of PTMSP/*p*-DCX MMMs reduced by only 2 % after 60 days of aging, while a 40 % reduction in N₂ permeability was observed for the as-cast membrane. It is noteworthy that such relative aging gives rise to outstanding CO₂/N₂ selectivity. NMR studies inferred that the fundamental anti-aging mechanisms of the HCP additives were similar to PAFs, namely that interactions between the *p*-DCX and the trimethylsilyl groups of PTMSP “froze” the main chains of the bulk polymer. HCPs (polystyrene) have also shown positive anti-aging effects when used as additives in PIM-based membranes.^[25b] Again, analogous aging experiments indicate that the loss of permeability of N₂ is more rapid than that of CO₂ over time, thus leading to an enhanced CO₂/N₂ selectivity from 7 to 12.

COFs are a class of extended porous materials that are defined by their crystalline structures.^[26] Given their high porosity, organic composition, and wide range of pore sizes it is surprising that their application as porous MMM additives has not been more widely explored. Only a few studies of 2D COFs as additives to polymer matrices have been reported; this may be in part due to challenging synthetic procedures and, for some COFs, limited stability under humid conditions. Recently, water-stable, exfoliated imine-based COFs were added to poly(ether imide) or polybenzimidazole (PBI) to

yield MMMs.^[24a] The as-synthesized COFs were exfoliated by sonication, thereby giving rise to sheets down to monolayer thickness with high aspect ratios. MMMs with up to 30 % COF filler were cast and, according to microscopy studies, the membranes were defect-free. This was attributed to good compatibility between the COF and the polymer matrix. In general, the COF additives lead to increased gas permeability and in some cases improvement in gas selectivity. A clear increase in the H₂/CO₂ selectivity from 9 up to 31 upon 20 wt % COF loading (surpassing the 2008 Robeson upper bound) was observed.

Similar, robust COFs (TPa-1 and TPBD)^[28] have been employed to synthesize MMMs with PBI.^[24b] In this case, membranes composed of up to 50 % COF could be cast before defects in the material were observed, once again indicating the excellent chemical compatibility of COFs and polymer hosts. These high COF loadings showed significant increases (almost sevenfold) in gas permeability for H₂, N₂, CH₄, and CO₂ compared to PBI. Furthermore, as may be expected, the gas permeability increased as the pore size of the COF increased. MMMs comprised of azine-linked COFs and the commercial polymer Matrimid have also been fabricated.^[24c] Once again, the addition of the COF material leads to a notable increase in gas permeability (130 % for CO₂ in the case of the 16 wt % loaded polymer) and, compared to the neat polymer, an increase in selectivity for CO₂/CH₄ from approximately 19 to 27.

2.3. Porous Molecular Compounds as Additives

The recent use of porous molecular compounds^[29,30] rather than extended porous materials as additives is outlined in this section, firstly summarizing the role of MOPs as fillers before discussing applications of the purely organic equivalents (POCs). In contrast to extended framework additives, here the porous molecular additive may be fully dispersed within the membrane support or be present as a suspension of crystallites (Scheme 1b).^[31c] Thus, the potential porosity of the molecular additive may be intrinsic (utilizing only the shape-persistent cavity of the species), extrinsic (relying on the voids formed from crystalline or frustrated amorphous packing of the cage units), or a combination.^[29c]

2.3.1. Metal-Organic Polyhedra as Additives

The alkyl chain decorated MOP-18 ([Cu₂₄(ddbdc)₂₄(S)₂₄], where ddbdc = 5-dodecyloxy-1,3-benzenedicarboxylate) was first reported as a component of MMMs only relatively recently.^[31a] Inspired by the work of Kim and co-workers, who used it as a membrane channel builder for cation transport,^[83] the authors sought to prepare MMMs by dispersing MOP-18 in Matrimid. MOP-18 is exohedrally decorated with alkyl chain substituents in the 5-position of the ligand, which enhances its solubility in organic solvents. The formation of homogeneous, phase-integrated MMMs with loadings as high as 80 wt % was shown by SEM data. Furthermore, there was no evidence of polymer rigidification at the MOP-18/polymer interface that characterizes MMMs prepared from extended

framework materials,^[16] with up to 44 wt % MOP-18/Matrimid MMMs retaining flexibility and low loadings (16 wt %) of MOP-18 increasing the strength of the composite. This was presumably due to the strong affinity of the polymer chains for the alkyl chains of MOP-18. The MOP-18/Matrimid composites became more permeable as the temperature was increased to 70°C and CO₂ plasticization was minimized. Permeability and solubility data showed that the pore, cage void, and alkyl chains of embedded MOP-18 introduced new sorption sites that significantly affected the gas transport properties of the membranes.

A similar approach was implemented by Ma et al.,^[84] who incorporated a soluble anionic MOP, Na₆H₁₈[Cu₂₄(5-SO₃-1,3-BDC)₂₄(S)₂₄]_xS (where S = methanol/N,N'-dimethylacetamide), as a filler in polysulfone (PSF). The design strategy was to use the aromatic rings of both the MOP additive and PSF to enhance the chemical compatibility as well as the sulfonate groups to augment CO₂ binding and deliver effective separation of CO₂/CH₄ mixtures. Similar strategies have been employed for MOF additives (see Section 2.1.1). Solution casting gave a MMM with homogeneous dispersion of the MOP cages which retained their chemical connectivity. Analysis of the separation performance for 8, 12, and 18 wt % MOP loadings revealed that the permeabilities of CO₂ and CH₄ both increased with an increase in MOP loading, with permeabilities up to 113% and 76% higher, respectively, than those in the pure PSF membrane. Moreover, the separation factor for CO₂ in the mixture also showed significant improvement compared to a pure PSF membrane (from 28 up to 45, a 60% increase). Although the higher permeability can be largely ascribed to new diffusion pathways, the improved separation factor was attributed to the polar -SO₃Na groups, which interact more strongly with quadrupolar CO₂. These observations were supported by corresponding data for a OH-functionalized MOP, which showed an increase in permeability but not selectivity with MOP loading.

Thus, MOPs can be incorporated into MMMs without phase segregation, and such materials, with the right composition, can deliver superior separation performance compared to a neat polymer membrane. With this in mind, Kitchin et al.^[31b] set about carefully controlling the interplay between components in a MMM at the molecular level to achieve control over the process of physical aging.^[85] The authors utilized PTMSP, which is highly prone to physical aging, and a series of soluble MOPs with various external chain lengths and polarities, namely a nonpolar tertiary butyl ('Bu-MOP), polar diethylene glycol (DEG MOP), polar triethylene glycol (TEG MOP), and nonpolar dodecane (MOP-18), to prepare MOP-MMMs. All the composites revealed homogeneous dispersion and intimate mixing between the polymer and the porous MOP additive at the loadings reported. It was observed that although all the MOP-PTMSP combinations had slightly lower initial CO₂ permeability, the MOP additives with shorter chains (i.e. 'Bu-MOP, DEG-MOP) had a reduced loss of permeability over a one year aging cycle (Figure 7): the 20% loaded 'Bu-MOP-MMM only lost 20% of its CO₂ permeability compared with the 73% loss exhibited by the pure PTMSP membrane. As a predictive tool, the anti-aging performance was found to correlate with the viscosity of the

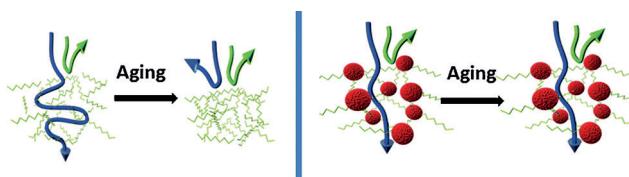


Figure 7. Schematic representation showing the postulated role that MOPs have in preventing aging and enhancing selectivity over time. Figure adapted from Ref. [31b] with permission. Copyright Royal Society of Chemistry, 2015.

casting solutions as well as the level of interaction between the polymer chains and the MOP additive.

Although not the main focus of this Review, MOP additives have been utilized to enhance the performance of pervaporation membranes for hydrocarbon separations. In one case, the reticular chemistry possible for MOPs was utilized to prepare a series of isostructural MOPs with different external functional groups. These were combined with a polymer to fabricate functionalized MOPs/hyperbranched polymer hybrid membranes^[86] whereby the selectivity was found to be governed primarily by the polarity of the MOP functional groups. In a similar manner, hybrid membranes of the 'Bu-MOP and hyperbranched polymer Boltorn W3000 were fabricated on a ceramic hollow tube by a simple immerse-coating method.^[87] These modules demonstrated excellent pervaporation separation performance for aromatic-aliphatic hydrocarbon mixtures.

2.3.2. Porous Organic Cages

Whereas MOPs have been of significant interest as a class of porous solids for some time, POCs have more recently attracted significant attention.^[29] These chemically stable, readily soluble, and solely organic additives should intimately mix with the polymer matrix, potentially ameliorating the gas transport issues that can befall other systems. Similar to MOPs, POCs also afford extremely high porosities but still retain their molecular identity, and can be readily processed into composite materials.^[29c] In addition to the close chemical complementarity of POCs to the polymer matrix, control over the interior and exterior chemical functionality as well as the intrinsic porosity of POCs is easily accomplished. Indeed, Song et al. demonstrated that it was possible to solution-process POCs into continuous and defect-free microporous thin films without the need for a supporting polymer.^[88] Although much remains to be explored in the field of POCs, their potential application as additives for MMMs is summarized in this section. There has, however, been previous interest in bowl-shaped and toroidal host molecules, such as calixarenes^[89] and cyclodextrins,^[90] which are also briefly discussed.

Studies on cyclodextrin fillers as components of pervaporation membranes have been reported.^[91] Jiang et al.^[90a] also investigated these Matrimid/β-cyclodextrin nanocomposite membranes for O₂/N₂ separation and found changes in permeability and selectivity that were dependent on the loading. Along these lines, Chapala et al.^[90b] systematically studied the effect of incorporating α-, β-, and γ-cyclodextrins

with Me or Me_3Si substituents into a poly(3-trimethylsilyl-tricyclononene-7) (PTCNSi1) matrix. Under these conditions, they observed that bulky Me_3Si groups led to minor reductions in the permeability coefficients for He and H_2 , while a marked decrease was found for other gases. Methyl-substituted cyclodextrins led to reductions in permeability for all the studied gases, although this effect was more significant for larger gas molecules. Thus, a MMM comprised of Me-substituted α -cyclodextrin resulted in an increase in selectivity for H_2/N_2 from 5.2 for the pure polymer to 9.1. An earlier study on substituted calixarenes by the same authors^[89b] showed these additives could also be blended with PTCNSi1. The advantage of such additives was that the nature of the substituents on both the upper and lower rims of the calixarenes could be used to modify the gas permeability and selectivity of the resulting membranes. The composites generally showed decreased permeability and increased selectivity towards different gas pairs compared with pure membranes; for example, a calixarene substituted on the upper rim with ethyl groups and the lower rim with ^1Bu groups showed a 104% increase in H_2/N_2 selectivity (to 11.4) but a near halving of permeability.

Bushell et al. reported the first synthesis of a POC composite membrane,^[31c] whereby the cage molecules were induced to crystallize within the membrane matrix. Starting from a solution of PIM-1 and POC, a dispersed but phase-separated composite was generated by *in situ* crystallization (Figure 8). The cage utilized was an imine POC formed from 1,3,5-triformylbenzene and (*R,R*)-1,2-diaminocyclohexane (CC3). The study showed that the incorporation of POCs significantly enhances the permeability, whereas nonporous cage molecules (in this case generated by chemical reduction

of the imine POC CC3) have the opposite effect; in the former case permeability increases with increasing weight percent of the porous cage, while in the latter permeability decreases as the concentration of the nonporous reduced cage increases. The effect of using preformed nanocrystals (PIM-1/nanocage) was also investigated. The authors concluded that the PIM-1/nanocage membranes extend the upper bound of performance for various relevant gas pairs, while the *in situ* crystallized systems provide better resistance towards physical aging.

In a computational study, Evans et al. assessed how POCs act as soluble additives that could ameliorate nonselective gas transport pathways in MMMs.^[92] Five POCs were investigated, comprising three different families of materials, including the tetrahedral imine cages (CC1, CC2, CC3) reported by Cooper and co-workers,^[93] an adamantoid cage from the group of Mastalerz,^[94] and the elongated, all-carbon-bonded, triangular dipyramidal cage.^[32a] The PIM-1/cage MMM composites were generated *in silico* and benchmarked against experimental data reported by Bushell et al.^[31c] The power of this approach was to allow analysis of numerous polymer/POC compositions, thereby generating the permeabilities and selectivities for 40% volume compositions of MMMs comprised of POCs and the polymer hosts Matrimid, Ultem, PIM-1, and PIM-7. This revealed that larger cage structures in the MMMs significantly improve the permeability for H_2/N_2 and H_2/CO_2 separations and is concomitant with a minor increase in the selectivity for H_2 .

Mao and Zhang^[31d] investigated MMM composites incorporating the waterwheel-shaped POC Noria. Noria was first synthesized^[95] from resorcinol and pentanediol and shown to be porous by Atwood and co-workers.^[96] The hydroxy groups render Noria soluble in polar solvents and allow its physical properties to be tailored by PSM. MMMs were prepared by incorporating Noria as well as its derivatives Noria-Boc and Noria-CO $'$ Bu as the fillers in the polyimide 6FDA-DAM. The substituted derivatives achieved better integration, giving a homogeneous dispersion of the nanoaggregates and close interfacial mixing of the phases, particularly in the cases where hydrophobic substituents were used. The separation performance of the resulting composites was strongly related to the chemical structures of the additives. Noria/6FDA-DAM composites gave a minor improvement in CO_2/CH_4 selectivity (15% increase) concomitant with a 53% decrease in permeability for CH_4 . In contrast, the introduction of Noria-CO $'$ Bu tends to increase the free volume and gas permeability of the MMMs (e.g. methane permeability increases by nearly 40%).

Cooper and co-workers have also recently utilized their tetrahedral imine cages to render materials porous by solution co-processing.^[97] Scrambled POC cage mixtures were prepared by a co-reaction approach that yields an amorphous material with a porosity almost twice that of the corresponding phase-pure POCs. A combinatorial approach was then used to explore the effect of doping with a series of nonporous polymers, including polyethyleneimine (PEI), polyvinylpyrrolidone (PVP), poly(methyl methacrylate) (PMMA), and polystyrene (PS). A notable observation was that the cage-polymer composites maintained their porosity

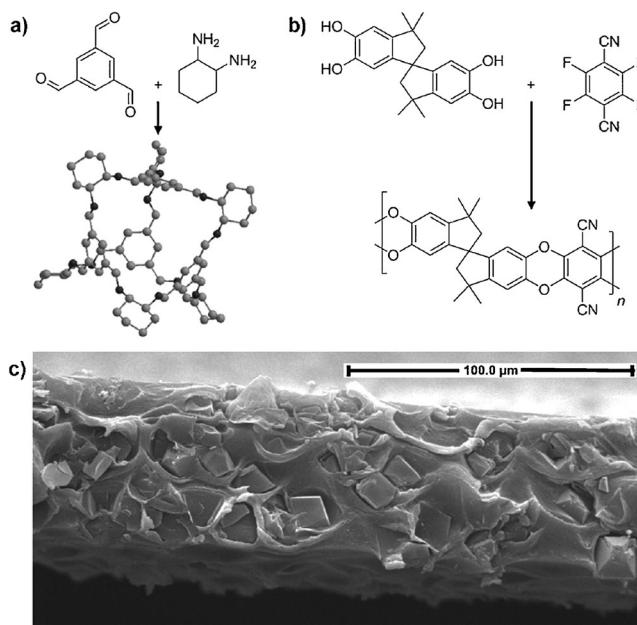


Figure 8. The syntheses of a) imine cage CC3, b) PIM-1, and c) a membrane produced by the *in situ* crystallization approach of Bushell et al.^[31c] Figure taken from Ref. [31c] with permission. Copyright John Wiley and Sons, 2013.

to N₂ up to 40 wt % polymer loading, which confirms the ability to convert nonporous commodity polymers into porous composites simply by combination with POCs. Desirable CO₂ uptake was achieved for a PEI/POC composite (17 wt % PEI), with the material delivering a higher CO₂ uptake than either of the two isolated organic components as well as an ideal CO₂/N₂ gas selectivity of 8 (295 K, 1 bar).

3. Scope and Outlook

The increased permselectivities obtained for many MOF-MMMs show that the choice of the MOF filler/polymer material combination, especially with certain MOF functional groups positioned on the linker or as a coating, can lead to better polymer-filler interactions and improved performance. Similarly, modified polymers displaying chemically complementary groups can achieve a comparable outcome. To understand this more fully, the polymer-filler interface can be modeled with integrated density functional theory calculations and force-field-based molecular dynamic simulations. This method has already been used successfully for MMMs from PIM-1 and ZIF-8, and has shown, for example, that the structure of the membrane at the polymer-filler interface is the result of chemical affinity between PIM-1 and ZIF-8, with a preferred interaction between the CN groups of PIM-1 and the terminal NH functionality of the organic linker on the ZIF-8 surface.^[98] Nonetheless, in general, these interactions are often not fully understood and clear spectroscopic evidence or the use of other appropriate characterization techniques is often lacking as a supplement to the theory. Thus, the development and utilization of advanced surface and material characterization techniques along with computational methods to simulate filler particle surfaces and their interactions with polymer chains will be needed. This knowledge will engender the design of better filler-polymer interfaces that should result in great improvements in separation performance.

Many of the reported studies on MOF-MMMs simply combine individual MOFs, which possess potentially desirable attributes, with commercially available polymers. These isolated studies do not readily facilitate the development of structure–performance relationships because of differences in the samples or experimental design. The growing number of filler material classes and examples makes it imperative to develop accurate testing and characterization protocols that are able to attribute specific properties associated with the fillers to the separation performance of the material. An example of this is a comparative study of gas separation using MMMs containing a variety of different nanoparticles.^[99] In this case, the gas permeation properties of a series of MMMs of Matrimid (fillers = Cu-BTC, ZIF-8, Carbon C, Carbon B, Carbon A, and POP-2) were measured to determine the dominant particle properties and explain the permeation by using a simple model based on the free volume. The gas permeabilities of all the MMMs were shown to increase as the filler loading increased without any reduction in the gas selectivity, with the enhancement for the MOF-MMMs at high volume fractions being significantly larger than for

carbon-MMMs. Analysis of the permeability data showed that, of all the membrane properties, the fractional free volumen (FFV) provided the strongest correlation to the permeability. Furthermore, the permeability of all the gas species was shown to be strongly correlated with the free volume of the MMM.

The MOF-related studies presented have also shown that the modification of the surface chemistry and texture, particle size and morphology, as well as dispersion of the filler particles have a significant influence on the separation properties of the MMMs. Thus, particles should be < 50 nm in size^[73] and their nature, shape, and orientation in the membrane should be known to be able to assign the separation properties. Techniques to probe these aspects are known, for example, Raman spectroscopy can be used to determine the homogeneity of the filler distribution in a MMM.^[100] By using this approach, the filler dispersion in the polymer can be determined at different locations of a sample. Additional advanced characterization techniques such as tomographic SEM/TEM, when used as quantification tools, can give great insight into the presence of large structural defects and particle orientation.^[20a,38b,101] In addition to these powerful visualization techniques, more care should be paid when studying the effect of filler addition on the intrinsic properties of the final composites. Changes in polymer rigidity or free volume can be responsible for changes in permeability, and these should be properly quantified.^[99,102]

The field of POF-based MMMs is in its infancy and further studies are required to assess the potential of these materials as additives in polymeric membranes. Nonetheless, the studies have shown that porous organic additives can afford remarkable, selective, anti-aging properties for glassy polymers. Further aging studies are essential to discover new combinations that provide enhanced effects and ultimately information about the long-term viability of these MMMs. However, from the available data, it appears that 3D amorphous materials offer greater enhancement in terms of anti-aging and selective transport than the 2D, crystalline COF materials that have been examined. Accordingly, it would be of interest to also examine 3D COFs as additives. Furthermore, studies aimed at uncovering why amorphous POF materials show such drastic enhancements in the performance characteristics of polymer membranes are essential. Given the chemical mutability of PAFs and HCPs it is anticipated that a vast library of novel MMMs with commercially interesting properties will be developed in the near future. The use of fully organic additives opens new challenges in the characterization of these composites, ruling out classical visualization techniques such as SEM or TEM and making the interpretation of other classical analyses such as thermogravimetry harder. Demonstrating the integrity of amorphous fillers upon inclusion in MMMs will not be trivial.

To date, all the MOPs used for the fabrication of MMMs are based on the archetypal Cu₂₄L₂₄ MOP-1 core developed by Yaghi and co-workers^[103] which is formed from a Cu^{II} paddlewheel unit and 1,3-benzene dicarboxylate linkers. Further opportunities lie in being able to tune the chemistry of the MOP exterior surface to match or complement that of

the pure polymer membrane.^[104] An additional opportunity to vary the MOP chemistry without changes to the cage topology also arises from studies on MOFs with alternative metals at the paddlewheel node,^[105] and also recent studies whereby MOFs were constructed from heterometallic Pd^{II}-M^{II} (M = Cu, Ni, Zn) paddlewheel nodes.^[106] MOFs with various topologies can also be prepared with different internal and external reactivities, internal void volumes, and pore windows.^[30,107] Along similar lines to the concept of a polyMOF, Hosono, Kitagawa et al.^[108] recently reported a strategy to utilize MOFs as building blocks for the formation of star-shaped polymers. Two strategies were elaborated: a divergent route relying on the synthesis of MOFs exohedrally decorated with dithiobenzoate or trithioester chain-transfer groups primed for polymerization, and a convergent route using polymer macroligands. Although the gas adsorption or separation potential of such materials has not been explored, the synthetic approaches elaborated will be useful for developing highly integrated MOF filler-polymer composite membranes.

The field of POCs is still in its infancy and exciting breakthroughs continue to emerge, including new cage types with increasingly porous structures. Thus, there are opportunities for the investigation of further POC/polymer compositions. In the field of MOF-MMMs, the external chemical functionality on the MOF cage has been instrumental in developing tight filler-polymer interfaces; similar variation is possible with several cage types, as exemplified by the imine-POCs with copper, where many exterior functional groups can be tolerated. As such, the chemical compatibility between the filler and continuous phase can be further tuned. An important breakthrough for potential industrial applications of POC-MMMs is the development of chemically robust cages, for example, all-carbon-bonded cages.^[29,32] As noted, hydrolytically stable fillers are preferred for the preparation of MMMs where a realistic technical application is targeted. Soluble, chemically robust additives also offer the possibility of chemical cross-linking of the polymer matrix or being chemically grafted onto a polymer chain.

Structural flexibility is widely known for MOF materials,^[109] and the weak packing that governs the solid-state arrangements of molecular porous structures also engenders flexibility.^[29] Thus, it is important to consider the flexibility of all filler additives, as weak packing forces define the pore structures in MOFs and POCs as well as the framework flexibility. For example, ZIF-8 and ZIF-90/Matrimid membranes show H₂/CH₄ selectivities that are significantly higher than predicted and the selectivity increase can be linked to hindered distortion of the imidazolate linkers in the ZIF frameworks.^[110]

The application of MMMs to industrial gas separations necessitates the production of the membrane modules on a commercial scale. Recent studies regarding the scale-up of MOF^[23] and POC^[32b] syntheses provides optimism that these promising additives can be delivered at scales necessary for commercial use. It should also be stressed at this point that most studies on MOF-MMMs to date are based on flat, self-supported membranes and that very little work has been done on the upscaling of such membranes to configurations

appropriate for industrial application,^[1c] which also necessitates the availability of the additives on larger scales.

The target for maximizing membrane productivity is the production of selective layers with thicknesses less than a micrometer. This is usually achieved in asymmetric configurations through the formation of a selective layer supported on a nonselective porous support that provides the necessary strength. Methods to manufacture asymmetric membranes are available, including phase separation, interfacial polymerization, solution-coating, and plasma polymerization.^[111] In particular, module geometries, such as spiral wound flat sheets, supported composites and hollow fiber (HFb) membrane modules are preferred,^[112] with the HFb architecture providing high densities and supporting transmembrane pressure differences of up to 70 bar. Given that there has been greater progress in the area of MOF-MMMs, it is not surprising that a number of reports already exist on MOF-based asymmetric MMMs. Notably, similar separation performance as that of self-supported membranes has been demonstrated.^[13,73,113] The field is advancing at a slower pace for the HFb configuration.^[111,112b,c,114] Nonetheless, impressive results on MOF-based HFb-MMMs have been published. For example, Dai et al. prepared dual-layer MOF-MMM-HFbs by using Ultem 100 and 200 nm ZIF-8 particles for CO₂/N₂ separation.^[16j] Gas permeation measurements demonstrated permeance and permselectivity higher than that of the polymer-only HFb membranes. The same group also reported the successful preparation of highly loaded ZIF-8 (up to 30% wt) MMM HFbs for the separation of different hydrocarbons with outstanding results.^[115] Given these observations, more attention should be devoted in the near future to the preparation of MMMs bearing desirable module configurations and to examine module fabrication with a broader range of polymer/additive combinations. Given that a focus is the preparation of even thinner separation layers able to achieve higher fluxes, the use of filler particles with very high aspect ratios will be instrumental.

Although many of the polymer continuous phases (e.g. polyimides, PSF) have excellent intrinsic mechanical stabilities that make them ideal for applications, the additive materials (MOFs, COF etc) typically display much poorer mechanical properties.^[15] In terms of MMMs, the introduction of an additive can often reduce the mechanical stability of the polymer support (dependent on the stability of the native polymer). Some reports provide data on mechanical stability as the filler composition is tuned, but a number of contributions lack these data. For MMMs formed from Matrimid and post-synthetically modified UiO-66-NH₂, however, the mechanical strength was reported to be better than that of the pure polymer and also to be tuned by the functional group grafted onto the MOF (which directly affects the MOF-polymer interface).^[56] The mechanical stability has also been reported for MOF-MMMs comprised of very high filler loadings.^[116] In this case, a unique approach to casting the MMMs was employed to form stable membranes with a polyvinylidene fluoride (PVDF) polymer. An "ink" was produced from MOF and PVDF in nonviscous solvents before casting and complete solvent removal. Mechanical stability was demonstrated by measuring the ultimate tensile strength

(UTS) for UiO-66-PVDF composites with 10–67 wt % loading. The UTS decreased in line with increasing MOF loading, but the elastic modulus initially increased over the neat polymer at low loadings.^[116a] Even better results were achieved with MMMs based on styrene/butadiene copolymers and high MOF loadings.^[116b] As an interesting aside, alternative approaches to MOF-MMM fabrication should be more widely explored to improve the mechanical strength (and other properties). For example, Sabic Global Technologies B.V. reported MMMs obtained by *in situ* cross-linking of short oligomers in the presence of the MOF filler.^[117] One of the drivers for the development of polyMOFs^[57] was to achieve improved mechanical stability for MOFs, although no quantitative mechanical data were presented. The mechanical properties with molecular porous additives have in some cases been reported. Noria-MMM composites maintained their tensile strength on addition of the filler but become more brittle at higher loadings (a reduction in the elongation at break measurements).^[31d] MOP-18/Matrimid MMMs show similar behavior to MOF additives: the Young's modulus was shown to increase as the loading increased up to a 16 wt % MOP-18 before a gradual decrease, consistent with aggregation of the filler and weakening of the MOP-polymer interface.^[31a] A common challenge for self-supporting membranes is that the thickness of the MMM required for mechanical stability creates resistance for gas molecules and lower permeability. Importantly, the asymmetric configurations discussed above can obviate this challenge and allow the development of usable membrane modules.

The types of gas separations already examined need to be considered for a focus on potential applications (Tables SI1 and 2 in the Supporting Information summarize these data). CO₂/CH₄ separations (natural gas sweetening, biogas purification) have been a common focus because of the combined filler and polymer performance and operating conditions being ideally suited to this separation.^[20a, 24c, 31d, 44, 48, 52, 71, 73, 77, 84] Additionally, pure polymer membranes have found application in this area, supplanting aqueous amine-based adsorbents and thereby easing the path for improved membrane technology. Activity in the patent literature points to a growing industrial interest in MOF- and MOP-based MMMs for natural gas sweetening.^[118, 119] CO₂/N₂ separations are commonly examined due to a ready availability of the data for this gas pair, but challenges such as the relatively low concentration of the target gas in flue streams, low pressure feed, and the large volumes needing to be processed, mean this still represents a major challenge to the field. A comprehensive review on CO₂-capturing MMMs has been published.^[18a] Precombustion capture of H₂/CO₂ also features commonly in the separations studied, and many MOF and COF additives have shown marked increases in separation performance.^[24a, 76, 92] A challenge here will be to balance the favorable separation characteristics that have been achieved with the likely engineering requirements (i.e. hydrogen may need to be preferentially retained in the gas feed rather than being allowed to permeate). This has been considered more generally for hydrogen recovery membranes, where non-porous additives can enhance the performance of so-called “reverse-selective” membranes.^[120] Air separation (O₂/N₂)

has also been examined,^[54, 90a] as MOF and related filler MMMs offer a potential way to overcome the small difference in the kinetic diameter of O₂ and N₂ (3.46 and 3.64 Å respectively) because of the potential tunability of the additive structure.

It is apparent that various performance enhancements and desirable membrane characteristics can be imparted by judicious choice of the additive and matrix. The research highlighted in this Review further suggests that novel filler materials may advance the field of MMMs and overcome long-standing challenges, such as polymer aging. Although many of the initial reports are promising, much work remains to be done before rational design principles can be established for any of the filler materials. In particular, systematic studies that employ identical conditions for testing gas permeation under industrially relevant conditions are required for a library of known polymers. Importantly, mixed-gas studies and investigations into the role contaminants play in separation performance need to be quantified. The mechanical properties of the resulting composites need to be routinely assessed and steps to perfect the fabrication of operating membrane modules with these bespoke fillers should be examined. Accordingly, this emerging field will provide chemists, materials scientists, and chemical engineers with many challenges over the coming years. Given that there is such a broad selection of filler materials, many with excellent separation performances themselves, facile processing, and excellent compatibility with the continuous phase, MMMs formed from these additives have exciting potential for clean energy applications and energy-efficient separations.

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Conflict of interest

The authors declare no conflict of interest.

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