ACCEPTED VERSION

Janina Dechnik, Jorge Gascon, Christian J. Doonan, Christoph Janiak and Christopher J. Sumby

Mixed-matrix membranes

http://hdl.handle.net/2440/105654

REVIEW

New directions for mixed-matrix membranes

Janina Dechnik,[a] Jorge Gascon,[b] Christian J. Doonan,[c] Christoph Janiak*[a] and Christopher J. Sumby*[c]

Abstract: Research into extended porous materials such as metal-organic frameworks (MOFs) and porous organic frameworks (POFs), and their molecular analogues, metal-organic polyhedra (MOPs) and porous organic cages (POCs), has blossomed over the last decade. Given their chemical and structural mutability and notable porosity, MOFs have been proposed as novel adsorbents for industrial gas separations. In this context they have also been identified as promising filler components for high-performance mixed matrix membranes (MMMs). Research in this area has focused on enhancing the chemical compatibility between the MOF and polymer phase by judiciously functionalising 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, unexpectedly, remarkable anti-aging performance and excellent chemical compatibility for commercially available polymers. This review briefly outlines the state-of-the-art in MOF-MMM fabrication, and the more recent use of porous organic frameworks and molecular additives for MMMs.

1. Introduction

Membrane processes are highly advantageous for chemical industry allowing energy to be saved in 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, 1b] Applied industrial membrane processes 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-
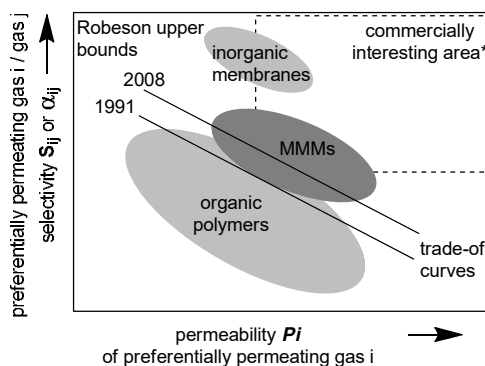

Figure 1. Schematic representation of the trade-off between permeability and selectivity with the 1991 and 2008 Robeson upper bounds shown. (*distance or position relative to upper bound can vary depending on the separation problem).

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 fast growing market potential. At present organic polymers are mostly used in the preparation of commercially applied membranes as they are cheap to produce and easy to process in comparison with inorganic materials.

While polymeric membranes have been used in industry for gas separation since the 1980s, they face challenges due to their compromise between gas permeability and selectivity. The well-known Robeson plot (log permeability vs log selectivity), states that as permeability increases the selectivity of the membranes decreases; the so-called upper bound of membrane performance (Fig. 1).[6] Enormous, ongoing efforts are being undertaken to meet this challenge through the development of new polymeric materials[7] and membranes of materials like 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 due to multi-step processing, while the permeability correlates with the productivity of the membrane and therefore determines the area or the number of membrane modules required (both affecting the capital expenditure of the process). For example, pre-combustion H_2/CO_2, oxy-combustion O_2/N_2 separation and natural gas treatments require high permeability 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

[a]   J. Dechnik, Prof. Dr C. Janiak
      Institut für Anorganische Chemie und Strukturchemie
      Universität Düsseldorf
      Düsseldorf, Germany
      E-mail: janiak@uni-duesseldorf.de
[b]   Prof. Dr J. Gascon
      Department of Chemical Engineering
      Technical University Delft
   Delft, The Netherlands
[c]   Prof. C. J. Doonan, Prof. C. J. Sumby
      Department of Chemistry and the Centre for Advanced
      Nanomaterials
      University of Adelaide
      Adelaide, Australia
      E-mail: christopher.sumby@adelaide.edu.au

      Supporting information for this article is given via a link at the end of the document.

Janina Dechnik (1986) graduated from Heinrich-Heine University with a Master degree in Chemistry in 2013. She is currently a PhD Student in the Institute of Bioinorganic Chemistry in Düsseldorf. Her research interest focuses on the development of MOF devices and the application and characterization of new MOF-based materials for gas separation and adsorption.

Jorge Gascon (1977) is 'Anthonie van Leeuwenhoek Professor' of Catalysis Engineering at TUDelft. Research interests include fundamental aspects and applications of new nano-structured materials and composites. He has co-authored over 170 publications and several patents. He has been the recipient of several I fellowships and awards, including VENI (2010), VIDI (2013) and ERC Starting (2013) personal grants and the 2013 ExxonMobil Chemical European Science and Engineering Award.
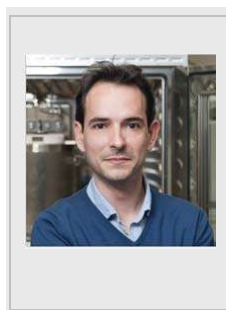
Christian Doonan is Director for the Centre for Advanced Nanomaterials and Professor of Chemistry at the University of Adelaide. His research interests encompass extended and molecular porous materials. Most days his favorite color is blue, the remainder of the time it is green. He enjoys playing guitar and watching any YouTube videos that contain cats.

Christoph Janiak is full professor for Bioinorganic Chemistry and catalysis at the University of Düsseldorf with research interests in the synthesis and properties of metal and porous organic frameworks (MOFs, COFs), metal nanoparticles, ionic liquids and catalysis. He has (co-)authored about 380 papers, book contributions, patents and teaching text books. Until 2018 he is visiting professor at Wuhan Univ. of Technology in China.

Christopher Sumby is Deputy Dean - Research and Professor of Chemistry at the University of Adelaide where he undertakes research into the synthesis and properties of nanomaterials for energy and environmental challenges. He has co-authored over 90 publications and been awarded various fellowships and awards, including an ARC Future Fellowship (2009) and a JSPS International Invitational Fellowship (2014).

manufacturing methods that would eventually allow for the reliable preparation of membranes (specially in case of zeolites and other molecular sieves) and to maintain the integrity of such membranes (avoid cracks or pinholes) which 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 selectivity and permeability which is typical for pure polymer membranes.
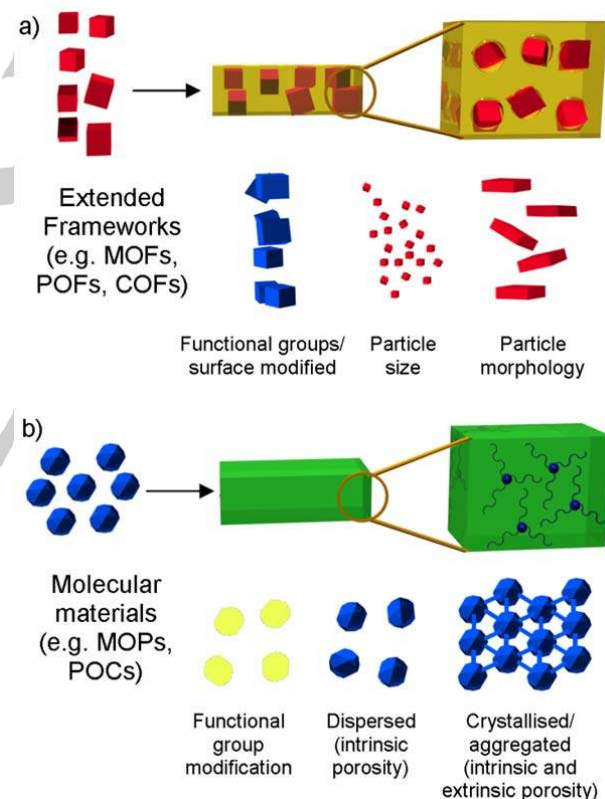
Scheme 1. Schematic representations of the structure of mixed-matrix membranes containing (a) extended framework or (b) molecular additives (fillers). A selection of parameters is shown for extended frameworks indicating different possible components for the filler materials, particle sizes and shapes. For molecular materials the intimate blending of continuous and filler phase is indicated by a change in membrane color and a lack of obvious 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.

Different types of inorganic additives, impermeable and permeable ones, have been used as filler materials.[16f, 16i-r, 17] In particular, improvements in gas permeation performance would be expected if nanostructured, highly porous additives such as zeolites or MOFs are used. Since a MMM is the dispersion of filler particles in a polymeric matrix, both polymer and filler properties affect the separation performance.[16f, 16i-r] Chemical structure, surface chemistry, particle size distribution and aspect ratio are other important variables 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 oxo 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 through judicious choice of ligands with appropriate chemical functionalities (Scheme 1a). Thus, the formation of micro gaps between inorganic and organic phase, which cause loss of selectivity, can 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 zeolites does not provide the level of tunability displayed by MOFs. In addition to 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 separation performance or facilitate stronger polymer-additive interactions. MOFs are not only tunable concerning their chemical groups, but also their pore volume, pore shapes and surface areas, enabling them to contribute to either the permeability or selectivity of the MMM.[19] In this regard, 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, issue for their potential applications in separation. In industrial gas separations moisture is a major concern and it is not economically feasible to use completely dry feed gas streams. Although in some cases synergy between both MMMs 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, which has recently been a research focus.[23] Zeolites by comparison are commercially available materials with a long history of use in industry due to their ready availability, and hydrothermal and chemical stability.

1.3. Alternative additives

While MOF fillers have attracted considerable attention, very recently alternative crystalline and non-crystalline organic porous materials, such as covalent organic frameworks (COFs),[24] and a broad category of porous organic polymers,[25] have also been also been explored. 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. PAFs, porous aromatic frameworks[27]). 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 like PAFs and PIMs. Selected COFs also have chemically robust structures due to chemical modifications post-synthesis.[28]

The majority of MMM additives that have been examined are extended solids, which possess strong directional bonding and open architectures with interconnected pores. However, recently, the use of molecular porous additives such as shape-persistent porous organic cage molecules (POCs)[29] and metal-organic polyhedra (MOPs)[30] have garnered attention (Scheme 1b).[31] POCs are discrete organic molecules, often formed via a dynamic chemistry approach, that possess a defined cage-like structure enveloping an intrinsic void volume, while MOPs are metal-organic variants. Through judicious control of the molecular precursors, organic cages and MOPs with a range of cage geometries can be procured. 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 ultra-high 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 filler and polymer can be achieved to facilitate homogenous 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. Like 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 MOF-MMM fabrication, examining how the chemical functionality of both the porous filler additive and organic chemical matrix combine to produce high performing MMMs. Newer aspects of MOF-MMMs, particularly the role of MOF particle size, distribution and importantly morphology will be examined, as will the role of MOF surface and post-synthetic modification. As part of this, new composites with higher filler compositions, or greater integration (e.g. so-called polyMOFs) between a crystalline MOF and the organic polymer component, will be discussed.

Additional sections of the review will assess the use of porous organic frameworks and molecular additives. These materials, such as COFs, POCs, and MOPs, provide potentially greater chemical compatibility with the organic polymer support

of a MMM than 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 is given in the supporting information.

2. Emerging Directions

2.1. MOF inclusion - significant strategies

MOF-MMMs have been intensively investigated,[16c, 18a, 33] as MOFs have been identified as excellent fillers with great potential due to their high porosity, tunable pore networks and chemical variability of their structures.[33c] The latter point provides opportunities to enhance performance, or avoid defects at the polymer/particle interface which result in loss of separation performance. While most current studies of MOF-based MMMs are fundamental in nature, directed toward understanding the interactions and processes which occur at the phase interface, these will ultimately assist the development of materials for industrial application. In the following sections, emerging aspects of MMM fabrication will be examined with a focus on recent, significant developments concerning MOFs (linker functionalization, surface modified and post-synthetically modified MOFs, polyMOFs), and choice of polymer continuous phase. An overview of newer aspects of particle size and shape control in MOF-MMM fabrication 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 MOF-MMM performance.[34] The interactions of the quadrupolar gas CO_2 with the linkers in MOFs can be enhanced by introducing $-NH_2$ and $-SO_3H$ groups in chemically stable MOFs like MIL-125(Ti)-NH_2[35] or MIL-101(Cr)-SO_3H.[36] Amine functionalized linkers are a common focus because of their preferential adsorption of the weakly acidic CO_2, and DFT (density functional theory) predictions that polar functional groups such as $-OH$, $-NO_2$ and $-NH_2$ would be advantageous for the separation of polar gases.[37] A second manner in which the functionality of the organic linker can be utilized is to achieve better compatibility with the polymer matrix and to enhance the polymer/particle interface morphology. In MMMs with the potential for hydrogen bonding between the polymer backbone and functional groups on the surface of the MOF filler particle, increased compatibility and improvements were observed in the gas separation properties of MMMs based on the amine-containing MOFs UiO-66-NH_2, MOF-199-NH_2,[16b] MIL-53(Al)-NH_2,[16a, 16r, 36] and MIL-101(Al)-NH_2.[38]

Detrimental performance can also be encountered when a titanium-based and amine functionalized MIL-125(Ti)-NH_2

($Ti_8O_8(OH)_4(NH_2\text{-}bdc)_6$) ($NH_2$-bdc = 2-amino-1,4-benzenedicarboxylate)[35] was investigated as a filler in MMMs for the separation of CO_2:CH_4 gas mixtures. With polysulfone (PSF) the selectivity dropped at high filler loadings (30 wt%) from 27 for neat PSF membranes to 6 with enhanced permeability from 7 to 37 Barrer caused by non-selective voids due to poor polymer-filler adhesion.[39] However, MIL-125-NH_2 MMMs with Matrimid® (30 wt% loading) gave significantly improved separation results, leading to a 550% increase in selectivity combined with 35% higher CO_2 permeability, as compared to the PSF-based MMMs previously reported. Also compared to pure Matrimid films (CO_2 permeability: 6 Barrer, CO_2/CH_4 selectivity: 30) the separation properties were enhanced for the MMMs with 30 wt% loading (CO_2 permeability: 50 Barrer, CO_2/CH_4 selectivity: 37).[40] Due to the linker amine group, covalent bonding between the polyimide and the filler was postulated, although not demonstrated, as the main reason for the better membrane performance.[41]

The presence of sulfonic acid groups in the polymer or MOF filler materials can also be effective for increasing the membrane separation performance.[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 CO_2/CH_4 gas selectivity compared with those loaded with unmodified MIL-101(Cr) fillers. The highest ideal selectivity for CO_2/CH_4 was 50 (at a CO_2 permeability of 2064 Barrer) with 40 wt% MIL101(Cr)-SO_3H loading in humidified state, compared to the pure SPEEK membrane with an ideal selectivity of 30 (at a CO_2 permeability of 540 Barrer) (Fig. 2). The sulfonic acid groups from both the polymer matrix and sulfonated MOF may construct facilitated transport pathways for CO_2 and, thereby, improve CO_2 solubility selectivity.[44]

2.1.2. Pre- and post-synthetic MOF modifications
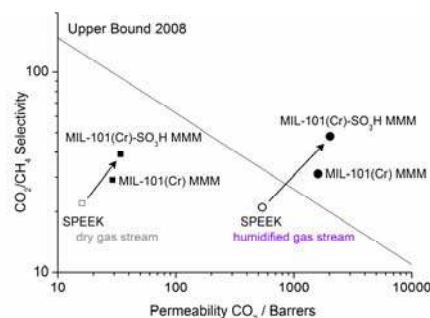
There are many strategies to overcome defective membrane

Figure 2. Example of a high-performing MMM from MIL101(Cr)-SO_3H/SPEEK with 40 wt% filler loading exceeding the Robeson Upper bound for CO_2/CH_4 separations compared to the pure polymer SPEEK and non-functionalized MIL-101(Cr) MMM. Permselectivity data obtained from ref [44] (Data measured and calculated from figures).

morphology or to influence the selectivity and permeability of particular MOF fillers in MMMs.[16h, 33a] For modified MOF-synthesis a distinction is drawn between *in-situ* modulation during formation of the MOF crystallites and post-synthetic modification (PSM, see later). Modulation of 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 allowing the surface of the particles to be better tuned for a desired application.[46]

Anjum *et al.* used the modulation approach during the synthesis of UiO-66 $[Zr_6O_4(OH)_4(bdc)_6]$[47] (bdc = 1,4-benzenedicarboxylate) and UiO-66-NH_2 $[Zr_6O_4(OH)_4(NH_2-bdc)_6]$[46a] to increase the affinity of the fillers for the Matrimid® matrix, thereby reducing leaks along the crystal–membrane interface. 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 MOF outer surface can interact with the imide groups of polyimides, as confirmed by ATR-FTIR spectroscopy of MMMs with high amino-MOF filler loadings. The membranes were tested for their performance in CO_2/CH_4 mixed-gas separations. The results showed that the combination of the amine-functionalized modulator and linker in UiO-66-NH_2-ABA gave the best performance among MMMs with different filler/modulator combination. The MMMs with 30 wt% filler loading (CO_2 permeability: 38 Barrer, CO_2/CH_4 selectivity: 48) were over 50% more selective and 540% more permeable than the reference Matrimid® membrane (CO_2 permeability: 6 Barrer, CO_2/CH_4 selectivity: 31) and 30% and 140% more selective and permeable than MMMs based on the reference UiO-66 (CO_2 permeability: 16 Barrer, CO_2/CH_4 selectivity: 36).[48]

Neat ZIF-8[49] membranes exhibit only moderate CO_2/CH_4 selectivities (kinetic diameter of CO_2 3.3 Å; CH_4 3.8 Å), much less than anticipated based on the pore aperture (~3.4 Å).[14b, 50] Thus, an *in-situ* ionothermal synthesis method was used to incorporate a room-temperature ionic liquid (RTIL), e.g. butyl-methyl imidazolium bis(trifluoromethyl-sulfonyl) imide [bmim][Tf_2N], into the nanocages of ZIF-8. RTILs are ideal cavity occupants due to their negligible vapor pressure, high thermal stability, good affinity to CO_2.[51] The sorption of N_2 and CH_4 by IL@ZIF-8 was notably decreased as a result of the reduced pore volume. In contrast, the uptake of CO_2 was enhanced, especially in the low relative pressure region, which can be attributed to the good solubility of CO_2 in [bmim][Tf_2N]. Gas permeability measurements on an IL@ZIF-8 MMM made with PSF showed that the selectivities of CO_2/N_2, and CO_2/CH_4 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 evaluated 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 the readers is 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. Using pH-dependent polymerization Cao *et al.*[54] coated a layer of polydopamine (PDA) on CAU-1-NH_2[55] by adding 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-NH_2 particles and the polymer matrix. These films were characterized as an oxygen-permeable layer for the air electrode of Li–air batteries working under real ambient atmosphere conditions. By repelling CO_2 and moisture in air the films enhanced the stability of the Li-air cell. Gas permeability measurements indicate that the MMMs exhibit a high O_2 permeability (627 Barrer) and low CO_2 permeability (114 Barrer). Additionally, the O_2/N_2 ideal selectivity of 3 for the MMM with PDA-coated MOF was higher than that (selectivity: 2) without PDA-coated MOF, facilitating O_2 enrichment from air.[54]

PSM UiO-66-NH_2 has been studied as a filler, trying to improve the mechanical and gas separation properties of MMMs.[56] Systematically three different functionalities: polar (acidic), non-polar (C10), or aromatic, were introduced to UiO-66-NH_2 and then PSM derivatives characterized as a filler in MMMs with Matrimid®. Analysis revealed that the two larger reactants, phenyl acetyl chloride and decanoyl chloride, do not diffuse inside the network and only react with the amine groups on the MOF crystallite surface. In contrast, succinic acid is smaller and its reaction with the internal amino groups was possible. The morphology of all MMMs from Matrimid® with the various UiO-66-NH_2-modified fillers showed good film formation and 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 a cage morphology). The influence of the different functionalities on the membrane morphology was shown with CO_2/N_2 single gas permeation measurements. An increased selectivity and permeability confirmed a defect free interface, with MMMs possessing 23 wt% filler compared to each other. MMMs with the phenyl acetyl functionalized UiO-66-NH_2 showed the strongest increase (approx. CO_2 permeability: 28 Barrer, CO_2/N_2 selectivity: 36), followed by the unmodified UiO-66-NH_2 (approx. CO_2 permeability: 23 Barrer, CO_2/N_2 selectivity: 35), decanoyl functionalized (approx. CO_2 permeability: 22 Barrer, CO_2/N_2 selectivity: 27), and the succinic acid functionalized UiO-66-NH_2 (approx. CO_2 permeability: 19 Barrer, CO_2/N_2 selectivity: 30). The favored interaction of MOF particles with NH_2 and phenyl acetyl functionalities was explained by the presence of aromatic and imide groups in the polymer (Fig. 3).
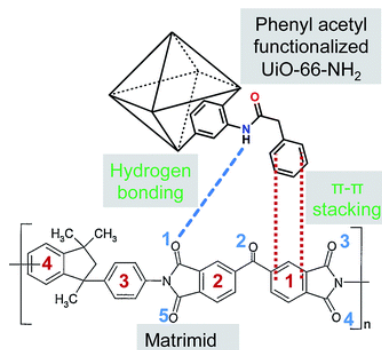
Figure 3. Scheme demonstrating the favorable interactions between the Matrimid® polymer and phenyl acetyl functionalized UiO-66-NH$_2$ based on surface functionality. Figure taken/adapted from ref.[56] with permission, copyright Royal Society of Chemistry, 2015.

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 whereby metal centers are linked to classic polymeric structures.[58] These newly developed polymer-MOF hybrid materials could be used as neat membrane materials if they possess high selectivity and porosity of their prototypical MOF structures, and at the same time have the capability to form films with high mechanical stability like 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 towards the fabrication of polymer-MOF hybrid materials. PSM approaches to form polymer monoliths (MOF-to-polymer conversion) have been followed and resulted in transformation of cubic MOF crystals to polymer gels via inner cross-linking of the organic linkers in the void space of MOF.[59] For example, an azide-tagged MOF was prepared from a functionalized ligand and subjected to reaction with a tetra-acetylene cross-linker to obtain a cross-linked MOF (CLM). In another post-synthetic approach, a Cu-based MOF with bifunctional linkers (2,5-divinylterephthalate) was synthesized such that they could participate in radical polymerization.[60] The radical polymerization of isolated parallel chains and their crosslinking 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 crosslinked polymer can be obtained easily by selective dissolution of MOF-matrix.[60] However, these strategies of polymerization within the pores of MOFs have not yet enabled the preparation of thin films for separation

applications or allowed the resulting polyMOFs to obtain the separation potential of their prototypical MOFs.

Stemming from an interest in the interface between MOF and polymer materials Zhang *et al.*[57] have developed a strategy to transform 1D, non-porous, amorphous polymers into three-dimensional, highly porous, crystalline MOFs. This synthetic approach can be seen as a pre-synthetic modification of MOFs because the ligands are polymerized before MOF synthesis (Fig. 4). IRMOF-1 (MOF-5) possesses a very high surface area (S_{BET} ~3000 m^2/g)[61] and selective adsorption of CO$_2$ over CH$_4$.[62] These characteristics make it interesting as a filler in MMMs for gas separation[63] but with the problem of its labile nature in humid conditions. To overcome this, new polymer-MOF hybrid materials were synthesized from 2,2'-cross-linked bdc^{2-} 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 from low synthesis temperatures (80°C) were also studied and revealed that they exhibit morphologies ranging from spherical superstructures to crystalline films. 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 separations but have not been characterized for this application.

The potential for industrial application of the IRMOF-1 derived polyMOFs was also examined. Contact angle measurements showed increased hydrophobicity of the IRMOF-1 polyMOFs while better stability against exposure to air/humidity was shown. Compared to MOF-5, which loses crystallinity and gas adsorption properties, the Zn-based carboxylate polyMOFs remained stable. This enhanced stability can be rationalized by the increased hydrophobicity which limits egress 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 where a humidified gas stream is used to test the separation performance of membranes. The IRMOF-1 derived polyMOFs exhibit much smaller BET surface areas than IRMOF-1 but were found to take up more CO$_2$ 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^{2-} and ligands like bpy = 4,4'-bipyridine and bpe = 1,2-bis(4-pyridyl)ethane are well investigated.[66]
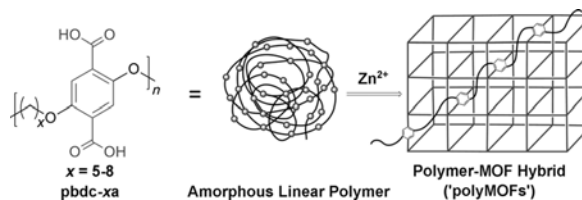

Figure 4. The synthesis of a polyMOF, isoreticular with MOF-5, from 2,5-connected bdc-polymeric ligands with different lengths (x) of methylene spacers. Figure taken from ref.[57a] with permission, copyright John Wiley and Sons, 2015.

These MOF topologies were used as a design template to synthesize new polyMOFs from a polyether dicarboxylate ligand in combination with N-donor co-ligands. Again, the polyMOFs were found to form particles, packed into uniform films. Experiments to determine the polymer to metal stoichiometry indicated that the polyMOFs may contain structural defects such that not all bdc units from the polymer ligands are coordinated to the SBUs. This also includes the possibility that polymer ligands extend outside the crystal domain and serves as a binder on the surface of the MOF particles. The polyMOF hybrids exhibit relatively high CO_2 sorption but very low N_2 sorption, making them promising materials for CO_2/N_2 separation. Added to this, the mixed ligand polyMOFs also demonstrate good water or water vapor stability in contrast to the parent materials.[57b]

2.1.4. Functionalized polymers

The application of polymers grafted with functional groups as continuous phase combined with suitable MOFs as the dispersed phase for MMMs is also expected to enhance the polymer–MOF interaction. Furthermore, the MOF particle distribution could be improved while also tuning the intrinsic permeability of the polymer. Grafting is a method wherein groups are covalently bonded (modified) onto the polymer chain.[67] Combining MIL-53(Al)-NH_2 with 6FDA–ODA (6FDA = 4,4′-hexafluoroisopropylidene diphthalic anhydride, ODA = 4,4′-oxidianiline), a non-functional polyimide with very low gas permeation (approx. CO_2 permeability: 14 Barrer, CO_2/CH_4 selectivity: 50), results in a MMM providing less than 15 Barrer for CO_2 permeability but enhanced selectivity to 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)-NH_2/ 6FDA–DAM (DAM = diaminomesitylene) membrane was prepared, in which the MOF-NH_2 particles also agglomerated into ca. 500 nm diameter clusters 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′-diamino-biphenyl) copolyimide (approx. CO_2 permeability: 46 Barrer, CO_2/CH_4 selectivity: 34) and 10 wt% MIL-53(Al)-NH_2 showed a permeability/selectivity behavior approaching the 2008 Robeson upper bound (approx. CO_2 permeability: 42 Barrer, CO_2/CH_4 selectivity: 78). Furthermore, the -OH groups on the polymer appeared to play a critical role in improving the interaction between the MOF-NH_2 particles and the polymer matrix, thereby enhancing the particle dispersion as well as effectively eliminating interfacial voids.[68]

2.1.5. MOF particle size and morphology control

In addition to changing the chemical properties of either the filler or the polymer, another powerful approach towards enhanced membrane performance consist 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 and distribution. Such multi-scale 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 CO_2 permeability of 720 Barrer with a CO_2/CH_4 selectivity of 37 (mixed gas, 1:1 CO_2/CH_4 mixture). The small size was deemed crucial for the permeability as ZIF-90 with 2.0± 0.6 µm particles in 6FDA-DAM (15 wt%) yielded a permeability of 590 Barrer with 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 CO_2 permeance of 100 GPU and selectivity of 15 for commercial CO_2/CH_4 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, nano-sized zeolitic imidazole framework ZIF-7 was incorporated into commercially available poly(amide-b-ethylene oxide) (Pebax®1657) formed on a porous polyacrylonitrile (PAN) support with a PTMSP gutter layer (CO_2/CH_4 selectivity: 14, CO_2/N_2 selectivity: 34).[73] ZIF-7 nano-particles with sizes around 30–35 nm were utilized as a suspension. The SEM data showed ideal blending between the two phases and no obvious voids or clusters. The separation performance of the composite membranes was investigated by single gas permeation experiments and analyzed for CO_2/N_2 and CO_2/CH_4 mixtures. Both, permeability (up to 145 Barrer from 72 Barrer) and gas selectivity (CO_2/N_2 up to 97 and CO_2/CH_4 up to 30) are increased at 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 Nair[74] and Tsaptsis[75] and colleagues, 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 CO_2 separation performance from CO_2/CH_4 gas mixtures, with the separation selectivity for nanosheet-CuBDC(8 wt%)@PI being 30-80% higher than for the pure polymeric membrane and 75-800% higher than for the bulk-CuBDC(8 wt%)@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 performance differential. Tomographic focused ion beam SEM, provided evidence for better occupation of the membrane cross-section by the MOF nanosheets as compared with isotropic crystals, and explains the improved separation efficiency (Fig. 5). Using

the same approach, Zhao et al.[76] developed a method for the preparation of [Cu$_2$(ndc)$_2$(dabco)]$_n$ in the morphologies of nanocubes and nanosheets and observed an improved performance of the nano-sheet based MMMs with polybenzimidazole (PBI) and 20 wt% lading, with the overall H$_2$/CO$_2$ separation performance (H$_2$ permeability: 6 Barrer, H$_2$/CO$_2$ selectivity: 27) exceeding the 2008 polymer upper bound.
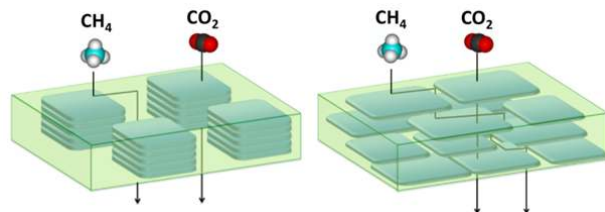

Figure 5. Representations of composite membranes containing bulk-type (left) and nanosheet (right) CuBDC MOF embedded in polyimide, showing how the morphology and dispersion of the nanosheet form in the MMM enhances separation performance.

A systematic investigation of particle morphology was recently reported.[77] MMMs composed of MIL-53(Al)-NH$_2$ in three different morphologies, nanoparticles, nanorods, and microneedles, and Matrimid® or 6FDA-DAM, at loadings between 5 and 20 wt%, have been prepared. Matrimid® membranes were tested for CO$_2$/CH$_4$ (1:1) separations at 3 bar and 298 K for 8 wt% MOF loading, where it was observed that incorporation of MIL-53(Al)-NH$_2$ nanoparticles gave the largest improvement in performance compared to nanorods and microneedles. It was also noted that the best performing morphology of nanofiller (particles) had a more pronounced performance improvement when incorporated into a highly permeable matrix (6FDA-DAM). The best performing membranes have a permeability of 660 Barrer, with a CO$_2$/CH$_4$ separation factor of 28, placing them close to the 2008 Robeson upper bound. Overall, these results demonstrate that particle morphology tuning is a very powerful approach to tune MMM performance.

2.2. Porous Organic Framework Additives

The term porous organic framework (POF) involves a number of porous solids based on only 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 using 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 via 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 that exhibits 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 CO$_2$ permeability of PTMSP decreases from 29,796 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, after 240 days CO$_2$ permeability decreased by approximately 7%, nearly 6 fold less than pure PTMSP membranes. Solid-state NMR experiments indicate that the PAF pore network incorporates the pendant methyl groups of the PTMSP polymer and, as a result, 'freeze' the polymer backbone in place (Fig. 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 (polymers of intrinsic microporosity)[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 H$_2$/N$_2$ selectivity increases approximately 3-fold 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 (-NH$_2$, -SO$_3$H, C60 and Li$_6$C60) showed a significant enhancement in permeability for industrially relevant gases (CH$_4$, CO$_2$, H$_2$, and N$_2$) compared to neat PAF MMMs.[80] The best performing composite was found to be PTMSP/PAF-Li$_6$C60 which showed both outstanding gas permeability and anti-aging properties. For example, PTMSP/PAF-Li$_6$C60 membranes showed an 85% increase in CO$_2$ permeability compared to their PTMSP/PAF counterparts.

Based on the excellent anti-aging properties of PAFs hyper-crosslinked polymers (HCP) have also been explored as MMM additives.[81] A clear advantage that this class of materials present is, relative to PAFs, facile synthesis.[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 CO$_2$ permeability. For example, after 60 days of aging the CO$_2$ permeability of PTMSP/p-DCX MMMs reduced by only 2% compared to the as cast membrane where a 40% reduction N$_2$ was observed. It is noteworthy that such relative aging gives rise to outstanding CO$_2$/N$_2$ selectivity. NMR studies inferred that the fundamental anti-aging mechanism of the HCP additives were similar to PAFs i.e., that interactions between 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 an additive to PIM-based membranes.[25b] Again, analogous aging experiments indicate that the loss of permeability of N$_2$ is more rapid than that of CO$_2$ with time, thus leading to enhanced CO$_2$/N$_2$ selectivity, increasing 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 in 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 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 H_2/CO_2 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 seven fold) in gas permeability for H_2, N_2, CH_4, and CO_2 compared to PBI. Furthermore, as may be expected, the gas permeability increased with increasing pore size of the COF. MMMs comprised of azine-linked COFs and the commercial polymer Matrimid® have also been fabricated.[24c] Once again addition of the COF material leads to a notable increase in gas permeability (130% for CO_2 for the 16 wt% loaded polymer) and, compared to the neat polymer, an increase in selectivity for CO_2/CH_4 from approximately 19 to 27.

2.3. Porous Molecular Additives

In this section the recent use of porous molecular compounds[29, 30] rather than extended porous materials as additives is outlined, firstly summarizing role of MOPs as fillers before discussing applications of the purely organic equivalents, POCs. As a point of distinction with 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

The alkyl chain decorated MOP-18 ($[Cu_{24}(ddbdc)_{24}(S)_{24}]$ 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 using this 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-
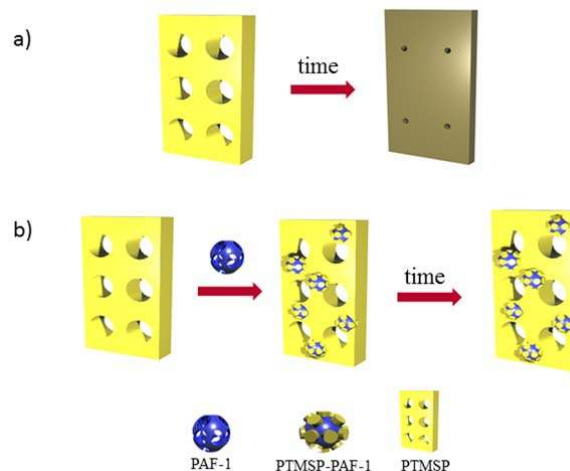

Figure 6. Schematic representations (a) the pronounced physical aging that occurs in pure PTMSP membranes and (b) how the PAF network anchors PTMSP sidechains to halt aging.

position of the ligand which enhances its solubility in organic solvents. Formation of homogenous, 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 CO_2 plasticization was minimized. Permeability and solubility data showed that the pore, core, 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, Na_6H_{18}-$[Cu_{24}(5$-SO_3-$1,3$-$BDC)_{24}(S)_{24}]$·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 chemical compatibility and the sulfonate groups to augment CO_2 binding and deliver effective separation of CO_2/CH_4 mixtures. Similar strategies have been employed for MOF additives (see 2.1.1). Solution casting gave a MMM with homogenous dispersion of the MOP cages which retained chemical connectivity. Analysis of the separation performance for 8, 12 and 18 wt% MOP loadings revealed that the permeabilities of CO_2 and CH_4 both increased with an increase in MOP loading, up to 113% and 76% higher than those in the pure PSF membrane, respectively. Moreover, the separation factor for CO_2 in the mixture also showed significant improvement compared to a pure PSF membrane (from 28 up to 45, a 60% increase). While the higher permeability can be largely ascribed to new diffusion pathways, the improved separation factor was attributed to the polar -SO_3Na groups, which more strongly

interacts with quadrupolar CO_2. 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 that such materials, given the right composition, can deliver superior separation performance with respect 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] For this work the authors utilized PTMSP, which is highly prone to physical aging, and a series of soluble MOPs of varying external chain length and polarity, namely a non-polar tertiary butyl (tBu-MOP), polar diethylene glycol (DEG MOP), polar triethylene glycol (TEG MOP) and non-polar dodecane (MOP-18), to prepare MOP-MMMs. All composites revealed homogenous dispersion and intimate mixing between the polymer and the porous additive of the MOP additive at the loadings reported. It was observed that while all MOP-PTMSP combinations had slightly lower initial CO_2 permeability, the MOP additives with shorter chains (i.e. tBu-MOP, DEG-MOP) had a reduced loss of permeability over a one year aging cycle (Fig. 7); the 20% loaded tBu-MOP-MMM only lost 20% of its CO_2 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 casting solutions and the level of interaction between the polymer chains and the MOP additive.

While not central to this review, MOP additives have been utilized to enhance pervaporation membranes performance for hydrocarbon separations. In one instance, 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] with the selectivity found to be governed primarily by the polarity of the MOP functional groups. In a similar manner hybrid membranes of the tBu 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.
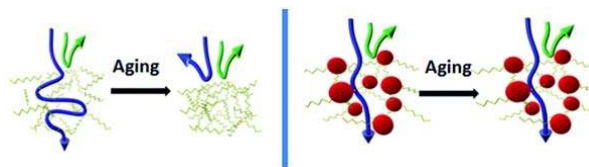

Figure 7. A schematic representation showing the postulated role MOPs have in preventing aging and enhancing selectivity over time. Figure adapted from ref.[31b] with permission, copyright Royal Society of Chemistry, 2015.

2.3.2. Porous Organic Cages

While 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. Like MOPs, POCs also afford extremely high porosities but still retain their molecular identity, and are readily able to be processed into composite materials.[29c] In addition to the close chemical complementarity POCs have to the polymer matrix, control the interior and exterior chemical functionality and 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] While much remains to be explored in the field of porous organic cages (POCs), their potential application as additives for MMMs are summarized. 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.

Work 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 O_2/N_2 separation, seeing changes and permeability and selectivity which were dependent on 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-trimethylsilyltricyclononene-7) (PTCNSi1) matrix. Under these conditions they observed that bulky Me_3Si-groups led to minor reductions of the permeability coefficients for He and H_2, while for other gases showed a marked decrease. Me-substituted cyclodextrins led to reductions in permeability for all the studied gases, although this effect was more significant for larger gas molecules. Thus, MMM comprised of Me-substituted α-cyclodextrin resulted in an increase in selectivity for H_2/N_2 from 5.2 for 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 substituents on both the upper and lower rims of 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 in comparison with pure membranes; in a typical result (for a calixarene substituted on the upper rim with ethyl and the lower rim with tBu) 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 (Fig. 8). The cage utilized was an imine POC formed from 1,3,5-triformylbenzene and (R,R)-1,2-diaminocyclohexane (CC3). The

work showed that the incorporation of POCs significantly enhances permeability, whereas non-porous cage molecules (in this instance 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 in line with increasing concentration of the non-porous reduced cage. The effect of using pre-formed nanocrystals (PIM-1/nanocage) was also investigated. The authors concluded that the nanocage membranes extend the upper bound of performance for various relevant gas pairs while the in-situ crystallized systems provide better resistance towards physical ageing.
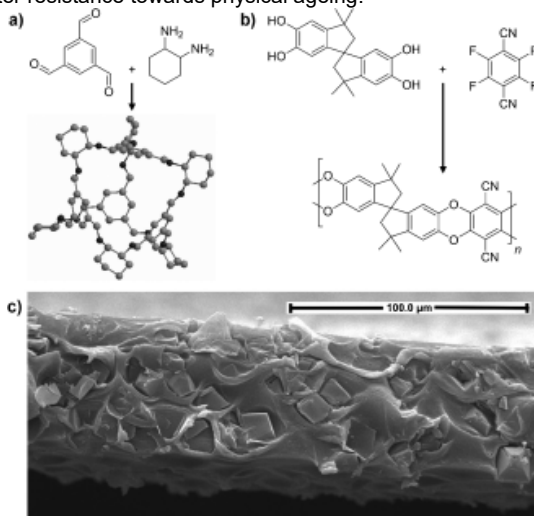

Figure 8. The syntheses of a) imine cage CC3 and b) PIM-1 and c) a membrane produce by the in-situ crystallization approach of Bushell *et al.*[31c]. Figure taken from ref. [31c] with permission, copyright John Wiley and Sons, 2013.

In a computational study Evans *et al.* assessed how POCs act as soluble additives that could ameliorate non-selective 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,[93] an adamantoid cage from the group of Masterlez,[94] and the elongated, all carbon-bonded, triangular dipyramidal cage.[32a] 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, 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 MMMs containing larger cage structures significantly improves 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 pentanedial and shown to be porous by Atwood *et al.*[96] The hydroxyl groups render

Noria soluble in polar solvents and allow the tailoring of its physical properties by PSM. MMMs were prepared incorporating Noria and its derivatives Noria-Boc and Noria-CO^{t}Bu as the fillers into the polyimide 6FDA-DAM. The substituted derivatives achieved better integration, giving a homogeneous dispersion of the nano-aggregates 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^{t}Bu tends to increase the free volume and gas permeability of the MMMs (e.g. methane permeability increases by nearly 40%).

Cooper and colleagues 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 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 to N_2 up to 40 wt% polymer loading and confirms the ability to convert non-porous commodity polymers into porous composites simply by combination with POCs. Desirable CO_2 uptake was achieved for a PEI/POC composite (17 wt% PEI) with the material delivering higher CO_2 uptakes than either of the two isolated organic components and an ideal CO_2/N_2 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/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, modelled descriptions of the polymer-filler interface can be achieved by computational means using integrated density-function theory calculations and force-field-based molecular dynamic simulations. This method has already been successfully used 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 NH-terminal 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. In this context, 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 shall result in great improvements in separation performance.

At this stage, many of the studies reported for MOF-MMMs simply combine individual MOFs, possessing potentially desirable attributes, with commercially available polymers. These isolated studies do not readily facilitate the development of structure/performance relationships due to sample or experimental design differences. Particularly with the growing number of filler material classes and examples, it is important to develop accurate testing and characterization protocols 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 instance, 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 using a simple free volume-based model. Gas permeabilities of all MMMs were shown to increase with increasing filler loading 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. The permeability data was then analyzed to determine which particle properties agreed best with the results, with particle surface area providing the strongest correlation to the permeability enhancement. The permeability of all gas species was shown to be strongly correlated with the fractional free volume (FFV) of the MMM.

The MOF-related studies presented have also shown that the modification of the surface chemistry and texture, particle size and morphology, and dispersion of the filler particles have a significant influence on the separation properties of the MMMs. Thus, with regard to the particle size, particles should be <50 nm in size[73] and their nature, shape and orientation in the membrane should be known in order to be able to assign the separation properties. Techniques to probe these aspects are known, for example the determination of the homogeneity of the filler distribution in a MMM by Raman spectroscopy.[100] 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 a 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 in studying the effect of filler addition into 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 MMM is in its infancy and further studies are required to assess the potential of these materials as additives to 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 obviously essential to unearth new combinations that provide enhanced effects and ultimately information about the long-term viability of these MMMs. However, from the available literature data, it appears that 3D amorphous materials offer more significant enhancement in 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, further studies aimed at uncovering why amorphous POP 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 of 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 trickier. Finally, demonstrating the integrity of amorphous fillers upon inclusion in MMMs will not be trivial.

To date, all MOPs used for MMM fabrication are based on the archetypal $Cu_{24}L_{24}$ MOP-1 core of Yaghi and co-workers,[103] formed from a Cu(II) paddle-wheel 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 work on MOPs with alternate metals at the paddlewheel node,[105] and even recent work whereby MOPs could be constructed from heterometallic Pd(II)–M(II) (M= Cu, Ni, Zn) paddlewheel nodes.[106] MOPs of various topologies can also be prepared that afford different internal and external chemistry, internal void volumes and pore windows.[30, 107] Along similar lines to the concept of a polyMOF, Hosono and Kitagawa[108] recently reported a strategy to utilize MOPs as building blocks for the formation of star-shaped polymers. Two strategies were elaborated, including a divergent route relying on the synthesis of MOPs exohedrally decorated with dithiobenzoate or trithioester chain transfer groups primed for polymerization, or a convergent route using polymer macro-ligands. While the gas adsorption or separation potential of such materials has not been explored, the synthetic approaches elaborated will be useful for developing highly integrated MOP 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 investigation of further POC/polymer compositions. In the field of MOP-MMMs, external chemical functionality on the MOP cage has been instrumental for developing tight filler-polymer interfaces; similar variation is possible for several cage types exemplified by the imine POCs of Copper where many exterior functional groups can be tolerated. As such, the chemical compatibility between 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 into 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 of consider the flexibility of all filler additives, as weak packing forces define the pore structures in MOPs and POCs and framework flexibility. For example, ZIF-8 and ZIF-90/Matrimid membranes show H_2/CH_4 selectivities significantly higher than the predicted and the selectivity increase can be linked to hindered linker distortion of the imidazolate linkers in the ZIF frameworks.[110]

Application of MMMs to industrial gas separations necessitates production of the membrane modules at a commercial scale. Recent work regarding 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 MOF-MMMs work to date is 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] this too necessitates availability of the additives on larger scales. In order to maximize membrane productivity, the target is the production of selective layers with thicknesses lower than a micrometer. This is usually achieved in asymmetric configurations with the formation of a selective layer supported on a non-selective 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 for thin separating layers,[112] with the HFb architecture providing high densities and supporting transmembrane pressure differences 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] For the HFb configuration, the field is advancing at a slower pace.[111, 112b-c, 114] Nonetheless, impressive results on MOF based HBf MMMs have been published. For example, Dai *et al.* prepared dual layer MOF-MMM-HFbs using Ultem®100 and 200 nm ZIF-8 particles for CO_2/N_2 separation.[16j] Gas permeation measurements demonstrated permeance and permselectivity higher than that of 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.

While many of the polymer continuous phases (e.g. polyimides, PSF) have excellent intrinsic mechanical stabilities that make them ideal for applications, commonly the additive materials (MOFs, COF etc) display much poorer mechanical properties.[15] In respect of MMMs, often the introduction of an additive can reduce the mechanical stability of the polymer support (dependent on the stability of the native polymer) and some reports provide data on mechanical stability as the filler composition is tuned; disappointingly, a number of contributions lack this 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 further to be tuned by the functional group grafted onto the MOF (which directly affects the MOF-polymer interface).[56] 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 polyvinylidene fluoride (PVDF) polymer. An 'ink' was produced from MOF and PVDF in non-viscous 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. UTS decreased in line with MOF loading but the elastic modulus actually increased at low loadings.[116a] Even better results were achieved for MMMs utilizing styrene/butadiene copolymers and high loadings of MOF.[116b] As an interesting aside, it could be suggested that alternative approaches to MOF-MMM fabrication should be more widely explored to improve mechanical strength (and other properties). For instance, Sabic Global Technologies B.V. reported MMMs obtained by in-situ cross-linking of short oligomers in the presence of the MOF filler.[117] Also, one of the drivers for the development of PolyMOFs[57] was to achieve improved mechanical stability for MOFs although no quantitative mechanical data was presented. For molecular porous additives some reporting of mechanical properties has featured. Noria-MMM composites maintained tensile strength with filler addition 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 loading increases up to a 16 wt% MOP-18 loading before a gradual decrease consistent with aggregation of the filler and weakening of the MOP-polymer interface.[31a] Finally it is worth noting, for self-supporting membranes a common challenge is that the thickness of MMM required for mechanical stability creates resistance for gas molecules and lower permeability. Importantly, the asymmetric configurations discussed above can obviate this challenge to the development of usable membrane modules.

It is relevant to consider the types of gas separations that have been examined with a focus on potential applications (tables in the supporting information, Tables SI 1 and 2, summarize this data). CO_2/CH_4 separations (natural gas

sweetening, biogas purification) has been a common focus due to 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] CO_2/N_2 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 CO_2 capture MMMs has been published.[18a] Precombustion H_2/CO_2 capture also features commonly amongst 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 (O_2/N_2) has also been examined[54, 90a] as MOF and related filler MMMs offer a potential way to overcome the small difference in kinetic diameter of O_2 and N_2 (3.46 and 3.64 Å respectively) due to the potential tunability of the structure of the additive.

It is apparent that various performance enhancements and desirable membrane characteristics can be imparted by judicious additive and matrix choice. 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. Mechanical properties of the resulting composites need to be routinely assessed and steps to perfect 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 such a broad selection of filler materials, many with excellent separation performance themselves, facile processing and excellent compatibility for the continuous phase, MMMs formed from these additives have exciting potential for clean energy applications and energy-efficient separations.

[1]   a) J. C. Davis, R. J. Valus, R. Eshragi, A. E. Velikoff, *Sep. Sci. Techn*. **1993**, *28*, 463-476; b) M. G. Buonomenna, *RSC Adv.* **2013**, *3*, 5694-5740; c) W. J. Koros, C. Zhang, *Nat. Mater.* **2017**, doi:10.1038/nmat4805.

[2]   a) X. He, M.-J. Hägg. *Membranes* **2012**, *2*, 706-726; b) W. J. Koros, R. Mahajan, *J. Membr. Sci.* **2000**, *175*, 181-196.

[3]   K. Ohlrogge, K. Stürken, *Membrane technology in the chemical industry*, (S. P. Nunez, K.-V. Peinemann, Eds.), Wiley-VCH, Weinheim, **2001**; pp. 69-94.

[4]   a) R. W. Baker, *Ind. Eng. Chem. Res.* **2002**, *41*, 1393-1411, b) BORSIG Membrane Technology GmbH, http://www.borsig-china.com/#productrecovery

[5]   Sulzer Chemtech AG, http://www.sulzer.com/en/Products-and-Services/Separation-Technology/Membrane-Technology/Organic-Solvent-Nanofiltration-OSN

[6]   L. M. Robeson, *J. Membr. Sci.* **2008**, *320*, 390–400.

[7]   S. Qiu, T. Ben, *Porous Polymers: Design, Synthesis and Applications*, RSC Publishing, Cambridge, **2015**.

[8]   a) M. E. Davis, *Ind. Eng. Chem. Res*., **1991**, *30*, 1675-1683; b) J. Liu, J. Yu, *Toward Greener and Designed Synthesis of Zeolite Materials*, (B. Sels and L. Kustov, Eds.), Elsevier, Amsterdam, **2016**; pp. 1-32; c) N. Kosinova, J. Gascon, F. Kapteijn, E. J.M. Hensen, *J. Membr. Sci.* **2016**, *499*, 65-79.

[9]   O. Shekhah, J. Liu, R. A. Fischer, C. Wöll, *Chem. Soc. Rev.* **2011**, *40*, 1081-1106.

[10]   a) S. M Saufi, A. F Ismail, *Carbon* **2004**, *42*, 241-259; b) M. Rungta, G. B. Wenz, C. Zhang, L. Xu, W. Qiu, J. S. Adams, W. J. Koros, *Carbon* **2017**, *115*, 237-248.

[11]   a) A. F. Ismaila, P. S. Goha, S. M. Sanipa, M. Aziz, *Sep. Purif. Tech.* **2009**, *70*, 12-26; b) D. Mattia, H. Leese, K. P. Lee, *J. Membr. Sci.* **2015**, *475*, 266-272.

[12]   a) G. Liu, W. Jin, N. Xu, *Chem. Soc. Rev.* **2015**, *44*, 5016-5030; b) H. Huang, Y. Ying, X. Peng, *J. Mater. Chem. A* **2014**, *2*, 13772-13782.

[13]   T. S. Chung, L. Y. Jiang, Y. Li, S. Kulprathipanja, *Progr. Polym. Sci.* **2007**, *32*, 483–507.

[14]   a) J. Caro, *Curr. Opin. Chem. Eng.* **2011**, *1*, 77-83. b) H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.* **2009**, *131*, 16000-16001.

[15]   S. R. Venna, M. A. Carreon, *Chem. Eng. Sci.* **2015**, *124*, 3-19.

[16]   a) B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, *Chem. Commun.* **2011**, *47*, 9522-9524; b) O. G. Nik, X. Y. Chen, S. Kaliaguine, *J. Membr. Sci.* **2012**, *413–414*, 48-61; c) H. B. Tanh Jeazet, C. Staudt, C. Janiak, *Dalton Trans.* **2012**, *41*, 14003-14027; d) K. Hunger, N. Schmeling, H. B. Jeazet, C. Janiak, C. Staudt, K. Kleinermanns, *Membranes* **2012**, *2*, 727-763; e) H. B. T. Jeazet, C. Janiak, in *Metal-Organic Framework*

Materials (Eds.: L. R. MacGillivray, C. Lukehart), UK: John Wiley & Sons, Ltd, Chichester, **2014**, pp. 1-15; f) B. Zornoza, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, *Micropor. Mesopor. Mater.* **2013**, *166*, 67-78; g) D. Bastani, N. Esmaeili, M. Asadollahi, *J. Ind. Eng. Chem.* **2013**, *19*, 375-393; h) G. Dong, H. Li, V. Chen, *J. Mater. Chem. A* **2013**, *1*, 4610-4630; i) M. J. C. Ordoñez, K. J. Balkus Jr, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2010**, *361*, 28-37; j) Y. Dai, J. R. Johnson, O. Karvan, D. S. Sholl, W. J. Koros, *J. Membr. Sci.* **2012**, *401–402*, 76-82; k) D. Zheng, X. Liu, D. Hu, M. Li, J. Zhang, G. Zeng, Y. Zhang, Y. Sun, *RSC Adv.* **2014**, *4*, 10140-10143; l) M. G. Buonomenna, W. Yave, G. Golemme, *RSC Adv.* **2012**, *2*, 10745-10773; m) X. Y. Chen, H. Vinh-Thang, D. Rodrigue, S. Kaliaguine, *RSC Adv.* **2014**, *4*, 12235-12244; n) S. Sorribas, B. Zornoza, C. Téllez, J. Coronas, *J. Membr. Sci.* **2014**, *452*, 184-192; o) P. Burmann, B. Zornoza, C. Téllez, J. Coronas, *Chem. Eng. Sci.* **2014**, *107*, 66-75; p) X. Y. Chen, H. Vinh-Thang, D. Rodrigue, S. Kaliaguine, *Ind. Eng. Chem. Res.* **2012**, *51*, 6895-6906; q) B. Seoane, J. M. Zamaro, C. Tellez, J. Coronas, *RSC Adv.* **2011**, *1*, 917-922; r) X. Y. Chen, V.-T. Hoang, D. Rodrigue, S. Kaliaguine, *RSC Adv.* **2013**, *3*, 24266-24279.

[17] a) G. Rebollar-Perez, E. Carretier, N. Lesage, P. Moulin, *Membranes* **2011**, *1*, 80-90; b) L. Dumee, L. Velleman, K. Sears, M. Hill, J. Schutz, N. Finn, M. Duke, S. Gray, *Membranes* **2010**, *1*, 25-36.

[18] a) B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascon, *Chem. Soc. Rev.* **2015**, *44*, 2421-2454; b) R. D. Noble, *J. Membr. Sci.* **2011**, *378*, 393-397.

[19] a) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444; b) C. Janiak, J. K. Vieth, *New J. Chem.* **2010**, *34*, 2366-2388.

[20] a) T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena, J. Gascon, *Nat. Mater.* **2015**, *14*, 48-55; b) J. B. DeCoste, J. M. S. Denny, G. W. Peterson, J. J. Mahle, S. M. Cohen, *Chem. Sci.* **2016**, *7*, 2711-2716.

[21] a) F. Jeremias, D. Frohlich, C. Janiak, S. K. Henninger, *New J. Chem.* **2014**, *38*, 1846-1852; b) C. Janiak, S. K. Henninger, *Chimia* **2013**, *67*, 419-424; c) J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem, R. R. Willis, *J. Am. Chem. Soc.* **2009**, *131*, 15834-15842.

[22] a) J. Ehrenmann, S. K. Henninger, C. Janiak, *Eur. J. Inorg. Chem.* **2011**, *2011*, 471-474; b) A. Khutia, H. U. Rammelberg, T. Schmidt, S. Henninger, C. Janiak, *Chem. Mater.* **2013**, *25*, 790-798; c) S. Karmakar, J. Dechnik, C. Janiak, S. De, *J. Hazard. Mater.* **2016**, *303*, 10-20; d) F. Jeremias, D. Frohlich, C. Janiak, S. K. Henninger, *RSC Adv.* **2014**, *4*, 24073-24082; e) D. Fröhlich, S. K. Henninger, C. Janiak, *Dalton Trans.* **2014**, *43*, 15300-15304; f) P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, *Micropor. Mesopor. Mater.* **2009**, *120*, 325-330; g) T. Wu, L. Shen, M. Luebbers, C. Hu, Q. Chen, Z. Ni, R. I. Masel, *Chem. Commun.* **2010**, *46*, 6120-6122.

[23] a) N. Stock, S. Biswas, *Chem. Rev.* **2012**, *112*, 933-969; b) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413-447; c) M. Rubio-Martinez, M. P. Batten, A. Polyzos, K.-C. Carey, J. I. Mardel, K.-S. Lim, M. R. Hill, *Sci. Rep.* **2014**, Article number: 5443.

[24] See, for examples: a) Z. Kang, Y. Peng, Y. Qian, D. Yuan, M. A. Addicoat, T. Heine, Z. Hu, L. Tee, Z. Guo, D. Zhao, *Chem. Mater.* **2016**, *28*, 1277-1285; b) B. Biswal, H. D. Chaudhari, R. Banerjee, U. K. Kharul, *Chem. Eur. J.* **2016**, 22, 4695-4699; c) M. Shan, B. Seoane, E. Rozhko, A. Dikhtiarenko, G. Clet, F. Kapteijn, J. Gascon, *Chem. Eur. J.* **2016**, *22*, 14467-14470.

[25] See, for examples: a) C. H. Lau, P. T. Nguyen, M. R. Hill, A. W. Thornton, K. Konstas, C. M. Doherty, R. J. Mulder, L. Bourgeois, A. C. Y. Liu, D. J. Sprouster, J. P. Sullivan, T. J. Bastow, A. J. Hill, D. L. Gin, R. D. Noble, *Angew. Chem. Int. Ed.* **2014**, *53*, 5322 –5326; T. Mitra, R. S. Bhavsar, D. J. Adams, P. M. Budd, A. I. Cooper, *Chem. Commun.* **2016**, *52*, 5581-5584.

[26] P. J. Waller, F. Gándara, O. M. Yaghi, *Acc. Chem. Res.* **2015**, *48*, 3053-3063.

[27] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, G. Zhu, *Angew. Chem. Int. Ed.* **2009**, *48*, 9457-9460.

[28] S. Chandra, S. Kandambeth, B. P. Biswal, B. Lukose, S. M. Kunjir, M. Chaudhary, R. Babarao, T. Heine, R. Banerjee *J. Am. Chem. Soc.* **2013**, *135*, 17853-17861.

[29] a) G. Zhang, M. Mastalerz, *Chem. Soc. Rev.* **2014**, *43*, 1934-1947; b) A. G. Slater, A. I. Cooper, *Science* **2015**, *348*, aaa8075; c) J. D. Evans, C. J. Sumby, C. J. Doonan, *Chem. Lett.* **2015**, *44*, 582-588; d) T. Hasell, A. I. Cooper, *Nat. Rev. Mater.* **2016**, *1*, Article number: 16053.

[30] D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem., Int. Ed.* **2008**, *47*, 5136-5147.

[31] See, for examples: a) E. V. Perez, K. J. Balkus Jr., J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2014**, *463*, 82-93; b) M. Kitchin, J. Teo, K. Konstas, C. Hon Lau, C. J. Sumby, A. W. Thornton, C. J. Doonan, M. R. Hill, *J. Mater. Chem. A* **2015**, *3*, 15241-15247; c) A. F. Bushell, P. M. Budd, M. P. Attfield, J. T. A. Jones, T. Hasell, A. I. Cooper, P. Bernardo, F. Bazzarelli, G. Clarizia, J. C. Jansen, *Angew. Chem. Int. Ed.* **2013**, *52*, 1253-1256; d) H. Mao, S. Zhang, *J. Colloid Interface Sci.* **2017**, *490*, 29-36.

[32] a) A. Avellaneda, P. Valente, A. Burgun, J. D. Evans, A. W. Markwell-Heys, M. R. Hill, D. J. Nielsen, C. J. Sumby, C. J. Doonan, *Angew. Chem. Int. Ed.* **2013**, *52*, 3746-3749. b) M. Kitchin, K. Konstas, C. J. Sumby, M. Czyz, P. Valente, M. R. Hill, A. Polyzos, C. J. Doonan, *Chem. Commun.* **2015**, *51*, 14231-14234.

[33] a) Y. Zhang, X. Feng, S. Yuan, J. Zhou, B. Wang, *Inorg. Chem. Front.* **2016**; b) W. Li, Y. Zhang, Q. Li, G. Zhang, *Chem. Eng. Sci.* **2015**, *135*, 232-257; c) N. Rangnekar, N. Mittal, B. Elyassi, J. Caro, M. Tsapatsis, *Chem. Soc. Rev.* **2015**, *44*, 7128-7154.

[34] G. E. Cmarik, M. Kim, S. M. Cohen, K. S. Walton, *Langmuir* **2012**, *28*, 15606-15613.

[35] C. Zlotea, D. Phanon, M. Mazaj, D. Heurtaux, V. Guillerm, C. Serre, P. Horcajada, T. Devic, E. Magnier, F. Cuevas, G. Ferey, P. L. Llewellyn, M. Latroche, *Dalton Trans.* **2011**, *40*, 4879-4881.

[36] M. G. Goesten, J. Juan-Alcañiz, E. V. Ramos-Fernandez, K. B. Sai Sankar Gupta, E. Stavitski, H. van Bekkum, J. Gascon, F. Kapteijn, *J. Catal.* **2011**, *281*, 177-187.

[37] A. Torrisi, C. Mellot-Draznieks, R. G. Bell, *J. Chem. Phys.* **2010**, *132*, 044705.

[38] a) B. Seoane, C. Téllez, J. Coronas, C. Staudt, *Sep. Purif. Technol.* **2013**, *111*, 72-81; b) T. Rodenas, M. van Dalen, P. Serra-Crespo, F. Kapteijn, J. Gascon, *Micropor. Mesopor. Mater.* **2014**, *192*, 35-42.

[39] X. Guo, H. Huang, Y. Ban, Q. Yang, Y. Xiao, Y. Li, W. Yang, C. Zhong, *J. Membr. Sci.* **2015**, *478*, 130-139.

[40] M. Waqas Anjum, B. Bueken, D. De Vos, I. F. J. Vankelecom, *J. Membr. Sci.* **2016**, *502*, 21-28.

[41] K. Vanherck, P. Vandezande, S. O. Aldea, I. F. J. Vankelecom, *J. Membr. Sci.* **2008**, *320*, 468-476.

[42] A. L. Khan, C. Klaysom, A. Gahlaut, X. Li, I. F. J. Vankelecom, *J. Mater. Chem.* **2012**, *22*, 20057-20064.

[43] Z. Li, G. He, Y. Zhao, Y. Cao, H. Wu, Y. Li, Z. Jiang, *J. Power Sources* **2014**, *262*, 372-379.

[44] Q. Xin, T. Liu, Z. Li, S. Wang, Y. Li, Z. Li, J. Ouyang, Z. Jiang, H. Wu, *J. Membr. Sci.* **2015**, *488*, 67-78.

[45] a) A. Umemura, S Diring, S. Furukawa, H. Uehara, T. Tsuruoka, S. Kitagawa, *J. Am. Chem. Soc.* **2011**, *133*, 15506-15513; b) C. V. McGuire, R. S. Forgan, *Chem. Commun.* **2015**, *51*, 5199-5217.

[46] a) A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, *Chem. Eur. J.* **2011**, *17*, 6643-6651; b) Q. Liu, L.-N. Jin, W.-Y. Sun, *CrystEngComm* **2013**, *15*, 8250-8254; c) G. Wißmann, A. Schaate, S. Lilienthal, I. Bremer, A. M. Schneider, P. Behrens, *Micropor. Mesopor. Mater.* **2012**, *152*, 64-70.

[47] F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, D. E. De Vos, *J. Am. Chem. Soc.* **2013**, *135*, 11465-11468.

[48] M. W. Anjum, F. Vermoortele, A. L. Khan, B. Bueken, D. E. De Vos, I. F. J. Vankelecom, *ACS Appl. Mater. Interfaces* **2015**, *7*, 25193-25201.

[49] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci.* **2006**, *103*, 10186-10191.

[50] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, T. Düren, *J. Am. Chem. Soc.* **2011**, *133*, 8900-8902.

[51] M. Hasib-ur-Rahman, M. Siaj, F. Larachi, *Chem. Eng. Process.* **2010**, *49*, 313-322.

[52] Y. Ban, Z. Li, Y. Li, Y. Peng, H. Jin, W. Jiao, A. Guo, P. Wang, Q. Yang, C. Zhong, W. Yang, *Angew. Chem.* **2015**, *127*, 15703-15707.

[53] a) S. M. Cohen, *Chem. Rev.* **2012**, *112*, 970-1000; b) Y.-F. Song, L. Cronin, *Angew. Chem., Int. Ed.* **2008**, *47*, 4635-4637; c) K. K. Tanabe, S. M. Cohen, *Chem. Soc. Rev.* **2011**, *40*, 498-519; d) Z. Wang, S. M. Cohen, *Chem. Soc. Rev.* **2009**, *38*, 1315-1329; e) J. D. Evans, C. J. Sumby, C. J. Doonan, *Chem. Soc. Rev.* **2014**, *43*, 5933-5951.

[54] L. Cao, F. Lv, Y. Liu, W. Wang, Y. Huo, X. Fu, R. Sun, Z. Lu, *Chem. Commun.* **2015**, *51*, 4364-4367.

[55] T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker, N. Stock, *Angew. Chem., Int. Ed.* **2009**, *48*, 5163-5166.

[56] S. R. Venna, M. Lartey, T. Li, A. Spore, S. Kumar, H. B. Nulwala, D. R. Luebke, N. L. Rosi, E. Albenze, *J. Mater. Chem. A* **2015**, *3*, 5014-5022.

[57] a) Z. Zhang, H. T. H. Nguyen, S. A. Miller, S. M. Cohen, *Angew. Chem., Int. Ed.* **2015**, *54*, 6152-6157; b) Z. Zhang, H. T. H. Nguyen, S. A. Miller, A. M. Ploskonka, J. B. DeCoste, S. M. Cohen, *J. Am. Chem. Soc.* **2016**, *138*, 920-925; c) Y. Zhang, X. Feng, H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang, B. Wang, *Angew. Chem., Int. Ed.* **2015**, *54*, 4259-4263.

[58] a) G. R. Whittell, I. Manners, *Adv. Mater.* **2007**, *19*, 3439-3468; b) J.-C. Eloi, L. Chabanne, G. R. Whittell, I. Manners, *Mater. Today* **2008**, *11*, 28-36.

[59] T. Ishiwata, Y. Furukawa, K. Sugikawa, K. Kokado, K. Sada, *J. Am. Chem. Soc.* **2013**, *135*, 5427-5432.

[60] G. Distefano, H. Suzuki, M. Tsujimoto, S. Isoda, S. Bracco, A. Comotti, P. Sozzani, T. Uemura, S. Kitagawa, *Nat. Chem.* **2013**, *5*, 335-341.

[61] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276-279; b) D. J. Tranchemontagne, J. R. Hunt, O. M. Yaghi, *Tetrahedron* **2008**, *64*, 8553-8557.

[62] D. Saha, Z. Bao, F. Jia, S. Deng, *Environ. Sci. Technol.* **2010**, *44*, 1820-1826.

[63] E. V. Perez, K. J. Balkus Jr, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2009**, *328*, 165-173.

[64] a) C. A. Allen, J. A. Boissonnault, J. Cirera, R. Gulland, F. Paesani, S. M. Cohen, *Chem. Commun.* **2013**, *49*, 3200-3202; b) C. A. Allen, S. M. Cohen, *Inorg. Chem.* **2014**, *53*, 7014-7019.

[65] P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature* **2013**, *495*, 80-84.

[66] a) S. Henke, A. Schneemann, S. Kapoor, R. Winter, R. A. Fischer, *J. Mater. Chem.* **2012**, *22*, 909-918; b) S. Henke, R. A. Fischer, *J. Am. Chem. Soc.* **2011**, *133*, 2064-2067; c) S. Henke, A. Schneemann, A. Wütscher, R. A. Fischer, *J. Am. Chem. Soc.* **2012**, *134*, 9464-9474.

[67] A. Bhattacharya, B. N. Misra, *Prog. Polym. Sci.* **2004**, *29*, 767-814.

[68] N. Tien-Binh, H. Vinh-Thang, X. Y. Chen, D. Rodrigue, S. Kaliaguine, *J. Mater. Chem. A* **2015**, *3*, 15202-15213.

[69] a) S. Furukawa, J. Reboul, S. Diring, K. Sumida, S. Kitagawa, *Chem. Soc. Rev.* **2014**, *43*, 5700-5734. b) R. Ricco, C. Pfeiffer, K. Sumida, C. J. Sumby, P. Falcaro, S. Furukawa, N. R. Champness, C. J. Doonan, *CrystEngComm* **2016**, *18*, 6532-6542.

[70] B. Seoane, S. Castellanos, A. Dikhtiarenko, F. Kapteijn, J. Gascon, *Coord. Chem. Rev.* **2016**, *307*, 147-187.

[71] T.-H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones, S. Nair, *Angew. Chem. Int. Ed.* **2010**, *49*, 9863-9866.

[72] T. C. Merkel, H. Q. Lin, X. T.Wei, R. Baker, *J. Membr. Sci.* **2010**, *359*, 126-139.

[73] T. Li, Y. Pan, K.-V. Peinemann, Z. Lai, *J. Memb. Sci.* **2013**, *425-426*, 235-242.

[74] S. Konduri, S. Nair, *J. Phys. Chem. C* **2007**, *111*, 2017-2024.

[75] S. Choi, J. Coronas, E. Jordan, W. Oh, S. Nair, F. Onorato, D. F. Shantz, M. Tsapatsis, *Angew. Chem. Int. Ed.* **2008**, *47*, 552-555.

[76] Z. Kang, Y. Peng, Z. Hu, Y. Qian, C. Chi, L. Y. Yeo, L. Tee, D. Zhao, *J. Mater. Chem. A* **2015**, 3, 20801-20810.

[77] A. Sabetghadam, B. Seoane, D. Keskin, N. Duim, T. Rodenas, S. Shahid, S. Sorribas, C. Le Guillouzer, G. Clet, C. Tellez, M. Daturi, J. Coronas, F. Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2016**, *26*, 3154-3163.

[78] G. Zhu, H. Ren, *Porous Organic Frameworks, Design, Synthesis and Their Advanced Applications*, Springer-Verlag GmbH Berlin, **2015**.

[79] N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, 35, 675-683.

[80] C. H. Lau, K. Konstas, C. M. Doherty, S. Kanehashi, B. Ozcelik, S. E. Kentish, A. J. Hill, M. R. Hill, *Chem. Mater.* **2015**, *27*, 4756-4762.

[81] C. H. Lau, X. Mulet, K. Konstas, C. M. Doherty, M.-A. Sani, F. Separovic, M. R. Hill, C. D. Wood, *Angew. Chem. Int. Ed.* **2016**, *55*, 1998-2001.

[82] R. Dawson, A. I. Cooper, D. J. Adams, *Prog. Polym. Sci.* **2012**, *37*, 530-563.

[83] M. Jung, H. Kim, K. Baek, K. Kim, *Angew. Chem. Int. Ed.* **2008**, *47*, 5755-5757.

[84] J. Ma, Y. Ying, Q. Yang, Y. Ban, H. Huang, X. Guo, Y. Xiao, D. Liu, Y. Li, W. Yang, C. Zhong, *Chem. Commun.* **2015**, *51*, 4249-4251.

[85] a) K. Nagai, T. Masuda, T. Nakagawa, B. D. Freeman, I. Pinnau, *Prog. Polym. Sci.* **2001**, *26*, 721-798. b) H. B. Park, C. H. Jung, Y. M. Lee, A. J. Jill, S. J. Pas, S. T. Mudie, E. V. Wagner, B. D. Freeman and D. J. Cookson, *Science* **2007**, 318, 254-258.

[86] C. Zhao, N. Wang, L. Wang, S. Sheng, H. Fan, F. Yang, S. Ji, J.-R. Li, J. Yu, *AIChE J.* **2016**, *62*, 3706-3716.

[87] C. Zhao, N. Wang, L. Wang, H. Huang, R. Zhang, F. Yang, Y. Xie, S. Ji, J.-R. Li, *Chem. Commun.* **2014**, *50*, 13921-13923.

[88] Q. Song, S. Jiang, T. Hasell, M. Liu, S. Sun, A. K. Cheetham, E. Sivaniah, A. I. Cooper, *Adv. Mater.* **2016**, *28*, 2629-2637.

[89] a) L. Liu, Z. Jiang, F. Pan, F. Peng, H. Wu, *J. Membr. Sci.* **2006**, *279*, 111-119. b) P. P. Chapala, M. V. Bermeshev, L. E. Starannikova, V. P. Shantarovich, N. N. Gavrilova, V. G. Avakyan, M. P. Filatova, Yu. P. Yampolskii, E. Sh. Finkelshtein, *J. Membr. Sci.* **2015**, *474*, 83-91.

[90] a) L. Y. Jiang, T. S. Chung, *J. Membr. Sci.* **2009**, *327*, 216-225. b) P. P. Chapala, M. V. Bermeshev, L. E. Starannikova, V. P. Shantarovich, N. N. Gavrilova, Yu. P. Yampolskii, E. Sh. Finkelshtein, *Polym. Compos.* **2015**, *36*, 1029-1038.

[91] See, for examples: a) H. L. Chen, L. G. Wu, J. Tan, C. L. Zhu, *Chem. Eng. J.* **2000**, *78*, 159-164. b) A. Yamasaki, K. Mizoguchi, *J. Appl. Polym. Sci.* **1994**, *53*, 1669-1674. c) S. J. Lue, S. H. Peng, *J. Membr. Sci.* **2003**, *222*, 203-210.

[92] J. D. Evans, D. M. Huang, M. R. Hill, C. J. Sumby, A. W. Thornton, C. J. Doonan, *J. Phys. Chem. C* **2014**, *118*, 1523-1529.

[93] T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973-978.

[94] M. W. Schneider, I. M. Oppel, H. Ott, L. G. Lechner, H. J. S. Hauswald, R. Stoll, M. Mastalerz, *Chem.-Eur. J.* **2012**, *18*, 836-847.

[95] H. Kudo, R. Hayashi, K. Mitani, T. Yokozawa, N. C. Kasuga, T. Nishikubo, *Angew. Chem. Int. Ed.* **2006**, *45*, 7948-7952.

[96] J. Tian, P. K. Thallapally, S. J. Dalgarno, P. B. McGrail, J. L. Atwood, *Angew. Chem. Int. Ed.* **2009**, 48, 5492-5495.

[97] S. Jiang, L. Chen, M. E. Briggs, T. Hasell, A. I. Cooper, *Chem. Commun.* **2016**, *52*, 6895-6898.

[98] M. Benzaqui, R. Semino, N. Menguy, F. Carn, T. Kundu, J.-M. Guigner, N. B. McKeown, K. J. Msayib, M. Carta, R. Malpass-Evans, C. Le Guillouzer, G. Clet, N. A. Ramsahye, C. Serre, G. Maurin, N. Steunou, *ACS Appl. Mater. Interfaces* **2016**, *8*, 27311-27321.

[99] a) S. Kanehashi, G. Q. Chen, C. A. Scholes, B. Ozcelik, C. Hua, L. Ciddor, P. D. Southon, D. M. D'Alessandro, S. E. Kentish, *J. Membr. Sci.* **2015**, *482*, 49-55; b) S. Kanehashi, G. Q. Chen, L. Ciddor, A. Chaffee, S. E. Kentish, *J. Membr. Sci.* **2015**, *492*, 471-477.

[100] A. Sabetghadam, B. Seoane, D. Keskin, N. Duim, T. Rodenas, S. Shahid, S. Sorribas, C. L. Guillouzer, G. Clet, C. Tellez, M. Daturi, J. Coronas, F. Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2016**, *26*, 3154-3163.

[101] T. Rodenas, M. van Dalen, E. García-Pérez, P. Serra-Crespo, B. Zornoza, F Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2014**, *24*, 249-256.

[102] S. J. D. Smith, C. H. Lau, J. I. Mardel, M. Kitchin, K. Konstas, B. P. Ladewig, M. R. Hill, *J. Mater. Chem. A* **2016**, *4*, 10627-10634.

[103] M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4368-4369.

[104] a) H. Furukawa, J. Kim, K. E. Plass, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 8398-8399. b) J. J. Perry, V. C. Kravtsov, M. J. Zaworotko, R. W. Larsen, *Cryst. Growth Des.* **2011**, *11*, 3183-3189. c) M. Tonigold, J. Hitzbleck, S. Bahnmuller, G. Langstein, D. Volkmer, *Dalton Trans.* **2009**, 1363-1371.

[105] a) Y. Ke, D. J. Collins and H.-C. Zhou, *Inorg. Chem.* **2005**, *44*, 4154-4156. b) S. Furukawa, N. Horike, M. Kondo, Y. Hijikata, A. Carné-Sánchez, P. Larpent, N. Louvain, S. Diring, H. Sato, R. Matsuda, R. Kawano, S. Kitagawa, *Inorg. Chem.* **2016**, *55*, 10843-10846.

[106] J. M. Teo, C. J. Coghlan, J. D. Evans, E. Tsivion, M. Head-Gordon, C. J. Sumby, C. J. Doonan, *Chem. Commun.* **2016**, *52*, 276-279.

[107] J.-R. Li, H.-C. Zhou, *Nat. Chem.* **2010**, *2*, 893-898.

[108] N. Hosono, M. Gochomori, R. Matsuda, H. Sato, S. Kitagawa, *J. Am. Chem. Soc.* **2016**, *138*, 6525-6531.

[109] S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695-704.

[110] L. Diestel, N. Wang, B. Schwiedland, F. Steinbach, U. Giese, J. Caro, *J. Membr. Sci.* **2015**, *492*, 181-186.

[111] R. W. Baker, *Membrane Technology and Applications*, John Wiley & Sons, England, 2nd edn., **2004**.

[112] a) M. F. A. Wahab, A. F. Ismail and S. J. Shilton, *Sep. Purif. Technol.* **2012**, *86*, 41-48. b) S. Husain and W. J. Koros, *J. Membr. Sci.* **2007**, *288*, 195-207. c) N. Peng, N. Widjojo, P. Sukitpaneenit, M. M. Teoh, G. G. Lipscomb, T.-S. Chung and J.-Y. Lai, *Prog. Polym. Sci.* **2012**, *37*, 1401-1424.

[113] a) S. Basu, A. Cano-Odena and I. F. J. Vankelecom, *J. Membr. Sci.* **2010**, *362*, 478-487. b) S. Basu, A. Cano-Odena and I. F. J. Vankelecom, *Sep. Purif. Technol.* **2011**, *81*, 31-40. c) H. Ren, J. Jin, J. Hu and H. Liu, *Ind. Eng. Chem. Res.* **2012**, *51*, 10156-10164. d) N. Nordin, A. Ismail and A. Mustafa, *J. Teknol.* **2014**, *69*, 73-76.

[114] S. Loeb and S. Sourirajan, in *Saline Water Conversion-II*, ACS, Washington DC, USA, **1963**, vol. 38, ch. 9, pp. 117-132.

[115] C. Zhang, K. Zhang, L. Xu, Y. Labreche, B. Kraftschik and W. J. Koros, *AIChE J.* **2014**, *60*, 2625-2635.

[116] a) M. S. Denny, S. M. Cohen, *Angew. Chem., Int. Ed.* **2015**, *54*, 9029-9032. b) J. C. Moreton , M. S. Denny Jr. and S. M. Cohen, *Chem. Commun.* **2016**, *52*, 14376-14379.

[117] I. N. Odeh, Y. Liu (Sabic Global Technologies B.V.), WO2017003661, **2017**.

[118] C. Li, B. McCulloch, S. T. Wilson, A. I. Benin, M. E. Schott (UOP LLC), US 7,637,983 B1, **2009**.

[119] R. R. Willis (UOP LLC), US 2011/0138999 A1, **2011**.

[120] T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin, A. J. Hill, *Science*, **2002**, *296*, 519-522.

REVIEW

Entry for the Table of Contents

REVIEW
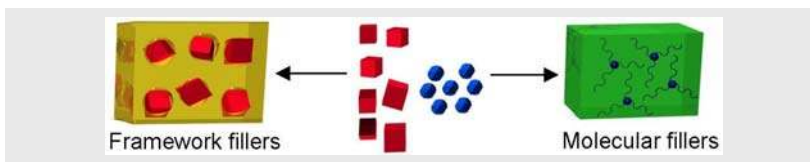
Framework fillers   Molecular fillers

The research highlighted in this review further suggests that novel filler materials will advance the field of MMMs and overcome long standing challenges such as polymer aging.

Janina Dechnik, Jorge Gascon, Christian J. Doonan, Christoph Janiak* and Christopher J. Sumby*