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Review

# A review on emerging organic-containing microporous material membranes for carbon capture and separation

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HIGHLIGHTS:

- Criteria in selecting microporous materials for $CO_2$ separation membrane is given.
- The membrane fabrication based on MOFs, POFs, TR polymers, and PIMs is summarized.
- The membrane performance in $CO_2$ separation under differents conditions is analyzed.
- The challenge and perspective for future development are pointed out.

GRAPHICAL ABSTRACT
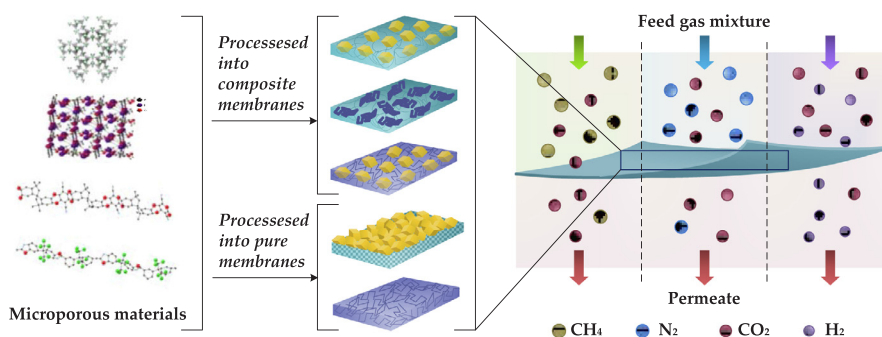


ARTICLE INFO

ABSTRACT

Membrane technology has gained great attention as one of the promising strategies for carbon capture and separation. Intended for such application, membrane fabrication from various materials has been attempted. While gas separation membranes based on dense polymeric materials have been long developed, there is a growing interest to use porous materials as the membrane material. This review then focuses on emerging organic-containing microporous materials to be used for the fabrication of membranes that are designed for $CO_2$ separation. Criteria for selecting the materials are first discussed, including physical and chemical properties, and parameters in membrane fabrication. Membranes based on these materials, such as metal-organic frameworks, porous organic frameworks, and microporous polymers, are then reviewed. Finally, special attention is given to recent advances, challenges, and perspectives in the development of such membranes for carbon capture and separation.

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## 1. Introduction

Increased attention to the environmental sustainability has encouraged global efforts to reduce carbon emissions from various industrial processes. For this reason, carbon dioxide ($CO_2$) separation is necessary to be applied in at least three important areas: pre-combustion to eliminate $CO_2$ from the main fuel ($CO_2/H_2$ separation), post-combustion where $CO_2$ will be separated from flue gases ($CO_2/N_2$ separation) and oxy-fuel combustion to produce a high concentration $CO_2$ gas stream from a combustion process of fuel and pure oxygen. In addition, $CO_2$ separation is also required in the natural gas processing and biogas upgrading ($CO_2/CH_4$ separation).

Currently, absorption technology using amine could be considered as the most mature option to accomplish the $CO_2$ capture and separation process [1]. However, the most crucial drawback with this process lies on the economical aspect and energy penalty to regenerate the absorbent [2]. There are then various alternative technologies to address the issue such as adsorption, carbonate looping, ionic liquids and membranes. Among the alternative technologies available, membrane technology could be considered as the most promising. Apart from its relative maturity compared with other technologies, this is also because membrane process could offer various advantages in terms of footprint,

energy consumption and cost [3–5]. Potential applications for membrane-based $CO_2$ separation are then depicted in Fig. 1. Various polymers (cellulose acetate, polysulfone, polyimide) and inorganic materials (alumina, YSZ) have been widely investigated to fabricate membrane both in flat-sheet and hollow fibre configuration for gas separation. However, the performance of the current membranes still needs to be further improved particularly to meet the targeted performance for industrial application and commercialization. For large application of $CO_2$ removal from natural gas, the $CO_2$ membrane permeance is targeted at more than 100 GPU (100 Barrer with 1 μm membrane thickness) with $CO_2/CH_4$ selectivity in the range of 20–30. Meanwhile for $CO_2$ capture from flue gas, the membrane is expected to have $CO_2$ permeance of more than 1000–5000 GPU with $CO_2/N_2$ selectivity in the range of 30–50. And for pre-combustion $CO_2$ capture, the $H_2$ membrane permeance is targeted to be more than 200 GPU with more than 10 in $H_2/CO_2$ selectivity [6]. In this respect, employment of new and advanced porous materials could be expected the satisfy these targets.

In general, porous materials could be classified into four different classes: inorganic (zeolite), carbon-based (carbon nanotube), organic-based (microporous polymers, porous organic frameworks) and hybrid (metal–organic frameworks) [7]. During the last two decades, there is a
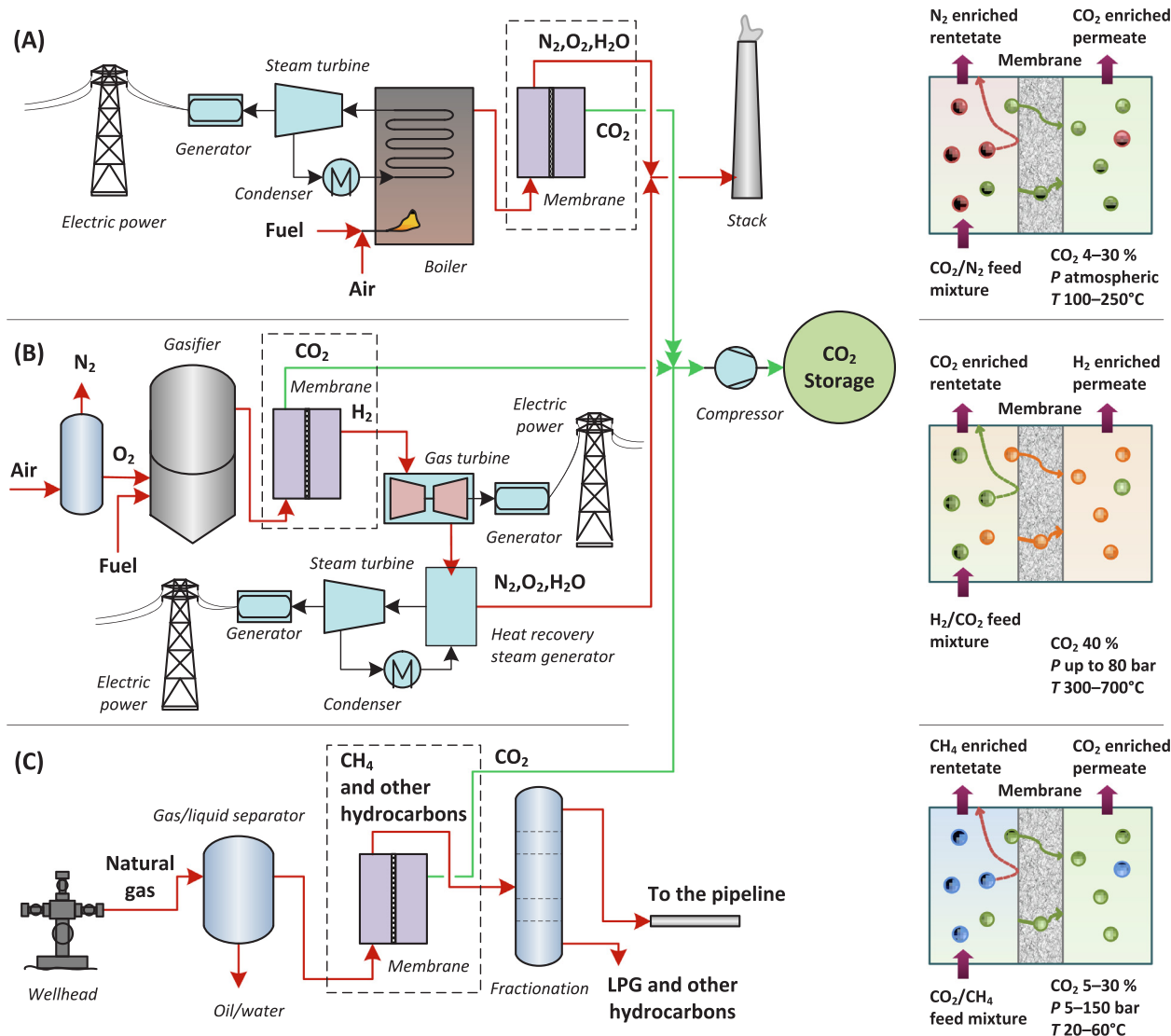


**Fig. 1.** Potential applications for membranes in $CO_2$ separation: (A) post-combustion, (B) pre-combustion, and (C) natural gas processing. The corresponding membrane gas separation and its process conditions are shown in the right picture.
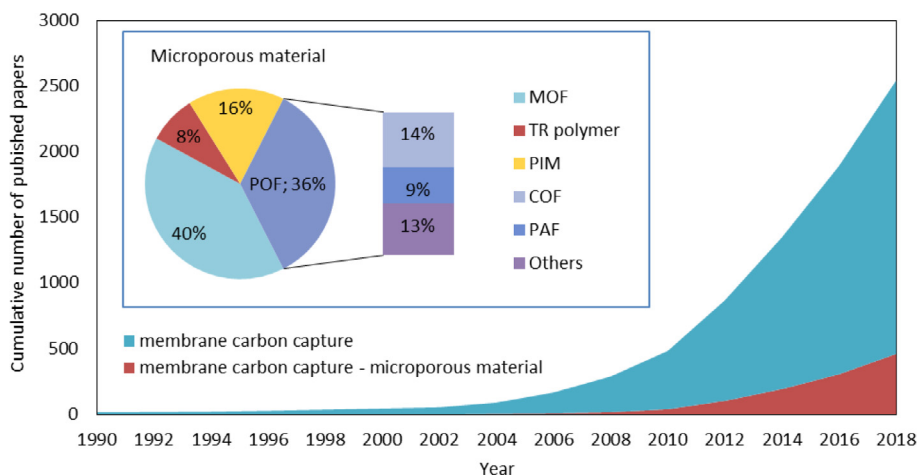
**Fig. 2.** The cumulative number of published articles related to the membranes and microporous material-based membranes for carbon capture. The inserted pie diagram presents the percentage of published articles reporting each type of microporous material.

growing interest in the development of the last two classes of the porous materials that contain organic compounds in their framework. Compared with the rest of the porous materials, this growing interest could be attributed to various factors but primarily because of their framework flexibility, pore size tailorability and the presence of organic components in their framework which could be utilized further for functionalization [8]. In particular for membrane field, these advantages could render them to have better performance in terms of molecular sieving effect and materials compatibility and thus makes them attractive to be an advanced membrane material. As can be seen in Fig. 2, although research in this field is still not a major constituent in the overall membrane carbon capture research field, the trend still reflects a growing research interest since the last decade with metal organic frameworks (MOF) and porous organic frameworks (POF) leading the trend. Therefore, in this review article, we choose to focus on the recent progresses on these last two classes of the porous materials that contains organic compounds. This will be then further classified into MOF, POF and microporous polymers which include polymer of intrinsic microporosity (PIM) and thermally-rearranged (TR) polymers. Although a number of review articles on porous materials and gas separation membranes have been published with various focuses [9–12], in this review article, we choose to focus on these organic-containing emerging porous materials that can be utilized further as a membrane material for $CO_2$ separation. This is important since we believe that membrane-based processes should be the next promising process for $CO_2$ separation and porous materials could significantly contribute in this field.

## 2. Microporous material selection criteria for $CO_2$ capture and membrane fabrication

### 2.1. Microporous materials criteria

Both physical and chemical properties could affect the $CO_2$ separation performance in microporous materials which, once applied in membrane, could also impact the membrane performance for $CO_2$ separation. This section will then concisely discuss both aspects.

### 2.1.1. Physical properties

In most gas separation membrane, the transport of gas molecules follows the solution-diffusion mechanism (Fig. 3). Based on this mechanism, the gas molecule will be firstly adsorbed on the feed side, diffuse through the membrane and desorbed at the permeate side. A judicious selection of microporous materials based on their physical properties is then expected to enhance the gas transport in membrane

both in the adsorption and diffusion steps. In this respect, employing a microporus material with high surface area and interconnected free volume is preferable. This is because the material will have high gas adsorption capacity and also able to effectively aid the adsorbed gas to diffuse through the membrane. This then results in faster gas transport across the membrane. Most of microporous materials have then satisfied this requirement since most of them have a very high surface area (in the.order of thousands of square metre per gram) and interconnected free volume [13,14].

However, this must also be accompanied with judicious selection of materials with correct pore size to also improve the gas selectivity. In this respect, different mechanisms can occur depending on the size of the pore and the gas molecule (Fig. 3). A material with a pore size close to the size of the targeted molecule is much preferred since thie will impart a confinement effect and thus enhancing the adsorption process [15]. This mechanism is called molecular sieving and occurs when the microporous material has the right pore size to exclude the larger gas molecules. Once the pore size increases and is suitable to accommodate both gases that are to be separated, various separation mechanisms could happen such as Knudsen diffusion and selective surface diffusion. Depending on the interaction between the gas molecule and the material, diffusion or equilibrium-based phenomenon would be the one dominating factor. The former happens if the pore size is just slightly larger than the largest gas molecule to be separated. In this phenomenon, a larger gas molecule would be excluded based on the diffusion mechanism since it diffuses slower than the smaller one. Meanwhile, the equilibrium based separation happens once both gases can diffuse easily inside the pore of the material and thus the separation is governed by the interaction between the framework and the gases [16]. In this case, a larger gas molecule could be more selectively adsorbed and passed through than the smaller gas molecule if the former has better interaction with the material. Therefore, designing microporous materials with correct pore aperture for $CO_2$ separation is important to improve the microporous material selectivity and the size is usually less than 1 nm and preferably around 3.0–7.0 Angstrom [17,18]. In addition to correct pore size, the selected microporous material should also have a narrow pore size distribution [19]. This is because a wide pore distribution could lead to unselective gas transport, particularly in the presence of a very large pore. When the pore size is too large, a viscous transport mechanism could occur when both gases could easily pass through the membrane without any resistance resulting in reduced membrane selectivity.

Apart from selecting the microporous materials with suitable physical properties, choosing materials with high $CO_2$ affinity is also crucial. This is because, for some cases, porous materials with an
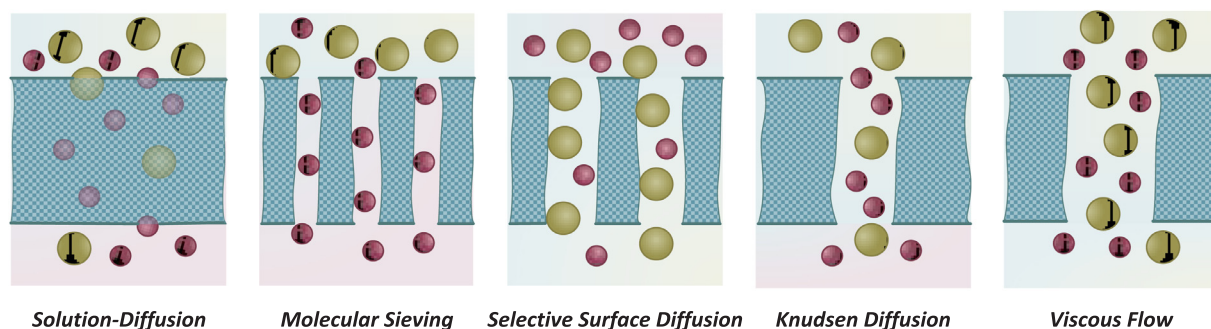
**Fig. 3.** Various separation mechanisms in microporous materials adsorbents and membrane.

exceptionally high surface area are not necessarily selective towards $CO_2$ [15]. Therefore, chemical properties of the materials needs to be considered before turning them into membrane.

### 2.1.2. Chemical properties

Compared to physical properties, chemical properties of emerging microporous materials are considered to be more important to enhance $CO_2$ capture performance [9]. A comprehensive review on this matter has been previously published such as for MOFs [20] and POFs [17]. For the purpose of this article, a concise explanation is necessary to justify the selection of the microporous materials.

For $CO_2$ separation, the functional groups that contain nitrogen, oxygen, sulfur or phosphorus can improve the affinity between $CO_2$ and the materials [21]. This beneficial aspect has been explored using various functional groups incorporated inside microporous materials. The common example is to use amine group. As in conventional absorption process, amine groups in microporous materials could enhance their $CO_2$ uptake and selectivity [22]. This is particularly important in low-pressure region where adsorption occurs in the most energetic region of the solid surface since $CO_2$ can readily make a C-N covalent bonding with the amine group through the chemisorption process [22].

Nitrogen-rich functional groups are also beneficial for $CO_2$ capture [23–25]. Microporous materials for $CO_2$ separation could then be functionalized using this functional group such as triazole [26], azobenzene [27,28] and benzimidazole [29]. The presence of nitrogen-rich microporous materials has been reported to improve the selectivity of $CO_2$ against $N_2$ and $CH_4$ through various mechanisms such as the dipole-quadrupole interaction [30] and nitrogen-phobicity environment [27]. A functional group that is not only rich in nitrogen but also has a $CO_2$-philic property such as tetrazole [31] is also beneficial in improving $CO_2$ separation since it provides a basic environment to attract more $CO_2$ into the pores.

The presence of polar functional groups is also beneficial for $CO_2$ capture to enhance $CO_2$ selectivity based on polarity. This has been proven for example in the family of Zeolitic Imidazolate Frameworks (ZIF) [32] and Covalent Organic Frameworks (COF) [33]. The polar functional groups can have a greater attraction towards $CO_2$ resulting from the quadrupole moment and thus resulting in a lower parasitic energy loss when applied in a carbon capture plant. Its benefit could even be doubled when using multiple functional groups in a porous material [33].

For MOFs in particular, open metal sites can also help to adsorb more $CO_2$ since it can behave as a Lewis acid site [34]. This usually comes from the removal of terminated solvent molecules inside the MOFs pore. Therefore, MOFs that have a denser population of open metal sites in a unit cell exhibit higher $CO_2$ uptake at low-pressure region than those with lower, or no open metal sites [35]. As open metal sites, the presence of heteroatoms in MOFs is also beneficial in improving the $CO_2$ capture performance [20]. This property is particularly important if the materials are going to be applied at low-pressure operating conditions such as post-combustion $CO_2$ capture [16].

Lastly, choosing materials with chemical property that could withstand the real application condition is necessary. This is because the presence of contaminants such as water vapor and acid gases in the real condition of $CO_2$ separation process cannot be neglected. In this case, microporous materials with a hydrophobic property could be a promising option. This is because its hydrophobicity could enhance the material resistance towards water vapour attack which could competitively adsorb to the active sites and lowering the $CO_2$ selectivity. This is particularly important for porous materials that are functionalized with polar functional groups since their tendency to be more easier in attracting water molecule [15,20].

### 2.2. Membrane fabrication

There are at least three core parameters need to be satisfied to turn a microporous material into a membrane: high permeability and selectivity, ease of fabrication, and robust structure. All of these properties and its relationship with the emerging microporous materials is discussed in the following section.

### 2.2.1. Permeability and selectivity

Performance in gas separation membranes is usually evaluated against the Robeson Upper Bound [36]. The graph depicts the trade-off between permeability and selectivity: membranes with higher permeability usually have lower selectivity, and vice versa. Research in gas separation membranes based on emerging microporous materials then aims to surpass this limit [36,37].

The membrane permeability in a polymeric membrane could be described by solution-diffusion model with Barrer as the permeability unit [1 Barrer = $10^{-10}$ $cm^3$(STP) cm $cm^{-2}$ $s^{-1}$ $cmHg^{-1}$] [38]. In this model, the permeability is affected by two parameters: solution and diffusion. The former is related to gas molecule solubility in a membrane material. Meanwhile, the latter is related to the size of each gas molecule. For most of the commercially available polymeric membranes, the permeability is mainly affected by the void space built from intermolecular space of the polymer which is called free volume [9,39]. The main drawback of the current polymeric membranes is their relatively low fractional free volume (FFV) since it is not interconnected, resulting in low membrane permeability [9,39]. As discussed above, this issue could then be addressed when using a microporous materials membrane since their pores are more interconnected as indicated by their high surface area and thus membrane with higher gas permeability could be obtained [17]. However, for practical application and commercialization, relying on membrane permeance is more relevant than membrane permeability since it reflects the real membrane productivity [40]. Membrane permeance is defined as the ratio between the permeability and membrane thickness. Thus, membrane thickness reduction is necessary to obtain a high permeance membrane. In this respect, the microporous materials compatibility to be constructed as a thin selective layer needs also to be carefully assessed so a high permeance membrane could be obtained.
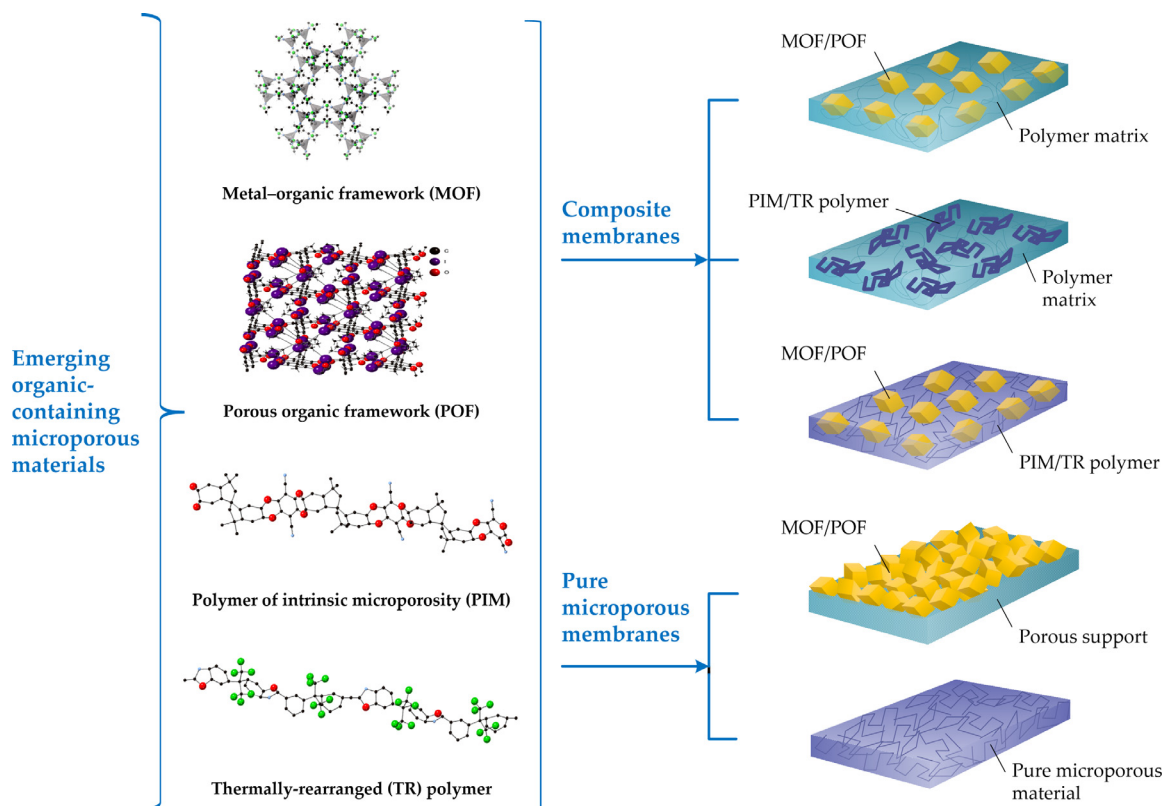
**Fig. 4.** Various approaches to fabricate $CO_2$ separation membranes based on microporous materials.

Selectivity is another important parameter in determining membrane gas separation performance. Selectivity is defined in a relative term between the permeability of one component against another, usually between the faster and the slower permeating gas. This depends on the permeation rate of each gas in the membrane. In post-combustion applications, a membrane with high $CO_2$ permeation is expected while impeding the $N_2$ transport. A membrane with similar property is also expected for natural gas purification where it must be selective in rejecting $CH_4$. In contrast, for pre-combustion application, the membrane should have high permeability towards $H_2$ and impede the $CO_2$ transport. For microporous materials-based membrane, both rational tuning of the pore size and pore functionalization are effective to improve this parameter since they contribute in enhancing both the molecular sieving ability and the surface interaction between the gas and the materials. [31,41].

### 2.2.2. Ease of fabrication

Emerging organic-containing microporous materials can be formed into a membrane either by fabricating a pure microporous membrane or a composite membrane as can be seen in Fig. 4. For a pure microporous membrane, the simplest approach is by employing solution-casting method. This might be the most suitable for materials that are solution-processable such as PIMs [42]. Meanwhile, for nonsolution-processable materials such as MOFs and COFs, turning them into a pure microporous membrane is usually accomplished by growing a continuous layer on a porous support. However, the main challenge for this technique lies in growing a defect-free membrane. This issue could be addressed, for example, by inducing a heterogeneous crystallization on the substrate [43], growing a multilayer structure [44] or by chemically altering the substrate to enhance the bonding between the materials and the substrate [45]

Because of this challenge, research has also explored composite membranes where two different materials are combined. This can be a composite of polymer and microporous materials (MOFs-polymer or

PIMs-polymer for example) or between microporous materials (MOFs-PIMs composite for example). The advantage of this method is the simplicity of the fabrication process. Because one of the components is usually solution-processable, the other components can be dispersed in the solution, followed by membrane casting. However, the major issue in this area is compatibility between the two different components. Poor compatibility between two different materials will result in membrane defects and non-selective voids. If a good compatibility between two different materials could be obtained, a satisfactory separation performance and improved mechanical properties such as tensile strength [46], Young modulus [46], and plasticization [47] could be obtained. In this case, emerging microporous materials such as MOFs and COFs contain organic compounds that will help to improve the compatibility with polymer. They could also be engineered to have 2D structure that could help in particle distribution in a polymer matrix [48]. In addition, both physical and chemical properties of either the microporous materials [49] or a polymer [50] could also be modified to improve their interaction.

### 2.2.3. Real-life performance

Applying membranes for $CO_2$ separation at industrial scale requires a robust testing condition. High pressure operating condition is required for membranes applied for pre-combustion $CO_2$ capture and natural gas sweetening. Meanwhile, both pre and post-combustion $CO_2$ capture requires operation at elevated temperature. Investigation at high operating pressure is also important since $CO_2$ is a condensable gas and at high operating pressure, the sorption of $CO_2$ starts to plasticize the membrane resulting in decrease of membrane selectivity [51].

The presence of feed impurities in $CO_2$ separation process must also be investigated [38,52]. This is because the presence of moisture and other contaminants can affect the membrane performance and thus the plant operating cost [53]. For $CO_2/CH_4$ separation, for instance, the natural gas stream usually contains a fraction of other hydrocarbons [54] and water vapour is also present in almost all $CO_2$ separation

processes [55]. This might impact the membrane separation performance. Competitive adsorption on the microporous-materials based membrane should also be investigated. This is because it could cause permanent damage to microporous-porous based membranes for $CO_2$ separation [53]. In this case, a mixed gas scenario is highly recommended to study the competitive sorption and diffusion.

Lastly, long-term membrane performance must also be evaluated since polymeric membranes for gas separation could suffer from physical aging [56]. Physical aging is a thermodynamic phenomenon experienced particularly in a polymer with a poor chain packing because of the chain relaxation and convergence leading to the reduction of fractional free volume of the membrane [51,57]. This phenomenon is commonly observed with PIMs-based membranes resulting in $CO_2$ permeability reduction and slightly enhanced selectivity. From the industrial perspective, aging is an unfavourable condition since it leads to productivity reduction and performance unpredictability.

## 3. Metal-organic frameworks-based membrane

Metal-organic frameworks (MOFs) are built from a metal or a metal cluster connected by organic linker as a ligand. MOFs have gained an increased interest because of their numerous positive aspects such as large surface area, adjustable pore size, and post-synthetic modification (PSM) potential. MOFs have also been investigated for membrane fabrication. Generally, there are two ways to turn MOFs into a membrane: incorporation of MOFs inside a polymer matrix to fabricate a mixed matrix membrane (MMMs) and growing of MOF thin film on a porous substrate which will be discussed below regarding their performance for $CO_2$ separation.

MOFs-based MMMs have been widely investigated and are considered as a promising candidate for $CO_2$ separation since it can outperform the performance of most of the polymeric membranes [20]. Various factors need to be considered to fabricate MOF-based MMMs with satisfactory $CO_2$ separation performance such as polymer selection, composition ratio, and MOF morphology. Polymer selection is crucial since incorporating MOF into rubbery polymers is not beneficial to increase both $CO_2$ permeability and selectivity compared to glassy polymers [58]. This might be caused by MOFs pore intrusion by the rubbery polymer resulting in MOF ineffectiveness.

Regarding MOF-polymer composition ratio, ideally, increasing MOFs loading in membranes should increase both membrane permeability and selectivity since they increase the free volume and enhance molecular sieving through chain rigidification [59,60]. However, up to a certain point, higher MOFs loading could only increase the membrane permeability but decrease the selectivity. This might be caused by several reasons such as particle agglomeration [61], particle sedimentation [62] and inhomogeneous particle dispersion leading to interfacial polymer-particle voids [63]. Thus, there is an optimum value for MOFs loading in a polymer matrix. Once the optimum value has been surpassed, inter-particle interaction starts to dominate which negatively impacts the MMMs performance [64].

Tailoring MOF property and morphology could also be an option to improve membrane performance. This could be done through various approaches such as PSM [65] and post-synthetic annealing (PSA) [66,67] to improve both MOF-polymer and MMM-$CO_2$ interaction. MOF's pores functionalization [68,69] and decoration with polymer [70] could also be used to improve the MMM molecular sieving ability and affinity towards $CO_2$. The MMMs performance could also be improved by designing MOFs to be in 2D structure. In case of $H_2/CO_2$ separation, the separation factor could be improved by incorporating MOF nanosheets since the nanosheets interlayer stacking creates a preferable pathway for $H_2$ to permeate compared to $CO_2$ [71]. MOF nanosheets could also enhance MMM productivity by the possibility to fabricate thinner membranes to increase the permeance [72]. Amorphous-MOF that was fabricated through in-situ thermal treatment in polymer matrix could also significantly improve the $CO_2/CH_4$

selectivity [73]. Apart from polymer cross linking, the thermal treatment on the ZIF-8-Matrimid MMMs turned the ZIF-8 to be amorphous but has not yet changed the overall structure and thus still retained its pore network to improve the molecular sieving property of the resulting membrane.

The MOF-based MMMs performance could also be enhanced by combining MOFs with other particles such as with other MOFs [74], graphene-based materials [75] and zeolites [76]. New MOF-composite fillers could also be synthesized such as ZIF-8-graphene oxide [77,78] and UiO-66-graphite oxide [79]. By combining MOF with other porous materials with different properties, it is expected that the molecular sieving property and $CO_2$ affinity of the composite membranes could be improved [75,78].

Once succesfully fabricated, the performance of MMMs for $CO_2$ separation is influenced by various operating conditions. High operating pressure could reduce both MOF-based MMMs $CO_2$ permeability because of saturation of Langmuir adsorption site [80] and selectivity because of plasticization and if the MOF has structural flexibility such as ZIF-8 [81]. Enhancement in selectivity, however, can be expected for $CO_2$ separation since higher pressure leads to higher $CO_2$ adsorption onto the MOFs and can prevent the active MOFs sites to be occupied fby other gases such as $CH_4$ [82]. Higher operating pressure can also be beneficial if flexible MOFs, such as MIL-53 (Al), is used which has higher $CO_2$ selectivity at higher pressure because of its breathable framework [81,83]. Temperature also affects the membrane performance. For MMMs built from glassy polymers, the increase in operating temperature is usually followed by the increase in polymer chain flexibility resulting in higher gases permeability [71,83]. Thus, it is important to maintain the operating condition where the membrane still retains high $CO_2$ selectivity since $CO_2$ permeance did not increase as fast as other gases such as $CH_4$ and $N_2$ resulting in lower selectivity [77,83]. The presence of contaminants will also impact the membrane performance. The presence of water vapour in the feed could negatively impact the permeation of light gases such as $CO_2$ and $CH_4$ [84]. Moreover, the negative impact is much more pronounced if the fillers used are more hydrophilic such as Cu-BTC and UiO-66 than in hydrophobic MOFs such as ZIF-8 since they are more attractive to water vapour [84].

MOF could also be turned into a MOF membrane by growing them onto a porous substrate. Growing a thin defect-free inter-crystalline layer is necessary to obtain a high flux and highly selective membrane which could be accomplished through various approaches [85]. One strategy is to focus on inducing heterogeneous nucleation on a porous substrate. This could be accomplished through seeding with MOF particles, to fabricate various MOF membranes such as MIL-53 (Al) [86], ZIF-7 [87], ZIF-8 [88], Mg-MOF-74[89], and UiO-66-$CH_3$ [90]. Seeding could also be accomplished by using other inorganic particles such as $TiO_2$ to assist the growing of ZIF-8 MOF and improve the overall mechanical structure (Fig. 5 (A), (B) and (C)). A seed-free technique can also be an option where both MOF nucleation and growing occur at the same time [91]. This could be done such as by preparing from an optimized and concentrated MOFs growing condition [92,93], a thermal ligand-deposition followed by crystal growing [94], gel-based processing [95], or utilization of substrate metal source to induce growing of MOF-film [96].

A defect-free MOFs membrane is expected to surpass the Knudsen selectivity value. The values for $H_2/CO_2$, $CO_2/N_2$ and $CO_2/CH_4$ are 4.7; 0.8 and 0.6, respectively. Although most MOF membranes could surpass these values, there are some cases where the separation performance could be negatively altered caused by preferential adsorption. This has been observed for $H_2/CO_2$ separation where $CO_2$ is preferentially adsorbed on the MOFs resulting in reverse selectivity [93,97]. For $CO_2/N_2$ and $CO_2/CH_4$ separation, high adsorption capacity of $CH_4$ could also result in a significantly lower $CO_2/CH_4$ selectivity than $CO_2/N_2$ because of less-available sites for $CO_2$ to get adsorbed and permeate through the membrane [98]. Therefore, understanding the adsorption-diffusion trade-off in MOF membranes is important to
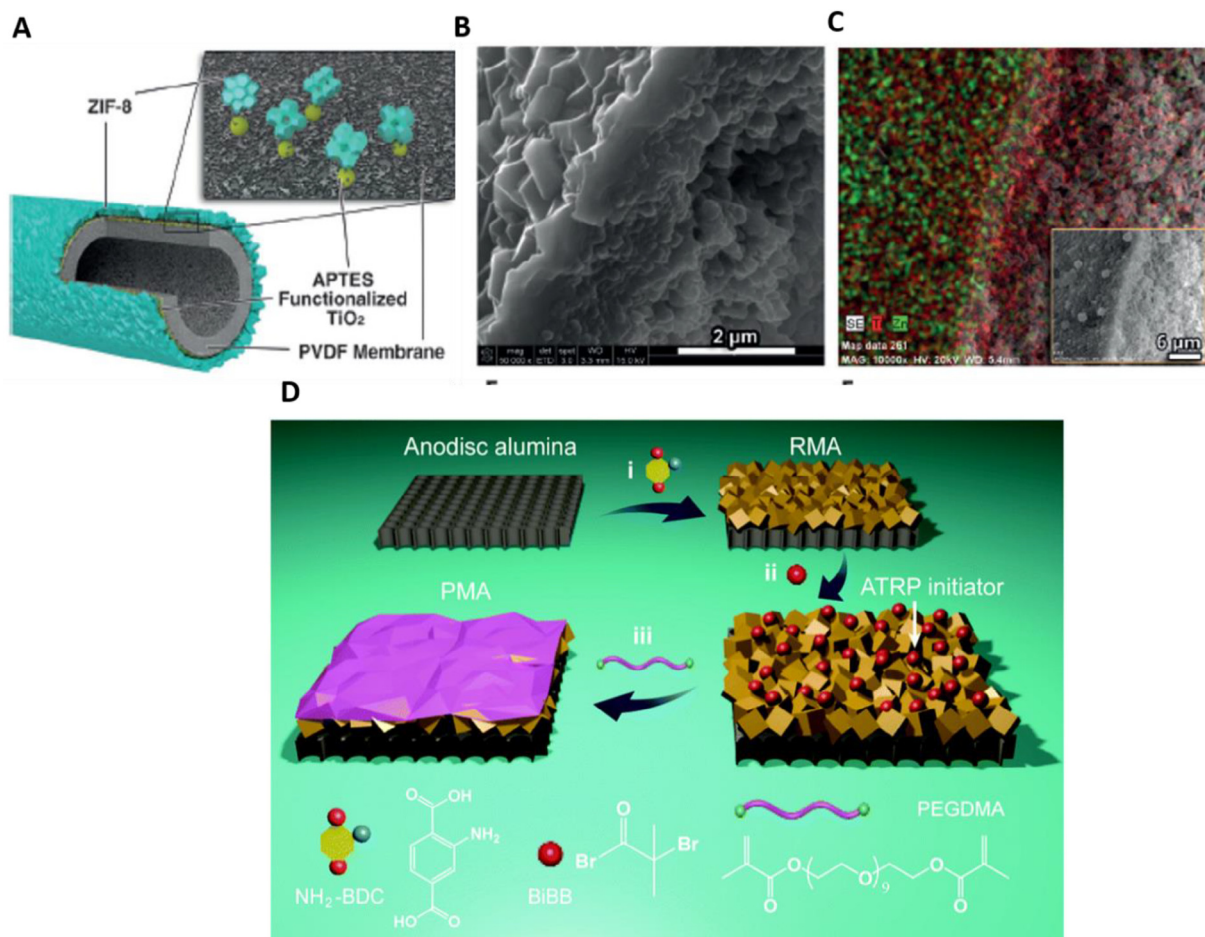
**Fig. 5.** Strategies for MOF membrane fabrications. Fabrication of ZIF-8 membrane on polymeric APTES-functionalized $TiO_2$ hollow fibre substrate (A) with its SEM cross sectional evaluation (B) and EDX mapping (C). Reprinted with permission from [111]. Copyright 2016, Wiley-VC. The bottom-up fabrication of the polymer/MOF composite architecture (PMA) using MOF as the gutter layer (D). Reprinted with permission from [109]. Copyright 2018, Royal Society of Chemistry.

obtain satisfactory $CO_2$ separation performance.

An increase in temperature does not always increase the gas permeability of MOF membranes, unlike the phenomenon usually observed in MOF-based MMM [89,99]. For instance, almost no change in $CO_2$ permeability was observed for ZIF-7 [100] and MOF-5 [101] membranes as the temperature was increased. In contrast, all gases permeance decreased with increasing temperature in a copper-based MOF membrane [102] and in a ZIF-90 membrane [98]. Meanwhile, in $Zn_2(bim)_4$ nanosheet membrane, the $CO_2$ permeation was observed to increase as temperature was increased [34]. This can be explained by the diffusion and adsorption phenomena in MOFs membrane. The former is a temperature-activated process, and an increase in diffusion and permeance is expected as the temperature is increased. However, the increase in temperature could also reduce the gas coverage on the MOFs surface because of lower adsorption at higher temperature [99]. As a result, each MOFs membrane has its own permeation activation energy. If this permeation activation energy is too small, temperature will barely affect the gas permeation through MOFs membrane. Despite this, it does seem that operating at high temperature for $H_2/CO_2$ separation might be beneficial for MOFs which adsorb $CO_2$ strongly, since higher temperature leads to less adsorbed $CO_2$ and higher free volume in the MOFs could be obtained for enhanced $H_2$ diffusion [103].

Differing from temperature, operating pressure in MOFs membrane permeation is more related to the adsorption. Increasing pressure usually results in higher gas flux but barely affects its normalized value [98,104]. A positive impact of higher operating pressure could be experienced in a highly $CO_2$-selective MOF membrane in the presence of

gas mixture. In this case, preferential adsorption towards $CO_2$ compared to other gases could improve the $CO_2/N_2$ or $CO_2/CH_4$ separation factor [104]. A contrasting situation, however, might be observed if there are different mechanisms taking place at the same time such as viscous flow in $CH_4$ leading to the reduction of $CO_2/CH_4$ selectivity at higher operating pressure [99,104].

Feed composition also affects the separation performance of MOF membranes. Increasing $CO_2$ concentration in $H_2/CO_2$ separation degrades its separation performance because of competitive adsorption [34]. Meanwhile, for $CO_2/N_2$ and $CO_2/CH_4$ separation, increasing the fraction of $CO_2$ is beneficial since it will saturate the MOFs pores with $CO_2$ and inhibits adsorption of both $N_2$ and $CH_4$, and their diffusion through the membrane resulting in an improvement of separation performance [99,105]. Despite this, a study using ZIF-8 membrane has also shown the possibility to obtain a satisfactory separation performance with low $CO_2$ partial pressure for $CO_2/CH_4$ separation when operated at low temperature and low pressure [104]. This is because the diffusion of $CH_4$ and other hydrocarbons will be limited while at the same time the surface of the MOF membrane is still saturated with $CO_2$ because of its preferential adsorption [99].

Apart from utilization of MOF as filler in MMM and fabrication as a selective layer, there are also other innovative approaches in turning MOF into a membrane. One approach is to fabricate a composite membrane containing MOF and other materials apart from polymer such as graphene oxide (GO) [106] and ionic liquid [107]. In this case, the MOF is fabricated as a selective layer and the role of the additional materials is to seal the inter-crystalline defects through both capillary
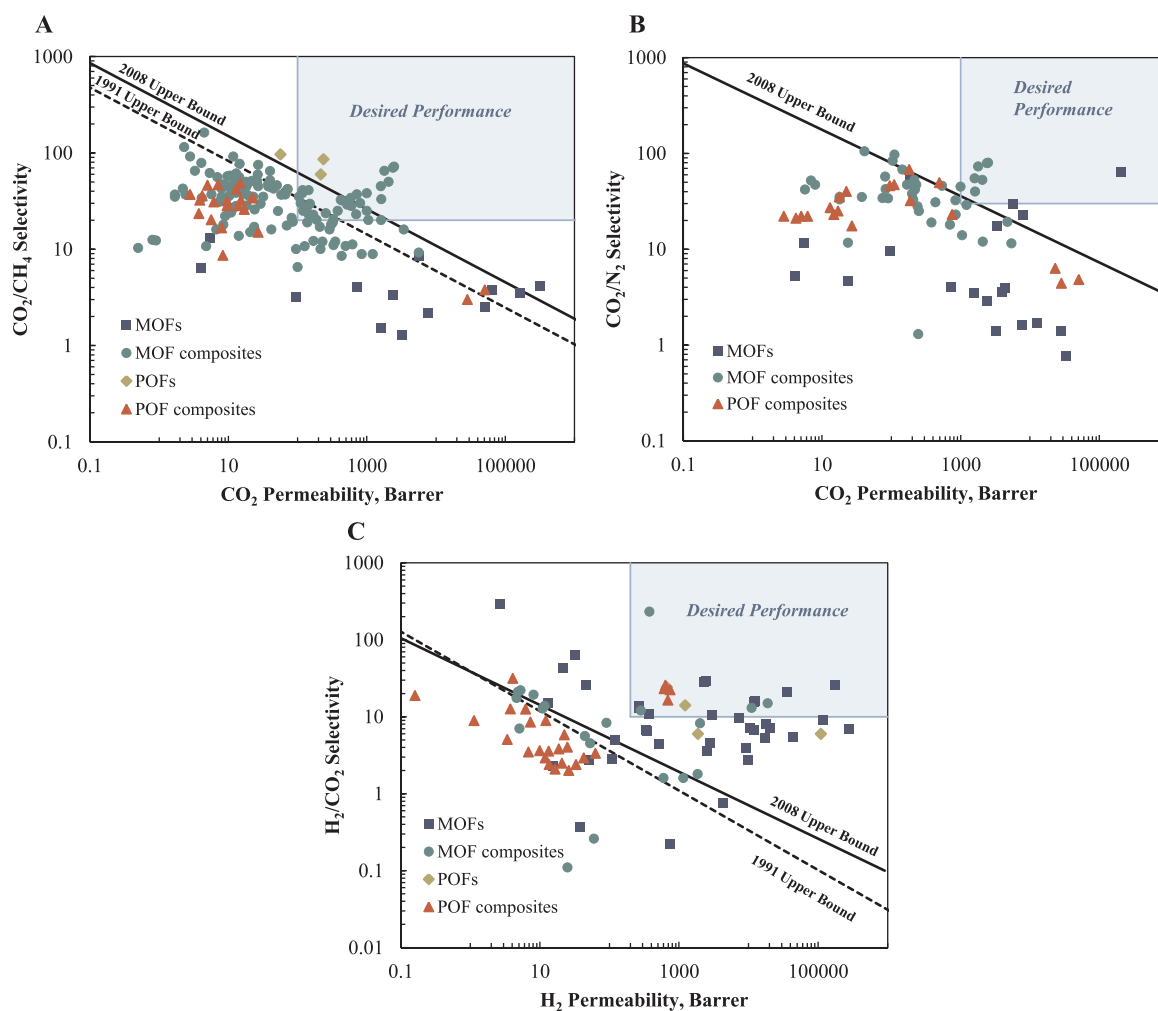
**Fig. 6.** Performance Summary of MOF and POF-based membranes for $CO_2/CH_4$ separation (A), $CO_2/N_2$ separation (B) and $H_2/CO_2$ separation (C). Data for the graph is availablefrom Table S1-S5 in the Supplementary Information.

force and covalent bonding and thus enhancing $CO_2$ selectivity [108]. However, the thickness of this additional material should be controlled so they will not add more resistance to the overall gas transport which could result in reduced $CO_2$ permeability [107]. Another innovative approach is to use MOFs as a gutter layer rather than as a selective layer. In this case, the MOF layer is then further covered by a more selective polymeric membrane layer [72,109,110] (Fig. 5 (D)). This can be accomplished by using spin coating [110] or cross-linking approach [109]. Apart from enhancing $CO_2$-selectivity in the membrane, employing MOF as the gutter layer could reduce the overall membrane resistance resulting in higher $CO_2$ permeability [110]. Further optimization in this approach is to produce a very thin selective layer on top of the MOF gutter layer to reduce the overall membrane resistance.

Having discussed the various approaches to turn MOF into membrane and factors affecting their $CO_2$ separation performance, the overall performance summary is then given in Fig. 6. For the $CO_2/N_2$ and $CO_2/CH_4$ separation, it could be clearly seen that just few MOF membranes could surpass the 2008 Robeson Upper Bound. Although they exhibit a superior $CO_2$ permeability up to 100,000 Barrer, the kinetic diameter similarities between the pairs might hinder the MOF membranes to have excellent selectivity which falls around 10. Meanwhile, most of composite MOF membranes fall in the middle region with $CO_2$ permeability range between 10 and 1000 which could depend on the property of the other constituent material. Despite its relatively lower permeability than MOF membrane, they exhibit satisfactory

selectivity which might be contributed from the combined properties of the constituent materials. For instance, with a judicious selection, a composite membrane fabricated sulfonated MIL-101 and sulfonated poly(ether ether ketone) (SPEEK) could reach permeability up to 2000 Barrer with more than 50 selectivity [112]. Meanwhile for $H_2/CO_2$ separation, both MOF membranes and composites have satisfactory performance in surpassing the 2008 Robeson Upper Bound. However, MOF membranes do seem to exhibit higher $H_2$ permeability and thus placing them to be closer in the desired performance region. Their high $H_2$ permeability which could reach up to 100,000 Barrer is accompanied with high selectivity more than 10 which satisfies the targeted performance. This then highlights the contribution of both the molecular sieving and pore environment of the MOF once a suitable MOF such as $Zn_2(bim)_4$ [34] and $NH_2$-Mg-MOF-74 [89] could be fabricated as a defect-free membrane.

## 4. Porous organic frameworks (POFs) based membrane

In addition to MOFs, there are other classes of porous material that are entirely built from organic compounds. They are classified with different names including covalent organic framework (COF), porous aromatic framework (PAF), covalent organic polymers (COP), porous organic polymers (POP), etc. For simplicity in this review, they are classified as porous organic frameworks (POF). This covers porous materials that are built from organic structures which can be crystalline
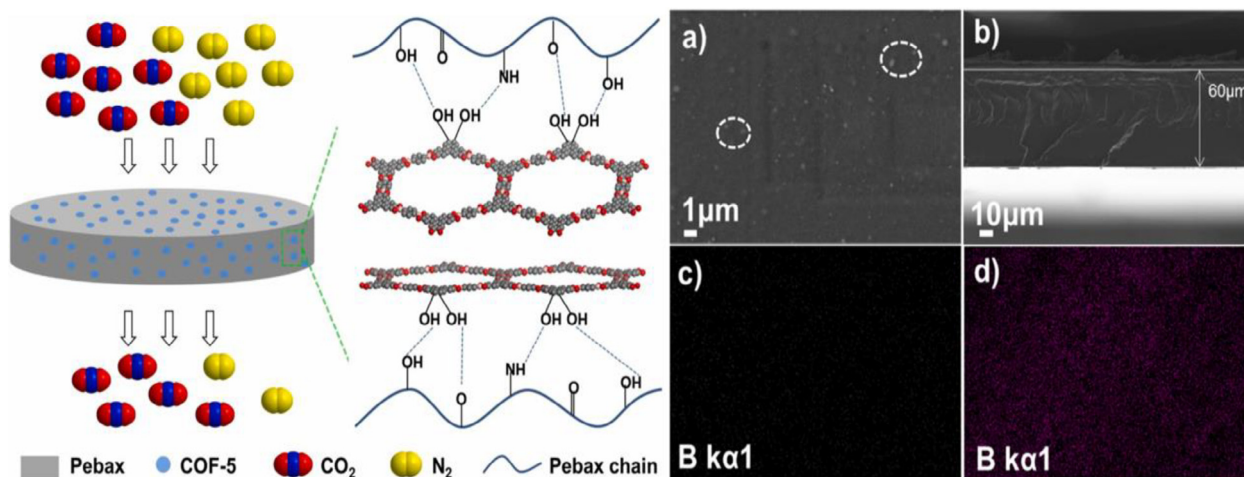
**Fig. 7.** Schematic diagram of functionalized-COF-5 – PEBAX MMM for $CO_2/N_2$ separation and its SEM images of (a) surface; (b) cross-section; EDS mapping images of B element (c) pristine Pebax membrane; (d) COF-5/Pebax membrane (0.4 wt%). Reprinted with permission from [114]. Copyright 2019, Elsevier B. V.

such as COF and PAF or amorphous such as COP and POP. As in MOFs, these materials have gained increased interest in the area of $CO_2$ capture as an adsorbent because of their high surface area and tailorability to be selective towards $CO_2$. Therefore, they are also promising to be turned into a membrane.

As in MOF, various studies for $CO_2$ capture using POFs have also been directed to the fabrication of POFs-based MMMs [17]. Since the POFs structure is entirely built from organic materials, it is expected that MMMs with a high particle loading could be obtained because of better POF-polymer interaction. This has been obtained by using PBI-BuI as the polymer matrix and TpBD and TpBA as fillers. Up to 50 wt% of a defect-free TpBA composite membrane could be obtained, resulting in high gas flux and $CO_2/CH_4$ selectivity [113]. Polymer-particle interaction can also be further enhanced by establishing hydrogen bonding from functionalized COFs (Fig. 7) [114]. Despite this, a similar threshold loading value in MMMs is also usually observed where further increase does not render any incremental positive impact to the resulting membranes [23,115].

POFs properties and morphology could then be tailored to improve the membrane performance. Employing POF with $CO_2$-philic groups is beneficial in enhancing both membrane permeability and selectivity since it has preferential $CO_2$ adsorption to induce continuous $CO_2$ adsorption–desorption [116–119]. They also contribute in blocking other gases such as $CH_4$ to permeate through [119]. A nitrogen-rich COF could be employed for $CO_2/N_2$ separation since they usually exhibit a higher $CO_2/N_2$ selectivity which could be translated to blocking $N_2$ permeation in the membrane [23,120]. Meanwhile, molecular sieving in POF's pores could also be enhanced through decoration with polymer [121] or with MOF [122] resulting in enhanced MMM $CO_2$ separation performance.

POFs with 2D morphology could also be used to improve the MMMs performance. This could be obtained through exfoliation (top-down approach) as in NUS-2 and NUS-3 [115] or bottom-up approach where they are prepared during synthesis as in NUS-8 [123]. Although the POF crystallinity might be lost in the former method, their in-phase structure and porosity could still be maintained to enhance the gas separation performance. This 2D COF approach has been proven to improve MMM performance for both pre- and post-combustion $CO_2$ capture, even at low loading below 10 wt% thanks to the molecular sieving improvement through polymer crystallinity enhancement [123].

Operating conditions then play a significant role in affecting the POFs-based MMMs performances. Higher temperature leads to higher polymer chain mobility resulting in increase in FFV and faster gas permeation [124]. This could result in lower $CO_2$ separation factor

which might be caused by enhanced diffusion rate of other gases such as $CH_4$ and $N_2$ compared with $CO_2$ [122,124]. Operating pressure can also affect the overall membrane performance. Once the pressure is increased, the Langmuir adsorption site of a membrane starts to be saturated and the adsorption site move to Henry sites. As a result, there will be a reduction in gas permeability caused by a decrease in gas solubility. This is more serious for strongly adsorbing gases such as $CO_2$ rather than the weakly-adsorbing ones such as $CH_4$ and $N_2$ and thus resulting in an overall decrease in $CO_2$ selectivity [122,125]. However, this might not be the case when a rubbery polymer is chosen as the continuous matrix since the permeability depends on the gas solubility and is directly proportional to pressure as the pressure is increased [125]. Lastly, different MMM performance is expected between single-gas and mixed-gas testing conditions. In the presence of other gases, competitive adsorption and diffusion occur inside the membrane which could usually lead to reduced membrane selectivity. However, employing POF with high $CO_2$-affinity could reverse the trend and higher $CO_2$ selectivity could be obtained [124].

One of the most interesting features investigated using POF as a filler in MMMs is their ability to improve the membrane resistance towards aging such as found in poly(1- trimethylsilyl-1-propyne) (PTMSP) [116], poly(4-methyl-2-pentyne) (PMP) [57] and PIM-1 [57,117]. In PAF-based MMM, selective aging phenomenon was even observed. During this phenomenon, the membrane selectivity improves as it ages but with a minimal decrease in membrane permeability. This feature is important since it can enhance the molecular sieving ability of the MMM and thus improves its separation performance such as for $CO_2/N_2$ separation [57].

Despite the limited reports, growing POFs-based membranes could be a very attractive approach for $CO_2$ separation. This is proven by simulation studies showing the potential of COF membrane to have superior $CO_2/N_2$ and $CO_2/CH_4$ separation performance once a defect-free membrane could be fabricated [126,127]. However, the POF material should be carefully selected to achieve this by fulfilling some criteria such as having the right pore aperture or the ability to be stacked to establish interpenetrating pore networks to establish molecular sieving and have $CO_2$-philic functional groups [127].

Once selected, there are various ways to fabricate POF-membranes. It could be fabricated through a solution processing method where the POFs are solubilized in a solvent followed by spin coating to deposit a POF film [128]. Substrate modification such as using (3-Aminopropyl) triethoxysilane (APTES) could also help to grow a defect-free POFs layer [45,129]. This technique could produce a bilayer COF membrane with enhanced molecular sieving from the interlaced pore built from two different COFs suitable for $H_2/CO_2$ separation [129]. POFs
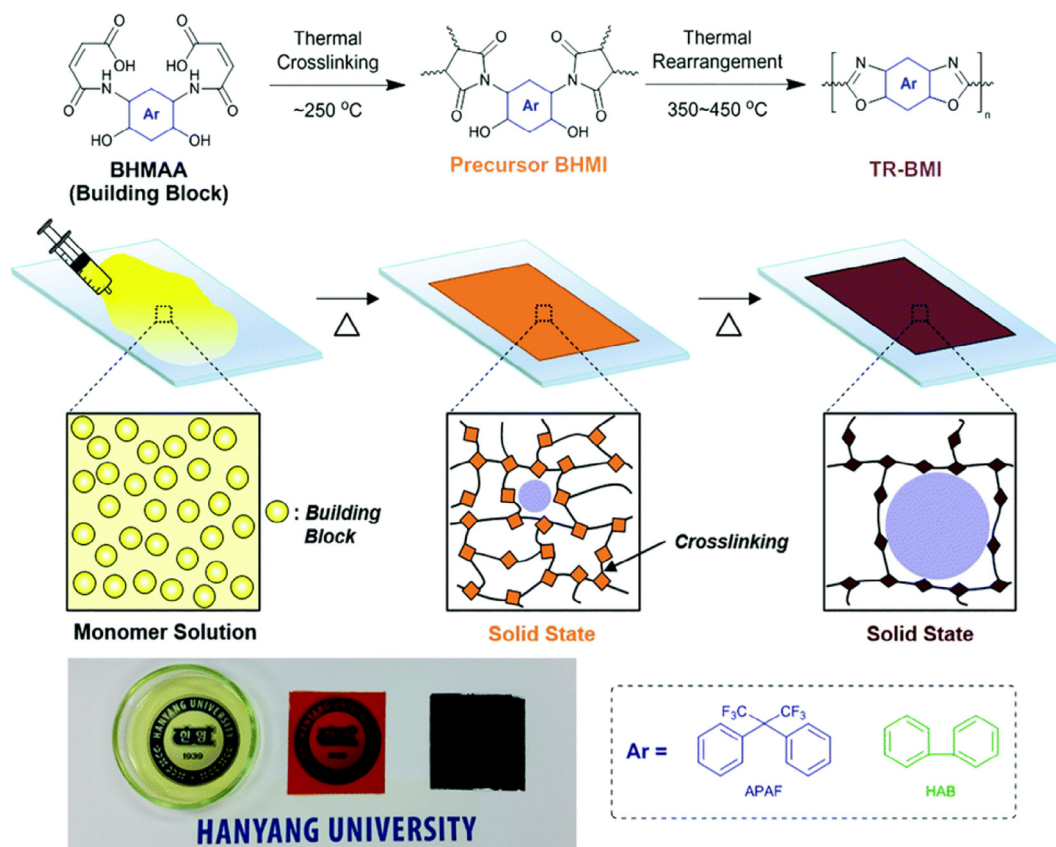
**Fig. 8.** Synthetic route and chemical structures of precursor BHMIs and TR-BMIs for membrane fabrication. Reprinted with permission from [134]. Copyright 2016, Royal Society of Chemistry.

membranes could also be fabricated using 2D POF which is directly stacked layer by layer [118] or aided by another inorganic particle such as GO which contributes to healing the membrane defects [130]. The narrow interlayer passages will act as a "gate" to achieve a molecular-sieving transport mechanism to enhance $H_2/CO_2$ selectivity. Interfacial polymerization (IP) is another technique investigated to fabricate a defect-free benzimidazole-linked polymers (BILPs) POF membrane suitable for pre-combustion $CO_2$ capture [131]. The robust nature of BILPs resulted in a membrane that could be operated up to 10 bar and 498 K which is a typical condition for pre-combustion $CO_2$ capture.

Various operating conditions could also influence the POF membrane performance. High operating pressure and temperature could deteriorate the membrane performance built from fragile POFs [128,131]. Meanwhile, the presence of water vapour could lead to framework hydrolysis [118,128]. This could then be mitigated by choosing robust POF frameworks or functionalized POFs as membrane material [118,126,128]. Aging could also be another issue for POF membranes, particularly when fabricated from amorphous POFs [128]. In this case, the thin layer of POF is in a *meta*-stable state which could not achieve its equilibrium state during membrane fabrication and thus tends to minimize their free volume once the fabrication process is finished. This could be addressed, for example, by establishing a stronger POF network to avoid POF chain movement after membrane fabrication [128].

The overall performance summary of POF-based membrane is then given in Fig. 6. As can be seen, differing from MOF membrane, research in POF membranes for $CO_2$ separation is still limited and more directed towards fabrication of POF composites. For $CO_2/N_2$ and $CO_2/CH_4$ separation, it could be seen that only few POF membranes have been fabricated and the best performance is exhibited by ACOF-1 with reported $CO_2/CH_4$ selectivity up to 86.4 [132]. Although its pore size is relatively big for molecular sieving, pore narrowing phenomenon

during intercrystalline growth might help to enhance the POF membrane selectivity. Meanwhile for POF membrane composites, most of them fall on the left side of the 2008 Robeson Upper Bound with reported permeability range around 10 Barrer with moderate selectivity. This might be contributed from fabrication of POF composites with glassy polymer matrix resulting in relatively low permeability and moderate selectivity. Despite this trend, employing POF with constricted pore size and $CO_2$-philic functionality seems promising as observed in a combination of POF-p-PVAm where more than 1000 GPU permeability with 68 selectivity could be obtained [121]. A similar trend could also be observed for the $H_2/CO_2$ separation. As can be seen, only a number of POF composites could satisfy the targeted performance. One of the best performers is the composite fabricated from CTF-1 and GO. In this case, the membrane with $CO_2$ permeability up to 745 Barrer and selectivity of 22 could be obtained [130].

## 5. Microporous polymer-based membrane

Developing new polymer-based materials with high permeability and selectivity is required to advance the material selection for $CO_2$ separation membrane. For this purpose, polymers with high FFV as well as a rigid structure are required. The recently developed membrane materials could then be classified as thermally rearranged (TR) polymers and polymers of intrinsic microporosity (PIMs).

### 5.1. Thermally rearranged polymers

Although aromatic polymers with heterocyclic rings, such as polybenzoxazole (PBO), polybenzimidazole (PBI), and polybenzothiazole (PBZ) have a rigid chain structure and good gas separation performance, they are poorly soluble in common solvents. Therefore, a thermal approach was proposed to fabricate the insoluble aromatic

polymer from a soluble polyimide precursor [133]. As the precursor polymers are soluble in common solvents, they can be easily processed into membranes using conventional solution casting method followed by heating to obtain aromatic polymeric membranes. The final membrane is called a TR polymer membrane.

The preparation of TR polymer membranes usually consists of three steps as visualized in Fig. 8: (i) synthesis of a soluble precursor polymer, which typically involves imidization process, (ii) membrane fabrication from the polymer precursor, and (iii) the thermal rearrangement of the membrane. The targeted characteristics of the final TR polymer membrane include FFV, microcavity size, and distribution, which can be manipulated by designing the polymer structure, synthesis route selection, and choosing the heat treatment protocols.

Different polymer structures can be controlled by varying the monomer structures. Two important criteria are chain rigidity and the presence of bulky bridging and/or pendant groups [135]. Monomers with high chain rigidity can minimize the chain relaxation during thermal treatment resulting in high FFV and gas permeability. The presence of bulky bridging and/or pendant groups on polymer chains can also increase free volume elements through disruption of the polymer chain packing density. Therefore, TR polymer membrane constructed from non-bulky and flexible polymer chains such as 4,4′-oxydiphthalic anhydride (OPDA) have the lowest $CO_2$ permeability and selectivity compared with other TR polymers constructed from a bulky and rigid structure [136].

Precursor polymers can be synthesized by thermal, azeotropic, chemical, or ester-acid imidization methods. The former is completed in the solid state while the rest are in liquid. Different imidization methods result in different precursor polymer structures which then influence the FFVs [137]. Compared with the rest, thermal imidization method favors the formation of FFV during imidization because of the low polymer chain mobility resulting in higher gas permeability once turned into a membrane. In case of $CO_2$ separation, TR-PBO prepared from chemically-imidized precursor (cTR-PBO) exhibited the highest $CO_2$ permeability followed by the thermally-imidized precursors (aTR-PBO). However, the latter had the highest $CO_2/N_2$ and $CO_2/CH_4$ selectivity [137,138]. Recently, intrinsically microporous polyimides (PIM-PIs) have also been used as the precursor polymer [139–141]. This strategy combines the PIMs and TR polymer structures to increase microporosity. The $CO_2$ permeability of the resulting membranes (PIM-TR-PBO or spiroTR-PBO) outperformed the PIM precursor and other TR-PBO membranes.

For thermal rearrangement, the precursor membranes are usually heated between 300 °C and 450 °C under a high-purity argon atmosphere [136]. During this process, the conversion of the polymer structure occurs and microcavities are formed which are influenced by the process parameters. Low temperature and short period rearrangement usually results in low-degree TR polymer formation [142], while high temperature formation could lead to precursor decomposition and brittle membrane [143]. Thermal treatment at optimum conditions then gives a high conversion to TR polymer resulting in increased FFV [141] and surface area [139,140]. The FFV in the resulting TR polymer membranes is usually in the range of 0.19–0.35 [136,137,141,144,145] which is comparable with high-free-volume glassy polymers such as PTMSP (0.29) [146], Teflon AF1600 (0.31), and Teflon AF2400 (0.33) [147]. Furthermore, the FFV in TR polymer membranes are three-dimensional interconnected microcavities that are analogues to micropores in certain adsorbents such as carbon molecular sieves [136]. This could then help in enhancing membrane gas permeability.

In selecting the best thermal treatment protocols, the chemical structure (chain rigidity) and the glass transition temperature ($T_g$) of the precursor polymer need to be considered since they influence the thermal conversion temperature [148,149]. For instance, using a bisphenol A type dianhydride (BisADA) in the polymer synthesis lowered the precursor $T_g$, which then successfully reduced the temperature of imide-to-benzoxazole conversion by about 100 °C [149]. The use of low

thermal treatment temperature is also desirable for manufacturing purpose and mechanical properties of the resulting membrane.

As stated before, thermal rearrangement can also bring a negative impact on the TR mechanical properties since the membrane can become brittle [150]. This can be addressed by incorporation of spiroobisindane [141], thermally labile units [151], and non-TR-able diamines [152,153] into TR polymer membranes. This could be attributed to the enhanced molecular chains by spiro kink group [141] and the presence of a flexible ether group from the non-TR-able unit [152]. In addition, formation of reduced GO scaffold inside TR polymer to create composite membranes can also provide mechanical robustness as well as remarkable $CO_2$ permeance [154].

The TR polymer membranes may also suffer physical aging because of their high FFV. Up to 50% decrease in $CO_2$ permeability was observed after 150 days of operation, which was accompanied by an increase in $CO_2/CH_4$ selectivity from 27 to 35 compared with the fresh TR membrane [139]. In-situ restoring procedure using methanol [155] and the addition of oxidized CNTs to the precursor solution [156] has been proposed to address this issue.

The separation performance of TR polymer membranes is also influenced by operating conditions such as pressure, temperature, and feed composition. There was a decline in pure $CO_2$ permeability as the upstream pressure was increased, while the permeabilities of less condensable gases were almost not affected by the pressure [142,157,158]. As a result, the selectivity also decreased [158]. When mixed-gas $CO_2/CH_4$ was used, the selectivity of TR polymer membranes improved because of the preferential competitive sorption [158], and even increased with the elevated pressure because of the enhanced sorption of $CO_2$ over $CH_4$ [159]. Furthermore, the TR polymer membranes offer good resistance to $CO_2$-induced plasticization. While the unconverted PI started to be plasticized at about 20 bar, the TR polymers only suffered mild plasticization and could even be resistant up to 50 bar [159]. They were also resistant against $SO_2$ and $H_2S$ plasticization which is important in real conditions with the presence of sulfur-based gases [160]. However, it seems that they still could not withstand the presence of water vapour, due to competitive adsorption [161]. Therefore, hydrophobic crosslinked TR polymer membranes are proposed to address this issue [162].

Performing $CO_2$ separation using TR polymer membrane at higher temperature resulted in increased $CO_2$ permeability, but in a lower extent compared to the other gases ($O_2$ and $N_2$), resulting in decreased selectivity [161]. This is attributable to the reduced solubility that is less favorable for $CO_2$ transport. In gas mixtures with $H_2$, the $CO_2$ permeability was significantly lower than $H_2$, resulting in a high $H_2/CO_2$ selectivity [163]. Thus, the TR polymer membrane has potential to be applied in pre-combustion $CO_2$ separation.

*5.2. Polymers of intrinsic microporosity*

Polymers of intrinsic microporosity (PIMs) were firstly developed by Budd and McKeown from a polycondensation reaction between tetrahydroxy-monomers containing spiro- or contorted centre with a tetrafluoro-monomers [164]. Differing from conventional polymers, the chain of PIMs has two distinguished properties: the absence of large-scale conformational change and the contorted structure. The former is caused by the rigidity of the PIMs backbone while the latter is caused by the random twisting of the polymer backbone [39]. As a result, gases could diffuse faster in PIMs-based membranes because of its high porosity. In addition, the presence of selective ultramicropores interconnected with big pores in PIMs also enhances its overall selectivity [165]. PIMs are considered as promising membrane material for $CO_2$ separation because of their satisfactory permeability and selectivity [42].

Since PIM is solution-processable, it could be easily turned into a membrane. In case of free-standing membrane, PIM could be used as the sole material or blended with other polymers or inorganic materials.

Another way is to use PIMs as the selective layer material as a thin film nanocomposite (TFN), in which the selective layer can be composed of PIM [166] or a nanocomposite [167]. As a neat membrane, PIMs have a very high gas permeability compared to other polymers because of its high FFV [168]. However, this FFV degree depends upon the preparation and treatment during membrane fabrication [168,169]. PIMs that are treated with alcohols usually have higher gas permeability than the untreated ones because of the complete solvent removal during membrane casting and increasing the FFV [39,169,170].

The $CO_2$ separation performance of PIMs-based membranes can then be improved by various ways. PIMs have nitrile groups on their backbones that can be further functionalized with amine [171], thioamide [170], beta-cyclodextrin [172], and tetrazole [173] to enhance its affinity with $CO_2$. Although becoming more selective, functionalized PIMs usually have lower $CO_2$ permeability because their pores are occupied by the functional groups. Cross-linking is another promising strategy. The cross-linking could be accomplished with UV-light illumination [174], thermal treatment [175] or by using chemical compounds such as pyrene [176]. The cross-linked PIMs membranes usually result in a reduction of the FFV and thus reduced gas permeability. However, this makes the PIM more diffusive-selective resulting in enhancement of $H_2/CO_2$, $CO_2/CH_4$ and $CO_2/N_2$ selectivity [175]. PIMs with enhanced $CO_2$ solubility could also be fabricated resulting in higher $CO_2/N_2$ selectivity during mixed gas separation since they could hinder the $N_2$ permeation [173].

PIMs could also be blended with other polymers such as polyetherimide [177], Torlon [178], matrimid [179], and Tröger's Base polymer [180] to improve their gas separation performance. Among various polymers, Tröger's Base polymer seems to match well with PIM-1 [180]. Since PIMs have high FFV, incorporation of other materials usually results in reduction of $CO_2$ permeability. However, this is usually followed by the improvement selectivity of $CO_2$ towards $CH_4$ and $N_2$ because the blended membrane will be more diffusive-selective [181].

Various fillers could also be incorporated inside PIMs to fabricate a PIM-based MMM. The fillers can be from MOFs [182,183], POFs [117,184,185] silica [186] and carbon nanotubes [187]. Once good interaction could be established, the additional void from the filers could contribute in improving the molecular sieving mechanism and $CO_2$ separation factor [184,188]. However, since PIMs already have high FFV, careful filler selection is required since without a correct pore size, the introduced voids could just decrease the $CO_2$ selectivity, particularly in the presence of interfacial defects [185]. This could then be mitigated in various ways, such as using a cross-linkeded PIM to establish a more robust cage for filler encapsulation (Fig. 9) or to cross-link the PIM with the filler [182].

Once used in $CO_2$ separation process, high operating pressure could lead to PIM-membrane swelling and plasticization resulting in the reduction of gas selectivity [190] and the onset of $CO_2$-induced plasticization pressure was lower for thinner membrane [191]. Therefore, in the presence of $CH_4$, lower $CO_2/CH_4$ selectivity is usually found in the plasticized membrane because of this phenomenon. Although the sorption selectivity barely changes, the $CO_2$-induced plasticization reduced the molecular sieveing ability of PIM membrane resulting in enhanced $CH_4$ diffusion and found to be more serious with ultramicroporous PIM [192,193]. The $CO_2$ permeance of PIM-1 membrane has been observed to decrease at higher temperature because of the negative activation energy [190]. This is in contrast with $CH_4$ permeance that has positive activation energy and thus resulting in $CO_2/CH_4$ selectivity reduction at higher operating temperature. This could be addressed, for example by introducing MOF into PIM resulting in improvement of $CO_2$ permeance [190]. With the prevalence of feed impurities in real $CO_2$ stream, the $CO_2$ separation performance of PIM membranes could also deteriorate significantly in high humidity condition and in the presence of contaminants, leading to permanent membrane damage [53]. The presence of water contributes to the

competitive sorption and permeation since it strongly interacts with the polar group resulting in less accessible sites for $CO_2$ adsorption while other contaminants might contribute in chemically altering the PIM structure [53].

Finally, physical aging is a serious problem in PIM-1 membranes. This is usually started with fast permeability reduction because of the presence of excess non-equilibrium FFV followed by a more gradual reduction since the polymer chain becomes less mobile after the first phase [193]. Membrane thickness and excess free volume could influence the PIM aging rate. Thinner PIM membranes age faster than the thicker ones [191]. PIM with high excess free volume (high current-specific-volume but low equilibrium-specific-volume) also ages faster because they have more driving force for aging to occur [193]. Although intrachain rigidity does not seem to address this issue [193], incorporating various fillers such as MOFs [188] and PAFs [57] are considered beneficial in suppressing the PIM aging rate by reducing the polymer chain mobility.

The overall performance of microporous polymers for $CO_2$ separation is then summarized in Fig. 10. For TR polymers, it could be seen that for $CO_2/N_2$ and $CO_2/CH_4$ separation, TR membranes $CO_2$ permeability fall in the range of 10–1000 Barrer with around 10–30 in selectivity. Although recent reports have shown that this membranes might not yet reach the satisfactory performance for $CO_2/N_2$ separation, its $CO_2/CH_4$ performance looks promising with up to 78 in selectivity and 540 membrane permeability once functionalized with amino group [194]. However, turning them into composite membranes do not seem to help in improving the overall performance as most TR composites only result in higher $CO_2$ permeability without significant change in selectivity. Differing from TR, although with comparable selectivity, PIM membranes have relatively higher $CO_2$ permeabiltiy. This renders PIM to be more promising for both $CO_2/N_2$ and $CO_2/CH_4$ separation. With this already satisfactory performance, turning them into a composite membrane such as by incorporation of functionalized MOFs, the PIM composite membrane $CO_2$ permeability could be enhanced to be more than 10,000 Barrer with around 20–30 selectivity and also with anti-aging property [68,182].

Meanwhile for $H_2/CO_2$ separation, researches in both pure and composite TR membranes have not shown any satisfactory performance. Their $H_2$ permeability does fall in the range of 100–1000 Barrer with a selectivity up to 3. This might indicate the poor molecular sieving ability in the membranes. In contrast, a rather promising performance is given by PIM-based membranes. As in $CO_2/N_2$ and $CO_2/CH_4$ separation, although with comparable selectivity, the $H_2$ permeabilty in PIM membranes are higher compared with TR. However, to further improve their selectivity to be close to 10, further cross-linking such as through UV treatment [174] or with other polymer such as Matrimid [195] is necessary to improve the molecular sieving within the PIM polymeric chain, although this must be accompanied with the sacrifice of $H_2$ permeability to be around 200 Barrer.

## 6. Challenges and future directions

Membranes fabricated from microporous materials are expected to satisfy at least four different aspects: performance (permeability and selectivity), structure and thickness, configuration, and system design [46]. In terms of membrane performance, it has been demonstrated that some of them have been able to surpass the 2008 Robeson Upper Bound. Interestingly, inorganic–organic frameworks seems promising for $H_2/CO_2$ separation, while microporous polymers are satisfactory for $CO_2/CH_4$ and $CO_2/N_2$ separation. This might be caused since the pore size in inorganic–organic hybrid frameworks is easier to be tuned than in microporous polymers resulting in enhanced molecular sieving. Therefore, apart from further pore fine-tuning, enhancement in the preferential adsorption should be further optimized to improve gas separation with similar sizes such as encountered in $CO_2/N_2$ and $CO_2/CH_4$ separation. Meanwhile for the microporous polymers, controlling
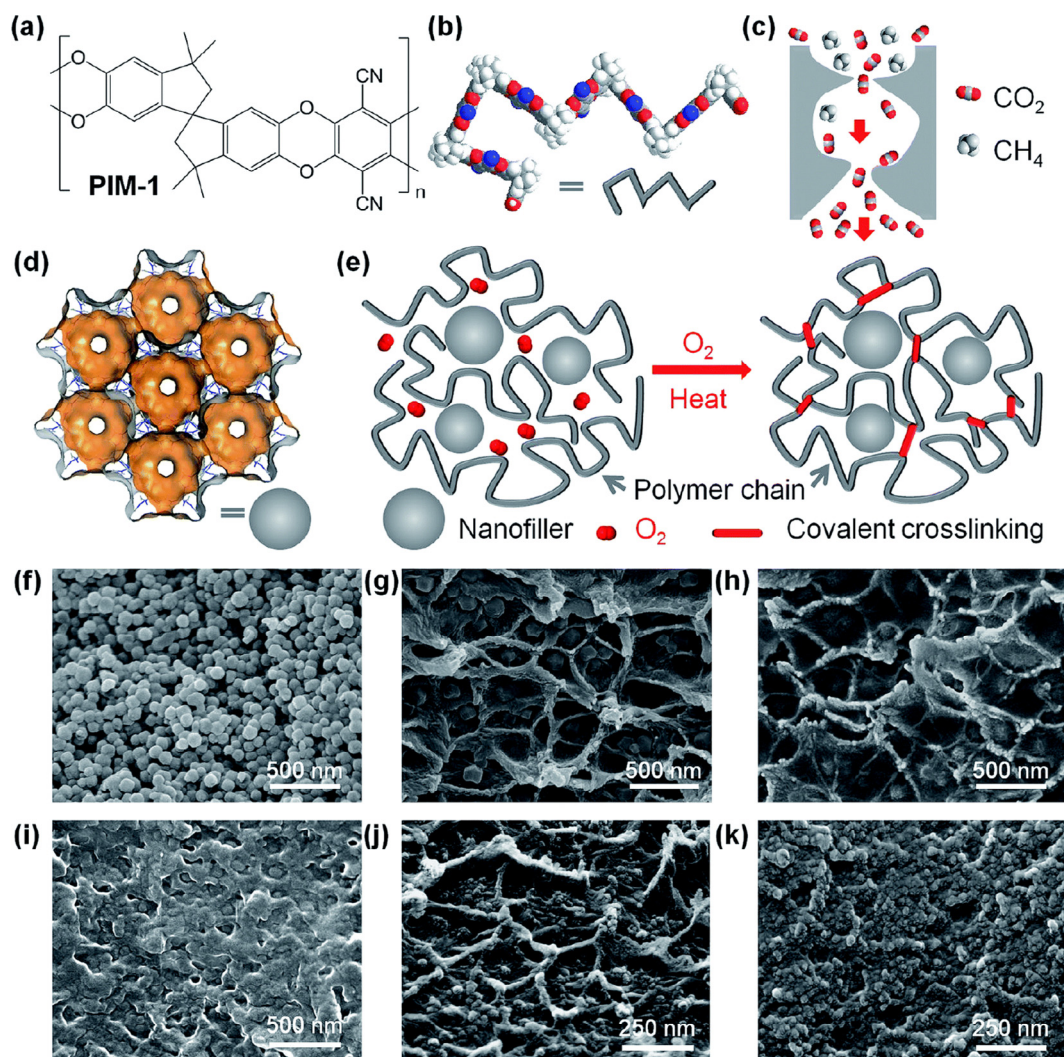
**Fig. 9.** Thermal-oxidative crosslinking of PIM-1 polymer nanocomposites incorporated with nanofillers. (a) Chemical structure of PIM-1 polymer. (b) 3D model of PIM-1 polymer chain segment. (c) Schematic diagram of molecular sieve membranes fabricated from PIMs polymer showing hour-glass-shaped interconnected cavities for rapid and selective transport of gas molecules (e.g. $CO_2$ and $CH_4$). (d) Molecular structure of ZIF-8. Yellow regions indicate Connolly surface probed by $H_2$ molecules. (e) Schematic diagram showing rigid polymer chains incorporated with nanofillers are covalently crosslinked to three-dimensional networks upon thermal-oxidative processing at suitable temperature (350–450 °C) in the presence of trace amount of oxygen. (f) SEM image of ZIF-8 nanocrystals. Cross-sectional SEM images of (g) PIM-1/ZIF-8 after annealing at 120 °C under vacuum (1 mbar), (h) TOX-PIM-1/ZIF-8 crosslinked at 385 °C for 24 h under vacuum (1 mbar), (i) PIM-1/ZIF-8 after annealing at 300 °C for 48 h under vacuum (1 mbar). (j) PIM-1/$SiO_2$ annealed at 120 °C, (k) TOX-PIM-1/$SiO_2$ annealed at 385 °C for 24 h under vacuum (1 mbar). Reprinted with permission from [189]. Copyright 2016, Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the interchain rigidity and spacing could be the key factors to enhance their molecular sieving property. Once the membranes have the satisfactory in terms of 2008 Robeson Upper Bond, the next crucial question is how to make them industrially-applicable both from the performance and economic point of view.

In this case, material selection is undoubtedly important regardless of the type of the microporous materials. They must be robust and could withstand harsh operating conditions. In case of a composite membrane, materials compatibility is also important to obtain membranes with satisfactory performance. A composite of robust microporous materials could then be a promising alternative. This could be, for example, by using microporous polymers as the continuous phase to obtain high permeability membrane while also loaded with MOF or POF to enhance the molecular sieving ability.

Most studies on microporous materials-based membranes were focused on flat sheet configuration because of the fabrication simplicity. However, hollow fibre membranes are more attractive for gas separation in industry, but there are only a few reports in this field

[133,196,197]. This still needs to be addressed in the future research of emerging microporous materials-based membranes. In case of MMMs for example, obtaining good particle dispersion to avoid agglomeration and membrane brittleness is important in successfully constructing hollow fibre configuration. Meanwhile, in hollow fibre TR polymer membranes, obtaining a defect-free skin layer is required with optimized process parameters [143,198]. For pure MOFs and COFs-based membranes, the major challenge is related to obtaining a defect-free membrane with reduced thickness to increase the gas permeance. If this could be obtained, their performance could be expected to be comparable with a single-crystal membrane which does not contain intercrystalline defects [199]. Several promising ways can be considered to address this issue, such as narrowing the particle size, and improving interaction between the support and the membrane layer [91].

Regarding membrane productivity, reducing membrane thickness is necessary to reduce membrane resistance and increase its permeance [200]. This is usually obtained by fabricating a membrane in an asymmetric structure with a selective thin and dense layer that is
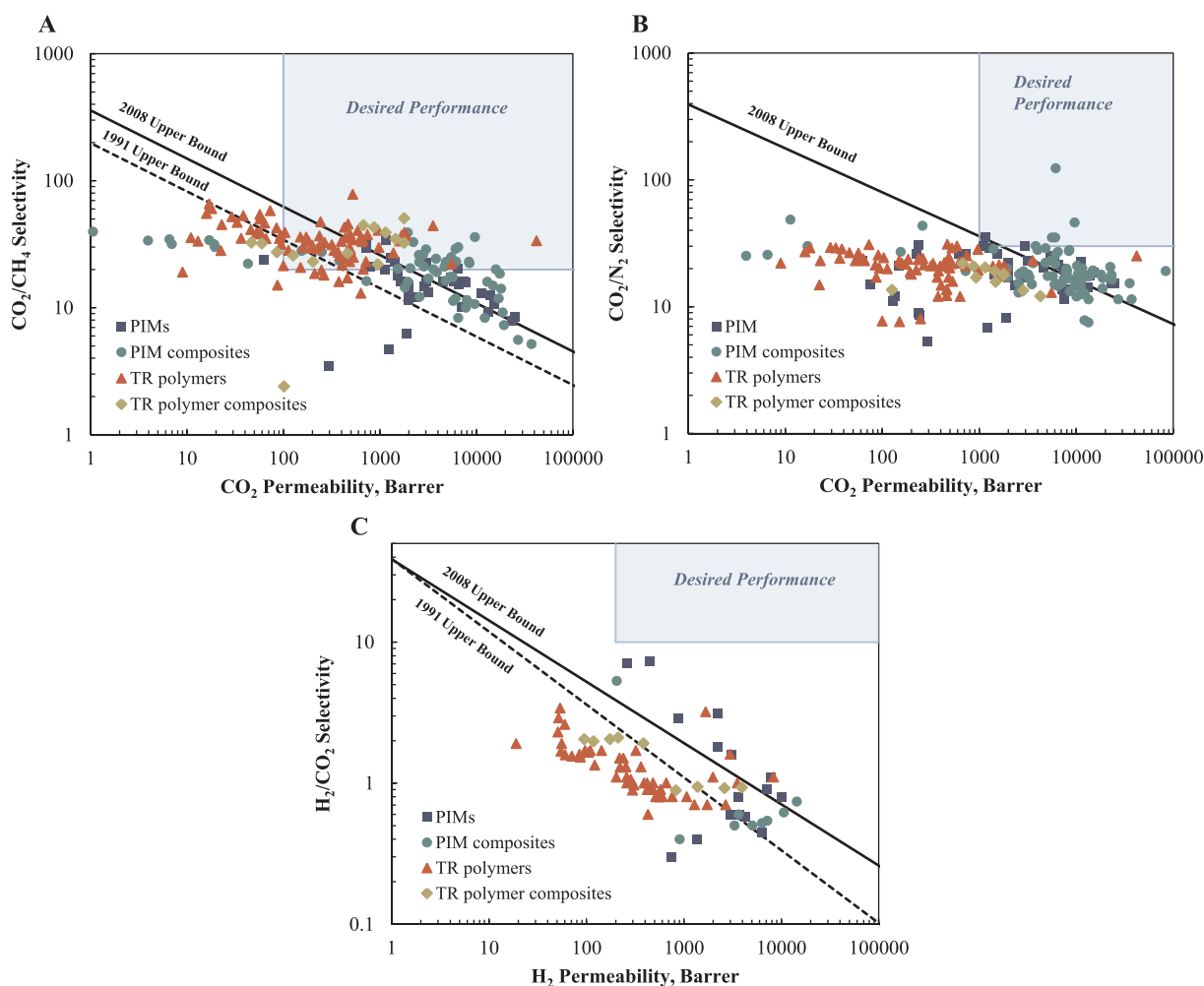
**Fig. 10.** Performance Summary of microporous polymers-based membranes for $CO_2/CH_4$ separation (A), $CO_2/N_2$ separation (B) and $H_2/CO_2$ separation (C). Data for the graph is available from Table S6-S9 in the Supplementary Informaiton.

supported by a porous structure. Whilst this strategy might work with solution-processable microporous polymers, this could be a major challenge with composite membranes. In this case, the particle size should be carefully controlled so they reside inside the selective layer and not on the porous layer [201]. This could be addressed, for instance, by constructing the material in 2D form to produce an ultrathin MMM wih less than 1 μm thickness [202].

Finally, some crucial issues relating to operating conditions must also be addressed. $CO_2$-induced plasticization is one of the major issues, particularly for polymeric membranes. It has been proven that TR polymer membranes with high degrees of TR conversion exhibit high resistance to $CO_2$-induced plasticization, even against $SO_2$ and $H_2S$ [159,160]. Meanwhile, this could still be a major issue for a PIM-based membrane since incorporating intrachain rigidity in their structure does not seem to significantly improve the resistance [192]. MOFs incorporation into a polymer matrix in the form of MMM could then address the issue since they could contribute in the reduction of polymer chain movement resulting in membrane with higher plasticization resistance [81,203]. Since $CO_2$ feed stream also usually contains other impurities such as water vapour, $NO_x$ and $SO_x$ [204], a study must also be conducted in this scenario since mixed-gas study alone does not seem to be sufficient [53]. This is particularly important to elucidate any permanent damage to the membrane structure once exposed to this harsh environment. Meanwhile, for long term operation, the physical aging is still one of the major issues [191]. This is particularly important for a thin membrane since it has a faster aging rate than a

thicker one. Incorporation of microporous materials such as PAF and MOFs could be an option to address this issue [116,182,205]. This is because they contribute to reduce the polymer chain movement resulting in performance stability as the membrane ages [116]. Interestingly, they could even also improve the $CO_2/CH_4$ selectivity during aging because the larger $CH_4$ gas permeation rate were more significantly reduced [116]. Despite this advantage, a stable membrane performance is still preferred [200]. The challenges and future research directions for the emerging organic-containing microporous materials are then summarized in Table 1.

## 7. Conclusions

During the last two decades, there is a growing interest in developing novel microporous materials. As a promising adsorbent, these emerging microporous materials have also advanced the research in the membrane field. This development is particularly important for $CO_2$ separation application, where membrane technology has been considered as one of the promising alternative processes to substitute the conventional processes.

This article has thoroughly reviewed four different classes of emerging organic-containing microporous materials that are considered promising for membrane application in $CO_2$ separation: metal–organic frameworks (MOFs), porous organic frameworks (POFs), polymers of intrinsic microporosity (PIMs) and thermally rearranged polymer (TR). All of them could be fabricated into a membrane either as a composite

**Table 1**
The challenges in development of microporous materials-based membranes for $CO_2$ separation.

| Microporous materials-based membrane type | Challenges | | |
|---|---|---|---|
| | Material selection | Membrane fabrication and module configuration | Membrane performance |
| Mixed matrix membranes (MOFs, POFs, PIMs) | • Selection of robust fillers (resistant towards water vapor, contaminants, etc) <br> • Selection of the best compatible materials (fillers and polymers) that can withstand harsh operating condition | • Optimization of particle loading to balance membrane performance and mechanical strength <br> • Asymmetric membrane production in a hollow fibre configuration | • Membrane thickness reduction for increased permeance <br> • Operating condition optimization <br> • Real-life condition and aging testing performance |
| Pure MOFs and POFs membrane | • Compatibility between the porous support and both MOF and POFs <br> • Selection of robust MOFs and POFs materials that can withstand harsh operating condition | • Growing a defect-free MOFs or POFs membrane in a benign way <br> • Development of hollow fibre configuration <br> • Consideration of polymeric substrate as a cheaper alternative for membrane support | |
| Microporous polymers | • Selection of robust materials that can withstand harsh operating condition | • Low-temperature thermal rearrangement for TR-based membrane <br> • Development of asymmetric membrane structure in a hollow fibre configuration | |

or as a pure microporous membrane. Once a perfect and defect-free membrane is obtained, almost all the emerging microporous material-based membrane have shown promising performance for $CO_2$ separation from $H_2$ (pre-combustion application), $CH_4$ (natural gas purification) and $N_2$ (post-combustion application). This is evident as most of the fabricated membranes are well located close or even surpass the 2008 Robeson Upper Bound.

However, translating this promising performance into a real industrial application for $CO_2$ separation is still a major challenge. There are several challenges that need to be addressed. From a membrane fabrication point of view, this includes membrane fabrication in hollow fibre form to enhance productivity and improving the interaction between two different components in a composite membrane. Mechanical strength could also be another issue, especially for composite membranes, since their tendency to have a brittle structure once loaded with higher particle loading. Another issue is the optimization of membrane operating condition. Optimum pressure and temperature should be investigated, particularly to address the $CO_2$-induced plasticization. It is also imperative to test the successful membranes in the mixed gas scenario or using the real feed gas to elucidate the membrane robustness. Finally, membrane aging should also be thoroughly investigated in order to evaluate its long-term performance.

Further research in the development of emerging microporous materials for membrane-based $CO_2$ separation is undoubtedly still required. The research should not be exclusively directed in discovering new microporous materials but also to optimize the recently developed materials since they have a promising $CO_2$ separation performance. In addition, a comprehensive economic feasibility analysis might also be required so assess their suitability from am industrial perspective. If these aspects can go hand in hand, microporous materials-based membrane technology can likely replace the conventional technology and contributing in making $CO_2$ separation processes more efficient.

Data Repository

The data presented is Figs. 6 and 10 (Robeson plots) are also available in tabular form, along with high-resolution versions of the Figures, from the following open repository: https://doi.org/10.5281/zenodo.3362810

**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.123575.

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