

Recent Advances in Metal-Organic Cages-Based Composite Membranes

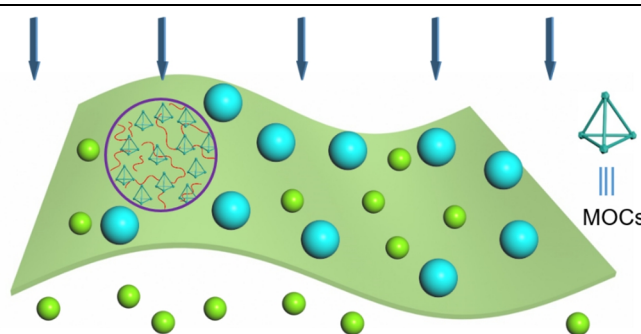
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ABSTRACT Conventional polymeric membranes face several limitations, such as the trade-off between permeability and selectivity, and physical aging or membrane fouling. In this case, fabrication of composite membranes, usually including mixed matrix membranes (MMMs) or thin film nanocomposite (TFN) membranes by introduction of porous materials as fillers has gained much attention. To achieve excellent membrane performance, it is of great importance to select proper porous materials to avoid agglomeration or precipitation during the composite membrane fabrication processes. Metal-organic cages (MOCs) have been explored as additives for the fabrication of defect-free composite membranes owing to their diversified topologies, well-defined pore structures, nanoscale size, and excellent solubility. This review mainly focuses on the recent advances in applications of MOCs for membrane separation, including synthetic artificial channels, reverse osmosis, nanofiltration, pervaporation and gas separation. Besides, two types of MOCs that have been extensively investigated for composite membrane fabrication are also highlighted. Furthermore, challenges and possible directions are also discussed in details, hoping to provide insightful guidance on the development of more MOC-based membranes with impressive separation performance.

Keywords: membrane separation, metal-organic cage, mixed matrix membranes, thin film nanocomposite membranes



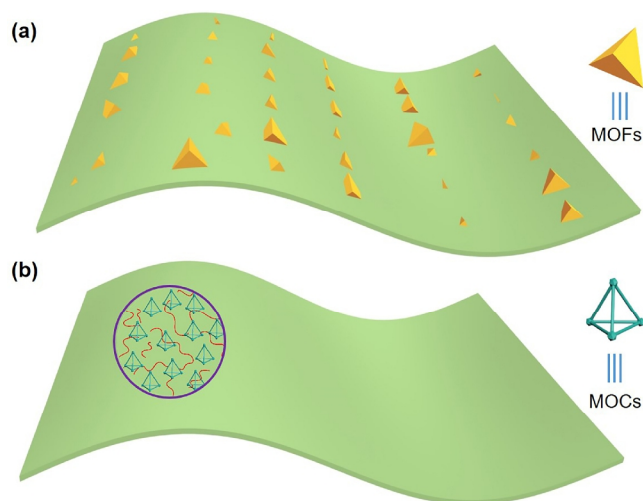
1 INTRODUCTION

Membrane separation technology has attracted much attention as an energy-efficient method for small molecular separation owing to its excellent separation efficiency, simple operation process, and environmentally benign merits. However, the polymeric membranes still face several limitations, such as the trade-off between permeability and selectivity, and physical aging or membrane fouling, even though they possess easy processability and mechanical stability features.^[1,2] Recently, membranes made from porous materials with well-defined pore structures, including zeolites, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), have displayed superior permeability and selectivity for small molecular separation.^[3-7] However, these membranes are intrinsically brittle and fragile, which largely limits their potential of being produced at a large scale without defects.^[8-15] Therefore, it is highly desired to fabricate membranes with large pore volume and good flexibility. The introduction of porous materials such as zeolites, MOFs and COFs as fillers into the polymeric matrix can lead to composite membranes, usually including mixed matrix membranes (MMMs) or thin film nanocomposite (TFN) membranes with both high permeability and good selectivity. These composite membranes combine merits of the easy large-scale processability of the polymer matrix and well-defined pore size of porous fillers.^[16-22] However, these porous fillers are insoluble in solvents and often demonstrate high tendency of agglomeration in the membrane at high filler loadings.

Therefore, porous fillers with both well-defined pores/apertures and high solubility in solvents are highly desired to achieve excellent dispersibility in the corresponding composite membranes.^[23]

MOCs, also referred to as metal-organic polyhedra (MOPs), are discrete molecule assemblies constructed from metal ions or metal clusters with organic ligands via coordination-driven self-assembly.^[24] MOCs have garnered considerable attention owing to their fascinating structures and have demonstrated great potentials in various applications, such as molecular recognition, cavity-induced catalysis, gas adsorption and separation, to mention a few.^[25-30] Similar to MOFs, MOCs also possess features, like tunable pore size and easy functionality. In this case, MOCs can be viewed as molecular MOF pore analogues.^[31] Different to the insoluble nature of MOFs, MOCs demonstrate impressive solubility in common solvents, which makes it promising as suitable fillers in composite membranes (Scheme 1).^[25,32,33] Besides, MOCs exhibit an average molecular size of 2.5-5.0 nm, highlighting their high surface-to-volume ratio. Consequently, MOCs can efficiently interact with polymer chains in the composite membrane, promoting the formation of defect-free membranes with good separation performance. Up to now, MOC-based composite membranes have demonstrated great potential for separation applications.

In this review, we will summarize the recent advances in MOC-based composite membranes regarding the judicious selection of MOCs and the potential applications of resultant membranes. We believe that offering a timely and critical review on this important



Scheme 1. Schematic illustration of the structure of composite membranes containing (a) MOFs or (b) molecular MOCs additives (fillers).

topic will provide insightful guidance on the rational design and fabrication of more MOC-based membranes with excellent separation performance in the future.

n MOCS OR MOPS USED AS FILLERS FOR COMPOSITE MEMBRANE FABRICATION

Careful choices of metal ions or clusters and organic linkers are the keys to build the desired MOCs. Metals such as Cu(II), Fe(III), Pd(II), Pt(II), Rh(II), Ti(IV), and Zr(IV) have been used as precursors for MOC synthesis. The obtained MOCs can be simply classified as Cu-MOPs, Fe-MOCs, Rh-MOPs, Zr-MOCs, etc. according to the corresponding metal precursors. Once the metal precursor is selected, different ligands possessing a variety of reaction centers, including carboxylate, and/or nitrogen donor groups have been successfully employed to direct suitable assemblies. The obtained MOCs can display diversified topologies, such as tetrahedron, octahedron, cube, icosahedron, cuboctahedron, and so on. Furthermore, the systematic introduction of different functional groups at the periphery of organic ligands can result in isostructural MOCs with tuned pore structure and functions. As discrete molecular assemblies, MOCs possess unique features compared to extended MOFs (Table 1). The nanoscale size and good processability of MOCs highlight their potential for the fabrication of composite membranes with impressive performance for diversified separation applications.

Different to the rapid development of MOF-based composite membranes, MOC-based composite membranes are at their

Table 1. Selected Characteristics of MOCs and MOFs

Characteristics	MOCs	MOFs
porosity	porous	porous
solubility	soluble in specific solvents	insoluble in solvents
size	2.5-5.0 nm	usually larger than 100 nm
structural tunability	good	good

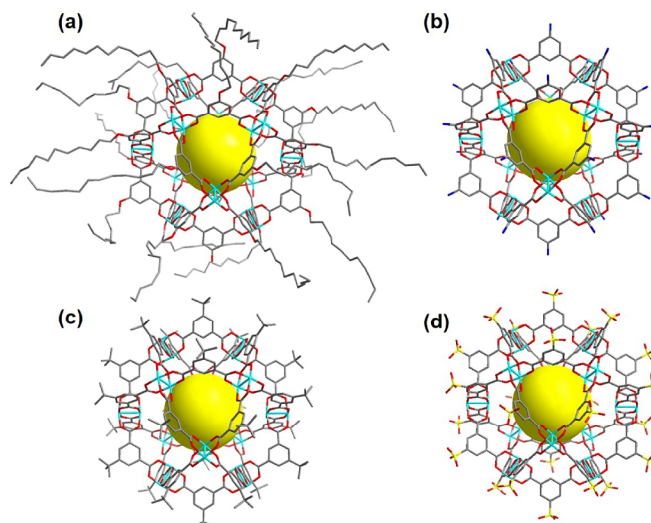


Figure 1. Crystal structures of Cu-MOPs commonly used for membrane fabrication. (a) $\text{Cu}_{24}(\text{dodecoxy-bdc})_{24}$ (MOP-18), (b) $\text{Cu}_{24}(\text{NH}_2\text{-bdc})_{24}$, (c) $\text{Cu}_{24}(\text{Bu-bdc})_{24}$ and (d) $\text{Cu}_{24}(\text{Na/H-SO}_3\text{-bdc})_{24}$.

infancy stage. Up till now, two types of MOCs, namely copper-based metal-organic polyhedra (Cu-MOPs) and zirconium-based metal-organic cages (Zr-MOCs), are mainly explored for membrane applications.

Cu-MOPs. Cu-MOPs were firstly reported by Yaghi and co-workers.^[34,35] In their study, discrete $\text{Cu}_{24}(\text{bdc})_{24}(\text{sol})_{24}$ was obtained when 1,3,5-benzenetricarboxylate was replaced by 1,3-benzenedicarboxylate during the synthesis of HKUST-1. $\text{Cu}_{24}(\text{bdc})_{24}$ features a cuboctahedron topology, in which 12 Cu_2 paddlewheel as nodes was bridged by 24 isophthalic acid ligands. Cu-MOPs with different topologies can be obtained by using proper polydentate carboxylate acids.^[36] Derivatives of Cu-MOPs with the same topologies are easily accessible where different functional groups are incorporated at the periphery of organic bridging ligands (Figure 1).^[37] The topological diversities and superior functionality tolerance impart Cu-MOPs with desired properties so that they can be deliberately synthesized for function-oriented applications.

Zr-MOCs. Zr-MOCs constructed from in-situ formed tri-nuclear zirconium clusters and polydentate carboxylate acids were firstly reported in 2013.^[38,39] Zr-MOCs with different topologies and various functional groups can be synthesized in a facile way (Figure 2).^[40,41] The judicious design of different Zr-MOCs with various functional groups can be interpreted by hard and soft acids and bases (HASB) theory.^[42,43] Following the HASB theory, Zr(IV) from the in-situ formed tri-nuclear zirconium cluster as the hard acid can selectively react with the hard base, deprotonated carboxylate acid groups, to afford Zr-MOCs during the coordination-driven self-assembly process. Zr-MOCs showed high stability in aqueous solutions with different pH values (typically ranging from 2.0-11.0).^[44,45] Besides, Zr-MOCs are cationic coordination cages and their positive charges are balanced by chloride ions. This ionic nature also imparts Zr-MOCs with good solubility in polar solvents, like methanol.^[46] Inspired by these merits, Zr-

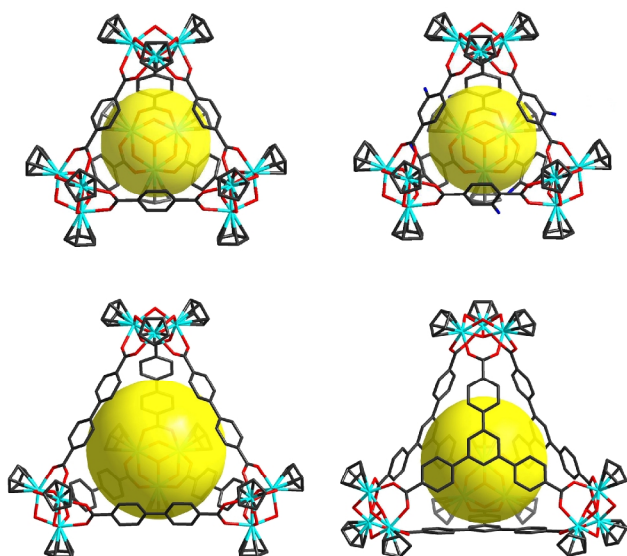


Figure 2. Crystal structures of Zr-MOCs. Reprinted with permission from ref.^[44] Copyright 2018 American Chemical Society.

MOCs have attracted much attention and have showed potential in various applications, such as molecular encapsulation and gas separation.^[45,47] Recently, Zr-MOCs were also used as molecular porous additives for advanced membrane fabrication owing to their good processability.

Rh-MOP, Fe-MOC, and Ti-MOC have also been investigated as additives for composite membrane fabrication and their structural features will be simply discussed later. It is anticipated that more novel types of MOCs with unique structural properties will be rationally designed and selected as fillers in composite membranes for challenging separation applications in the future.

n ADVANCED MOCs OR MOPS-BASED COMPOSITE MEMBRANES FOR SMALL MOLECULE SEPARATION

Synthetic Artificial Channels. In 2008, Kim and co-workers firstly reported the incorporation of Cu-MOP, namely MOP-18 with a chemical formula of $\text{Cu}_{24}(\text{dodecoxy-bdc})_{24}$ into lipid bilayer as cation selective channels. It is the first example of artificial ion channels based on MOPs across lipid membranes, which can selectively transport protons and alkali-metal ions with good selectivity based on cation size.^[48] Except Cu-MOP, a kind of rhodium based MOP (abbreviated as Rh-MOP) was also explored to fabricate artificial ion channels.^[49] In this study, the membrane displayed two conductance states by dynamically exposing either triangular or square apertures of Rh-MOP. The dynamic process was optimized by alkoxy chain length introduced at the periphery of Rh-MOPs. It is anticipated that superior performance can be achieved as the facile accessibility of Rh-MOPs decorated with various peripheral functional groups. Zr-MOCs have also been investigated as nano-porous fillers for artificial membrane fabri-

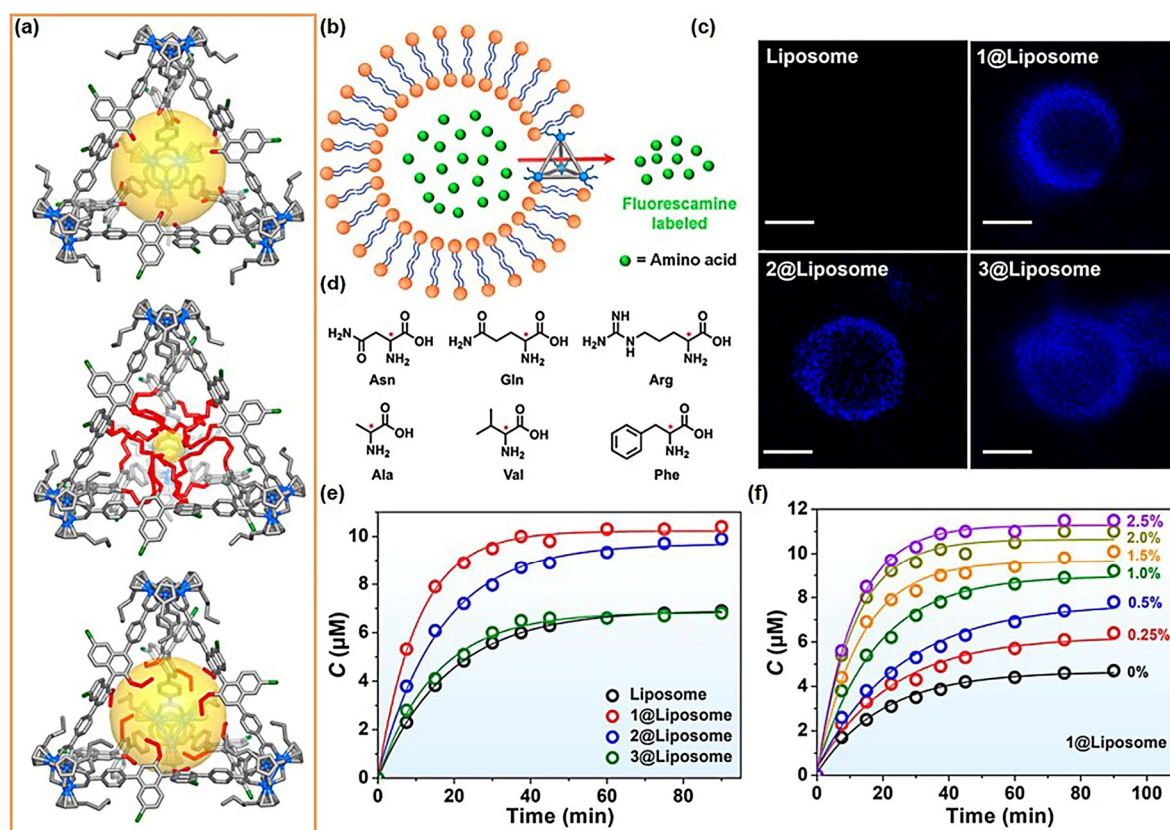


Figure 3. (a) Crystal structures of Zr-MOCs 1-3 investigated in the corresponding literature for membrane fabrication. (b-f) Schematic illustration of enantioselective transmembrane transport of amino acids by cage-embedded liposomes. Reprinted with permission from ref.^[50] Copyright 2021 American Chemical Society.

cation. The Zr-MOCs can be incorporated and dispersed into lipid membranes at a molecular level by taking advantages of their structural stability and great biocompatibility. Performance evaluation indicated that the resultant composite membranes could serve as biomolecular channels for enantioselective transport of natural amino acids (Figure 3).^[50] More significantly, subtle structural adjustments of Zr-MOCs can alter the membrane performance significantly as demonstrated by the fact that cage-1 decorated with hydroxyl groups spontaneously favors the passage of L-asparagine, whereas cage-2 functionalized with crown ether groups preferentially transports D-arginine. This result indicates that the superior structural tunability of MOCs can provide opportunities to achieve optimized performance.

Reverse Osmosis Membranes for Desalination. Zr-MOCs are suitable candidates for the fabrication of TFN reverse osmosis membranes for desalination as the nanoscale size of Zr-MOCs is far below the thickness of the polyamide selective layer (about 100 nm). Following this assumption, Zhao and co-workers reported the chemically crosslinking one Zr-MOC, named as ZrT-1-NH₂, with ideal stability, solubility, and porosity characteristics, into the TFN membranes (Figure 4).^[51] The optimized TFN membranes exhibit enhanced water flux while the salt rejection was maintained compared to the pristine thin film composite (TFC) membrane. As a continuing effort in this field, the same group further reported the anti-fouling property of Zr-MOC-incorporated TFN membranes.^[52] Introduction of Zr-MOCs into the TFN membranes can significantly improve the antifouling properties towards both protein and positively charged foulants.

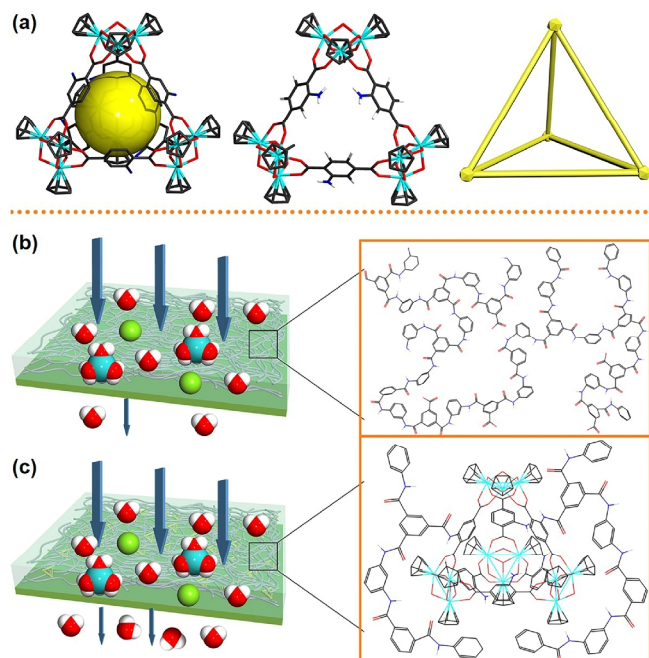


Figure 4. (a) Crystal structure of ZrT-1-NH₂. (b) Schematic representation of TFC membrane and the proposed chemical structure of the polyamide selective layer. (c) Schematic representation of TFN membrane and the proposed chemical structure of cage-containing selective polyamide layer. Reprinted with permission from ref.^[51] Copyright 2021 American Chemical Society.

Similar anti-fouling property was also observed when titanium-based MOC (abbreviated as Ti-MOC) was used as the filler for TFN membrane fabrication due to the improved hydrophilicity and electrostatic interactions. These results indicated that MOCs are better filler materials for improving the membrane performance by offering additional benefits, such as the enhanced anti-fouling property, to reverse osmosis membranes, aside from serving as water transport highways. The performance improvement and anti-fouling property push forward a significant step for the practical application of MOCs incorporated reverse osmosis membranes.

Nanofiltration. Fabrication of a polyamide TFN membrane with highly improved nanofiltration performance has been achieved by using iron-based MOC (abbreviated as Fe-MOC) as the molecular filler. The optimal TFN membrane showed a 3-time water flux enhancement and simultaneously improved rejection for Na₂SO₄ and congo red compared to the neat TFC membrane.^[53] The significant performance enhancement can be ascribed to the inner pore of Fe-MOC which can be served as fast transport pathways and the -SO₃Na group of the Fe-MOC, which can interact with water molecules with high affinity. Besides, the membrane anti-fouling property was significantly enhanced owing to both increased hydrophilicity and smoother surface microstructure of the TFN membrane. This result indicated the potential of MOCs for the construction of nanofiltration membranes. ZrT-1-NH₂ has also been used for the fabrication of nanofiltration membranes by crosslinking ZrT-1-NH₂ with trimesoyl chloride (TMC) via interfacial polymerization.^[54] The water permeance

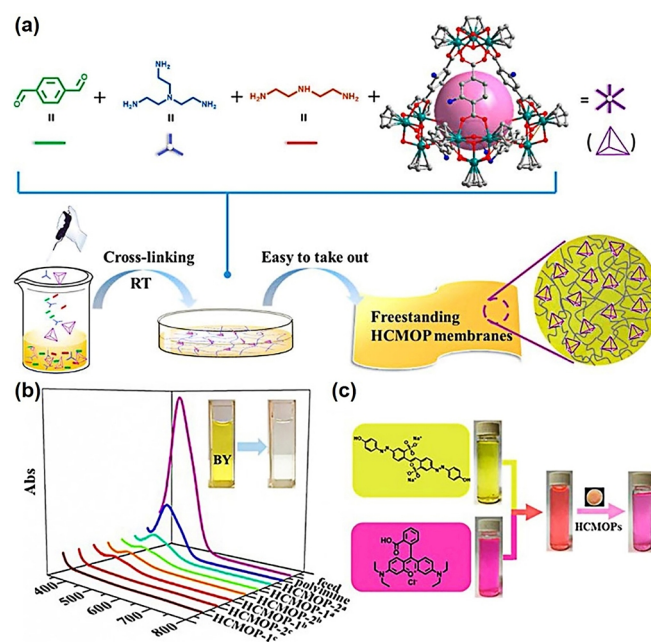


Figure 5. (a) Schematic illustration of the fabrication of HCMOPs membranes by using Zr-MOCs as high connectivity nodes. (b) UV-Vis spectra of feed and permeate Brilliant Yellow (BY) solution. (c) The photograph to show the selective separation of BY from BY/Rhodamine B mixture. Reprinted with permission from ref.^[56] Copyright 2019 American Chemical Society.

can be up to $82.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and the rejection rate for congo red can reach 99.7% owing to the improved pore volume after ZrT-1-NH₂ incorporation, accompanied by the concurrent enhancements in dye/salt rejections. Moreover, the TFN membrane also exhibited good antifouling and antibacterial properties. The same group also reported the fabrication of TFN membranes through in-situ interfacial polymerization of lysine and TMC in the presence of ZrT-1-NH₂ as the nano-porous filler.^[55] The TFN membranes feature striped structure induced by the participation of ZrT-1-NH₂ in polymerization, which can greatly enhance the water permeance owing to the enlarged permeation area of the separation layer. In 2018, Zhang and co-workers reported the selection of Zr-MOCs functionalized with amino groups as high connectivity nodes for hyper-cross-linked metal-organic polyhedra (HCMOPs) membrane fabrication.^[56] The HCMOPs membranes possess multiple merits imparted by both Zr-MOCs and polyimide matrix. Specifically, good water permeability, self-healing ability, antimicrobial activity, and better separation and mechanical performance can be obtained compared to the pristine polyimide membranes (Figure 5).

Pervaporation. MOC-based MMMs have also been investigated for pervaporation processes. In 2014, Li and co-workers reported the application of Cu-MOP with a chemical formula of Cu₂₄(^tBu-bdc)₂₄ for MMM fabrication.^[57] The membrane was synthesized by mixing Cu₂₄(^tBu-bdc)₂₄ with hyperbranched polymer (Boltorn W3000) and excellent pervaporation separation performance towards aromatic and aliphatic hydrocarbons was achieved. As a continuous project, the same group also introduced isostructural Cu-MOPs decorated with sulfonic (Cu₂₄(Na/H-SO₃-bdc)₂₄) and hydroxyl groups (Cu₂₄(OH-bdc)₂₄) as additives for membrane fabrication by using the same Boltorn W3000 polymer (Figure 6).^[58] More significant performance enhancement was obtained for Cu₂₄(Na/H-SO₃-bdc)₂₄/Boltorn W3000 membrane, highlighting the advantage of MOCs for membrane separation optimization.

Gas Separation. In addition to ions and small organic molecular

separation, MOC-based MMMs have also been intensively explored for gas separation. MOP-18 based membranes have also been explored for gas separation by mixing with Matrimid® 5218 for MMM fabrication.^[59] Scanning electron microscopy analysis indicated that MOP-18 could distribute evenly in the polymer matrix without aggregation even at a high loading, which can be attributed to the improved dispersibility imparted by long alkyl chains in cages. The membranes showed enhanced permeability and anti-plasticization properties. The permeability of propylene, propane and methane increased 7, 4.3 and 3.3-fold, respectively. However, the gas pair selectivity cannot be retained after the incorporation of MOP-18. Polymers are well-known for their aging property, which seriously affects the membrane permeability and selectivity owing to the increased chain packing density and decreased fractional pore volume along with time. An interesting project presented by Hill and co-workers suggested that the incorporation of Cu-MOPs as fillers can provide anti-aging performance for membranes based on a super glassy polymer, poly(1-trimethylsilyl-1)propyne.^[60] Anti-aging properties have also been observed in another project in which Cu₂₄(NH₂-bdc)₂₄, a Cu-MOP functionalized with amino groups, was explored as a filler for MMM fabrication.^[61] Besides, a large performance enhancement in permeability and selectivity can be obtained upon the addition of 1.6 wt% of Cu₂₄(NH₂-bdc)₂₄, which can meet the commercial standard for postcombustion CO₂ sequestration. Owing to the excellent anti-aging property, the performance of the composite membrane could still meet the commercial target even after 100 days of aging. Besides, cross-sectional focused ion beam scanning electron microscopy characterization indicated the selected Cu-MOP could be well distributed as molecular units when a low concentration of filler was used. Zhong and co-workers reported the construction of MMMs for natural gas upgrading by mixing a soluble Cu-MOP with a chemical formula of Cu₂₄(Na/H-SO₃-bdc)₂₄ with polysulfone and the resultant MMMs showed that a loading of 12 wt% filler can increase the permeability and separation factor of CO₂ by 81% and 60%, respectively.^[62] These enhancements can be attributed to the

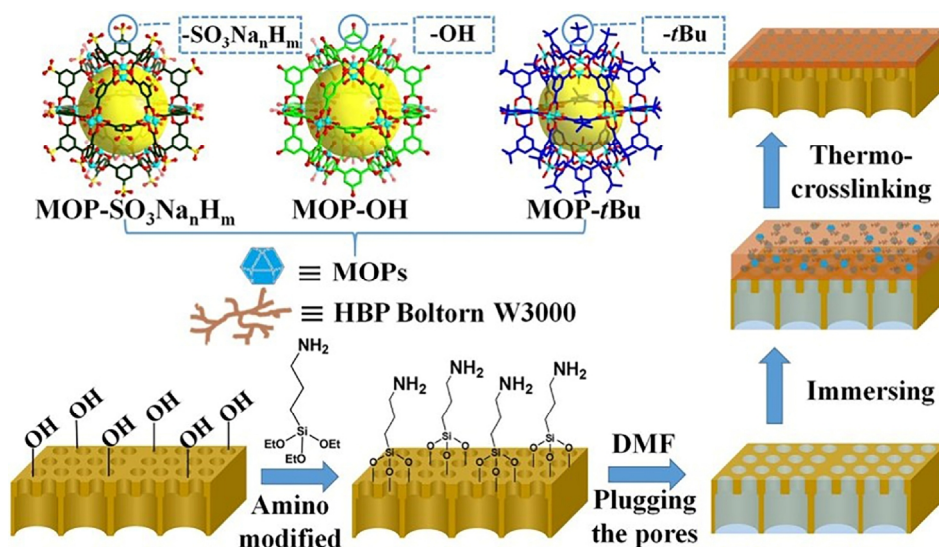


Figure 6. Schematic illustration of fabricating MOPs/Boltorn W3000 hybrid membranes. Reprinted with permission from ref.^[58] Copyright 2022 Wiley-VCH.

strong interaction between sulfonate groups of the deliberately selected Cu-MOP and CO₂. Apart from the polymer matrix, graphene oxide (GO) has also been used as a matrix for MOCs-based membrane fabrication. Peng and co-workers reported the mixing of MOP-18 with 15-crown-5 to construct type II porous liquids.^[63] After mixing cages with GO matrix, the resultant membranes showed enhanced permeability because of the reduced gas diffusion barriers imparted by the inner porous cavity of MOP-18.

The solvent evaporation method has been widely used to fabricate MMMs. However, even for MOCs, they are still prone to aggregation during the evaporation process at a considerably high filler loading. The agglomeration of MOCs will restrict the further improvement of membrane performance. To address this, many strategies have been used to improve the compatibility between MOC fillers and the polymer matrix. Hosono and co-workers reported the usage of polyethylene glycol (PEG)-grafted Cu-MOP for the synthesis of defect-free MMMs through the solution casting method.^[64] The membranes prepared with PEG-grafted MOPs displayed enhanced gas permeation for CO₂ and the CO₂/CH₄ selectivity can be well-preserved compared to the neat PEG-based membranes. Recently, a novel photo-induced polymerization process has also been utilized to construct MMMs. The nano-porous fillers were firstly mixed with polymer precursor and then subjected to UV irradiation. The membranes could be cured instantaneously within very short time, which is helpful to avoid the agglomeration of nano-porous fillers.^[65,66] Kim and co-workers reported the construction of cross-linked polyethylene glycol (XLPEO) membranes via UV-induced polymerization.^[67,68] Compared to conventional neat XLPEO, a modest CO₂ permeability enhancement of 30.5 barrer was observed for MMMs. Besides, the resultant membrane showed increased selectivity of 26.5 towards CO₂/N₂ compared to 19.6 of pristine XLPEO. Lin and co-workers also reported a bottom-up approach to synthesize the MMMs by dispersing Cu₂₄(Na/H-SO₃-bdc)₂₄ as molecular

dopants in polymer precursor solutions before rapid photo-polymerization to form interpenetrating networks.^[69] The distribution of Cu₂₄(Na/H-SO₃-bdc)₂₄ with a particle size of about 5 nm was checked by transmission electron microscope analysis. The introduced Cu₂₄(Na/H-SO₃-bdc)₂₄ dopant can decrease the glass transition temperatures of membranes and even induce the crystallization of polymer matrix at high loadings. Performance evaluation suggested that increasing the MOP loading could increase CO₂ permeability with a slight decrease in CO₂/gas selectivity. Kim and co-workers reported the fabrication of MMMs in which EG₃-MOP nanocages as CO₂-philic fillers were homogeneously distributed in the poly(poly(ethylene glycol) dimethacrylate glycol) dimethacrylate matrix. The good compatibility between EG₃-MOP nanocages and the polymer matrix was achieved at a filler loading up to 5 wt% owing to the strong interactions between the two phases in resultant membranes.^[70] In 2021, Zhao and co-workers reported the fabrication of homoporous hybrid membranes (HHMs) for natural gas upgrading. The HHMs were prepared by chemically crosslinking polymerizable Zr-MOC, ZrT-1-AA^[71] into polymeric precursors via a UV-induced polymerization strategy (Figure 7).^[72] The ZrT-1-AA was evenly distributed in the in-situ formed XLPEO matrix at a molecular level with superior interfacial compatibility. This is different to the MOF-based composite membranes fabricated by the same UV-induced polymerization strategy, in which MOF particles are randomly embedded in the polymer matrix.^[73] The HHM with a proper ZrT-1-AA loading showed an enhanced CO₂ permeability and a comparable selectivity towards CO₂/CH₄ separation because of the increased CO₂ solubility and diffusivity with the addition of MOCs.

n CONCLUSIONS AND PERSPECTIVE

In this review, recent developments of the incorporation of MOCs, especially Zr-MOCs and Cu-MOPs, as additives for membrane separation are summarized. With fewer amounts of MOCs doped

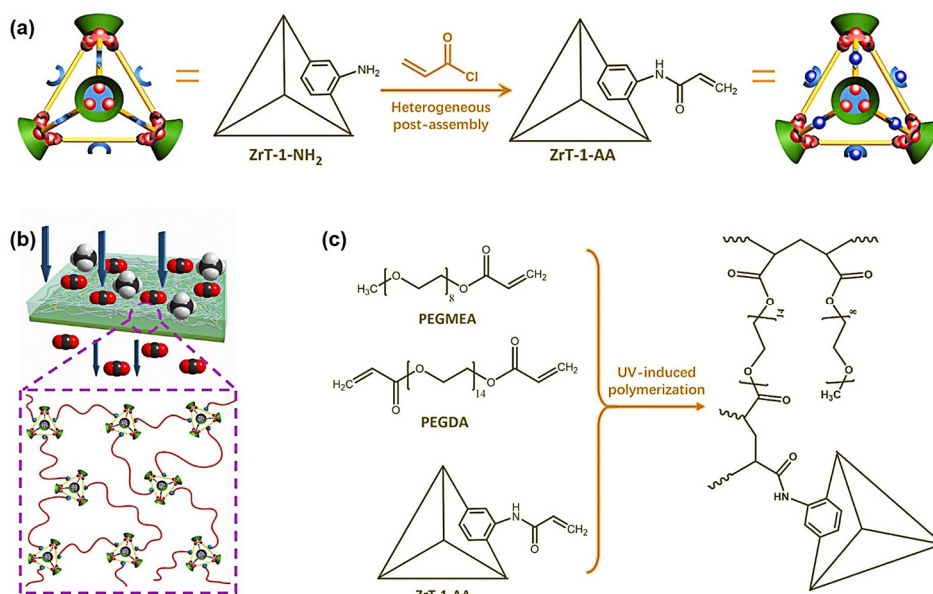


Figure 7. (a) The synthetic route and structure of ZrT-1-AA. (b) Schematic diagram of HHMs constructed by crosslinking ZrT-1-AA with in-situ formed XLPEO polymer matrix. (c) The synthetic route and structures of HHMs. Reprinted with permission from ref.^[72] Copyright 2021 Elsevier Inc.

in the polymer matrix, the resultant membranes with improved pore volume showed performance enhancement compared to the pristine ones. Besides, better anti-aging or anti-fouling properties can also be realized in resultant composite membranes. These features indicate the practical application of MOC-based composite membranes for small molecule separation. Although a series of significant advances have been achieved, it is clear that MOC-based composite membranes are still in their infancy and more efforts are needed. For further performance improvement, there are still some issues that should be taken into account. For instance, 1) The agglomeration of MOCs during the membrane fabrication process is still a formidable problem, which will hamper the development of advanced membranes. We should note that membranes would become more brittle with the incorporation of more MOC additives considering the rigid nature of MOCs. The fragile nature is similar to zeolites, MOFs and COFs based membranes. To address this issue, novel membrane fabrication methods such as layer by layer self-assembly and contra-diffusion method may be considered.^[74-76] Decorating MOCs with flexible PEG chains to improve the compatibility with the polymer matrix has been proposed as a possible strategy to solve this problem. However, the pore windows of MOCs may be partially blocked by the flexible polymer chains and this will influence the accessibility of MOCs.^[77] To address this issue, the design and synthesis of MOCs decorated with both rigid and flexible motifs may be considered. 2) Membrane activation is another challenging issue. MOCs can be incorporated into membranes by delicate designs. Considering the solubility differences between MOCs and polymers, solvents with proper dissolving capacity for both MOCs and polymer are deliberately screened. It is well-known that porous MOCs may encapsulate solvents. In MOC-based composite membranes, the pore apertures of MOCs will be surrounded by flexible polymer chains and more energies will be needed to remove the encapsulated guest solvents.^[78] 3) Different kinds of MOCs, such as well-known palladium-based MOCs (abbreviated as Pd-MOCs), should be introduced into the membrane as additives owing to their excellent structural diversity.^[79,80] 4) Compared to the MOC-based composite membranes, pure MOC-based membranes have been less investigated.^[81,82] More efforts should be devoted to that direction as well. Hierarchical self-assembly of MOCs results into the supramolecular frameworks that possess interpenetrated porosity and some of the stable supramolecular frameworks can retain the pore structure even after the removal of guest molecules. This provides a platform for the fabrication of pure MOC-based membranes and novel advanced properties may be achieved. Considering the rapid developments in MOC chemistry, we believe that these molecular cages will offer tremendous possibilities for the development of membranes. It is expected that this review will be helpful in designing and fabricating more novel MOC-based membranes for practical applications.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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