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2	MOF-based membranes for pervaporation
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#### 24 Abstract

25 Pervaporation competes with conventional separation techniques, such as distillation and 26 adsorption in organic liquid dehydration, removal or recovery of organic compounds from aqueous solutions, and separation of organic-organic mixtures. Pervaporation is a separation technique 27 relying on the concentration gradient, often expressed as partial vapor pressures, across 28 29 polymeric or polymer-composite membranes. Those membranes often exhibit a strong trade-off 30 between permeability and selectivity of target compounds, making the search for alternative 31 materials with advanced performance characteristics highly desirable. Metal-organic frameworks 32 (MOFs), a sub-group of porous functionalised materials, have recently demonstrated potential to 33 become a valuable building block in the fabrication of future high-performance pervaporation 34 membranes. MOFs feature unique properties, such as molecular sieve effects, preferential adsorption to the target molecular compounds, and thermal and chemical stability, being suitable 35 for direct applications in pervaporation separation of liquid mixtures. This paper comprehensively 36 37 examines the current design strategies of MOF-based membranes in pervaporation. The main developments of MOF-based membranes in pervaporation are discussed and the performance 38 39 of pervaporation processes using MOF-based membranes is also analysed. Furthermore, some 40 perspectives for future development of MOF-based membranes in pervaporation are given.

### Keywords: metal-organic frameworks; mixed-matrix membranes; solvent dehydration; solvent recovery; pervaporation.

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### 70 Abbreviations

AA	Alginic acid
AAm	Acrylamide
ALG-c-HDM	Alginate cross-linked with 1,6-hexanediamine
a-PVA	Amino-polyvinyl alcohol
CA	Cellulose acetate
CS	Chitosan
СТА	Cellulose triacetate
ddPDMS	Dihydroxypolydimethylsiloxane
GEL	Gelatin
HBP	Hyperbranched polymer
HEMA	Hydroxyethyl Methacrylate
HVA-c-N-4	Hydrolyzed vinyl acetate coated Nylon-4
MAC	Maleic anhydride modified chitosan
mm-PEMA	Monomethyl polyoxyethylene methacrylate
PA	Polvamide
PAA	Polvacrylic acid
PAA-a-PP	Poly (acrylic acid) grafted polypropylene
PAL	Polvamide imide
PAI-S	Polvamide imide sulfone
PANI	Polvaniline
PASAs	Polv(amide-sulfonamide)s
PBI	Polvbenzimidazole
PBLG	Polv(v-benzvl-L-glutamate)
PDA	Polydopamine
PDD-co-TFE	Perfluoro-2.2-dimethyl-1.1.3-dioxole copolymerized with tetrafluoro ethylene
PDMS	Polvdimethylsiloxane
PDMS-I	Polydimethylsiloxane-imide
PEBA	Polyether block amide
PEEK-WC	Poly(oxa-p-phenilene-3,3-phthalido-p-phenylene-oxy-phenylene)
PEG	Polyethylene Glycol
PEI	Poly(ether imide)
PEK-C	Sulfonated cardo polyetherketone
PEMA	Polyoxyethylene methacrylates
PES	Polvethersulfone
PEtl	Poly(ethyleneimine)
PHS	Poly(4-hydroxystyrene)
PI	Polyimide
PIMs	The polymers of intrinsic microporosity materials
PLA	Polylactic acid
pmPAN	Photo-modified poly(acrylonitrile)
PMPS	Polymethylphenylsiloxane
PP	Polypropylene
PPMS	Poly (phenyl methyl siloxane)
PPSU	Polyphenylsulfone
PS	Polystyrene
PSU	Polysulfone
PTES	$CF_3(CF_2)_5(CH_2)_2Si(OCH_2CH_3)_3$
PTFE	Polytetrafluoroethylene
PTMSP	Poly(1-trimethylsilyl-1-propyne)

	PUR PUU PVA PVA-m-MA PVDF PVP SA SC SFA SPES-C a DVA	Polyurethane Polyurethaneurea Poly(vinyl alcohol) Poly (vinyl alcohol) modified with malic acid Polyvinylidene fluoride Poly(N-vinyl-2-pyrrolidone) Sodium alginate Sericin Sulfosuccinic acid Sulfonated Polyarylethersulfone with cardo
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#### 1. Introduction

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The early 20<sup>th</sup> century saw membrane-based processes emerging as an advanced separation technology, though its importance in the industry has not been recognised until 1970s [1]. Since then, a variety of membrane-based processes has swiftly been implemented for the purification, concentration, separation, and fractionation of gaseous or liquid mixed streams. This rapid adoption of membrane processes made microfiltration, ultrafiltration, nanofiltration, reverse osmosis, forward osmosis, membrane distillation and pervaporation being recognised on industrial level [2-4].

102 Pervaporation allows an economic and efficient separation of azeotropic mixtures, volatile aroma compounds, and organic-organic mixtures, as well as the removal and recovery of dilute 103 104 organic compounds from aqueous solutions. Compared to traditional evaporation or membrane 105 distillation, pervaporation is a low-energy process because the pervaporation separation 106 mechanism is not based on the relative volatility associated with distillation. The separation in the 107 pervaporation process relies on the interaction of the permeate and the membrane material, only 108 a small part of the permeate penetrates through the membrane in the form of a phase transition (liquid to vapor)[5, 6]. As a result, pervaporation has lower energy consumption and more cost-109 110 efficient than traditional evaporation and distillation processes[7]. The first pervaporation concept was published by Kober in 1917 who observed the water transport from the mixture of albumin, 111 112 toluene and water through a membrane. The combination of the words of 'permeation' and 113 'evaporation' was done to define the term 'pervaporation' [8]. The known quantitative work about pervaporation appeared in 1956 by Heisler et al. [9] which was later further elaborated by Binning 114 et al. in the period from 1956 to 1962 [10-12], establishing the principles of pervaporation, and 115 emphasized the pervaporation potential for industrial application. Since then, the academic 116 117 interest in pervaporation has never been interrupted, although sometimes their poor performance has hindered its large-scale industrial application. In 1980s, Gesellschaft für Trenntechnik (GFT) 118 launched the first industrial pervaporation membrane to separate the ethanol-water azeotrope 119 120 mixture [13]. After that, the large-scale applications of pervaporation in industrialization had ushered in rapid development. DeltaMem AG (formerly known as Sulzer Chemtech), one of the 121 122 market leaders in supplying pervaporation plants and equipment, had installed more than 110 123 pervaporation plants worldwide up to the year of 2000 [14, 15]. In 2012, it was estimated that 124 DeltaMem AG had expanded the number of installations to more than 250. Nearly 90% of these 125 plants were used for the dehydration of ethanol or isopropanol [16, 17]. New membrane materials

and new methods of synthesis are continuously being developed to cope with challengingmixtures.

128 The pervaporation process involves phase transition from liquid to gas phase, resulting not only in mass transfer, but also in heat transfer during the separation process. In pervaporation, 129 130 the chemical potential gradient between the feed side and the permeate side, which is usually 131 created by applying pump and a condenser on the permeate side, driving some of the components in the liquid mixtures (feed) through the membrane, and the permeate is concentrated and 132 133 collected (Figure 1). Pervaporation is perceived to be a promising solution, based on several advantages, such as small footprint, simplicity, environmental sustainability, flexibility and cost-134 135 efficiency, for the dehydration of aqueous-organic mixtures [18, 19], the treatment of 136 wastewater[20], the separation of azeotropic or close-boiling mixtures [21], etc. All these 137 separation processes can mainly be classified according to three categories: (i) the dehydration 138 of organic liquids, (ii) the removal or recovery of organic compounds from aqueous solutions, and 139 (iii) the separation of organic-organic mixtures. In the recent years, pervaporation membranes 140 have been developed rapidly for desalination because of their potential for supplying fresh 141 water[22-27]. However, there are only few reports on the application of MOF-based membranes 142 for pervaporation desalination, so it will not be discussed this sub-area in this review.

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Figure 1 Schematic diagram of the vacuum pervaporation process.

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Polymeric membranes are commonly chosen and synthesized for pervaporation due to their diversified structural and chemical functionalities, superior selectivity, excellent film-forming properties for membrane preparation and cost-benefits. Nevertheless, in addition to the inherent trade-off between selectivity and permeability (i.e., highly permeable membranes usually have 149 low selectivity and vice versa), common to all membrane materials, an important limitation on 150 design and fabrication of polymeric membranes is their strong tendency to swell, which hampers 151 the diffusion selectivity [28]. Moreover, some polymeric membranes are also susceptible to severe plasticization and physical aging processes inflicted by the organic vapours permeating through 152 153 the membrane [29, 30]. To combat those limitations and to further enhance the efficiency of 154 polymer membranes, metal-organic frameworks (MOFs) have been suggested as promising 155 building blocks to fabricate high-performance pervaporation membranes combining the 156 processability of polymers and separation properties of MOFs [31]. Metal-organic frameworks 157 (MOFs), also described as porous coordination polymers (PCPs) or porous coordination networks 158 (PCNs), are an emerging class of organic-inorganic hybrid materials formed grounded on 159 coordination bonds between metal atoms or metal clusters (nodes) and organic ligands (linkers). 160 Although at first glance, MOFs and zeolites are very similar, MOFs show greater potential as the fillers utilized in mixed matrix membranes (MMMs) compared to zeolites because of their hybrid 161 162 metal - organic nature, allowing the organic ligands to couple with polymers and to increase the affinity between the fillers and polymer matrixes [32, 33]. In MMMs, the pores of MOF particles 163 164 can serve as molecular sieves or preferential channels for target molecules to obtain high 165 selectivity. The incorporation of porous fillers can also improve the permeation properties by 166 adjusting the polymer chain packing and enlarging the free volume of polymer matrix[34-36]. 167 Therefore, the separation performance of MMMs exceeds the inherent trade-off of polymer 168 membranes in terms of permeability and selectivity[37]. In the past few years, MOFs have attracted immense attention. This is because they are a class of porous materials with unique 169 170 structural properties, large surface areas, uniformly adjustable sized pores and high void volumes, 171 which have led to a large variety of interesting structures and widespread applications in a number 172 of fields including molecular separation[38], catalysis[39], gas storage[40], drug delivery[41], and  $CO_2$  capture [42]. 173

174 Pervaporation separation using MOF-based membranes is mostly realized by the utilization of 175 molecular sieving effect and/or preferential adsorption of MOFs to certain compounds. In the 176 former mechanism, certain molecules of a liquid mixture are blocked outside of the pores of MOFs 177 while other molecules are allowed to pass through the pores of MOFs [43]. And in the latter 178 mechanism, the pores of the MOF are large enough to allow all molecules of a liquid mixture to 179 pass through. In this case, the membrane performance mainly depends on the interactions 180 between molecules and the MOF crystal surface. These interactions ( $E_{int} = \mu \cdot E_{x, y, z}$ ) rely on the 181 permanent dipole moments ( $\mu$ ) of the polar molecules and the strength of the electric field by the 182 MOF ( $E_{x, y, z}$ ). Here, the strength of the electric field depends on the local spatial charge density

183 of the framework (for example, the cations present in the framework produce larger electric field 184 and organic aromatic compounds produce a smaller electric field) and the electric field can be 185 regarded as the derivative of the electrostatic potential of the framework. For nonpolar molecules without dipole permanent moments, the interactions are determined by the instantaneous dipole 186 187 of the guest compound ( $\mu_i$ ). The instantaneous dipole is induced by exposing the guest compound to an external electric field, thereby causing polarization. The polarization is the product of orbital 188 189 mixing between occupied and higher quantum number unoccupied orbitals. The instantaneous dipole ( $\mu_i = \alpha \cdot E_{x, y, z}$ ) can be obtained by multiplying polarizability ( $\alpha$ ) and the electric field applied 190 191 in all directions (Ex, y, z)[44]. Error! Reference source not found. and Table 2 list physical parameters of typical liquid solvents commonly used in pervaporation and structural parameters 192 193 of MOFs used in MOF-based membranes. In addition to the above two common mechanisms, 194 there exists the chemical adsorption between transition metal based-MOFs and unsaturated molecules mechanism in pervaporation. For example, in the pervaporative desulfurization, 195 196 coordinative metal sites within transition metal-based MOFs can promote the transport of thiophene molecules through reversible  $\pi$ -complexation interaction[45-47]. 197

198	Table 1 Physical	parameters of	commonly used	liquid solvents	in pervap	ooration
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Solvent	Kinetic diameter / Å	Dipole moment / µ (D)	Polarizability /
Water	2.65 [48]	2.95±0.2 [49]	14.5 [43]
Methanol (MeOH)	3.8 [48]	2.8 [50]	32.3–33.2 [43]
Ethanol	4.3 [48]	3.1 [51]	51.1–54.1 [43]
Isopropanol	4.6 [48]	1.63 [52]	66.7 [53]
Acetic acid	4.4 [54]	1.70 ± 0.03 [55]	51.49 [53]
Toluene	5.85 [54]	0.375 [56]	118–123 [43]
N-butanol	4.63 [57]	2.84 [58]	85.7 [53]
I-butanol	5.5 [59]	2.96 [60]	90.7 [61]
Thiophene	4.6 [59]	0.55 ±0.01[55]	90.1 [53]
Methyl tert-butyl ether (MTBE)	6.2 [62]	1.2 [63]	108.8 [64]
N-heptane	4.3 [65]	0 [66]	136.1 [43]
N-octane	4.3 [67]	0 [68]	159 [43]

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200 Table 2. Brief overview of Structural Parameters of MOFs utilized in pervaporation

MOF name	Metal	Ligand	Formula Composition	Pore volume (cm <sup>3</sup> /g)	BET surface area (N <sub>2</sub> ) (m <sup>2</sup> /g)	Window size (Å)	Structure	Ref.
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[Cu2(bdc)2(bpy)]n	Cu	1,4- benzenedicarboxylate (BDC) and 4,4'-	[Cu <sub>2</sub> (BDC) <sub>2</sub> (BPY)] <sup>n</sup>	0.462	305.5	3.4 A ×3.4 Å		[69- 71]
CAU-10-H	AI	bipyfiaine (BPY) benzene-1,3- dicarboxylate (1,3- H <sub>2</sub> BDC)	[Al(OH)(benzene- 1,3- dicarboxylate)]∙nH ₂O	0.43	635	7		[72, 73]
CAU-11	AI	4,4'- sulfonyldibenzoate anion (SBA)	[Al(OH)(SBA)]	0.95	529	10.69 Å × 9.18 Å		[74]
Co-formate	Со	НСООН	Co <sub>3</sub> (HCOO) <sub>6</sub>	0.15	300	5	ΞĤ.	[75- 77]
CPO-27 (MOF-74)	Ni	2,5- dihydroxyterephthalic acid (H₄dhtp)	Ni₂(dhtp)(H₂O)₂∙8 H₂O	0.582	1532	11		[75, 78]
CYCU-7	AI	diphenylmethane- 4,4'-dicarboxylate anion (MBA)	[AI(OH)(MBA)]	0.44	338	10.70 Å × 8.67 Å		[74]
DUT-5	AI	4,40 -biphenyldicarboxylic acid (H <sub>2</sub> BPDC)	AI(OH)( BPDC)	0.81	1613	11.1 Å × 11.1 Å	$\Leftrightarrow$	[79]
EuBTB	Eu	4,4',4"-benzene-1,3,5- triyl-tribenzoic acid (H <sub>3</sub> BTB)	Eu(BTB)	N/A	338	5–8	à.	[80, 81]
HKUST-1	Cu	benzene-1,3,5- tricarboxylate (BTC)	Cu <sub>3</sub> (BTC) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	0.75	1663	9		[82, 83]
MAF-6	Zn	2-ethylimidazole	Zn(eim) <sub>2</sub>	0.63	1343	7.6		[84, 85]
MIL-101	Cr	terephthalic acid (H <sub>2</sub> BDC)	[Cr <sub>3</sub> (O)X(BDC) <sub>3</sub> (H 2O)2]·nH2O X=(OH or F)	1.22	2500	12 and 15	£3	[86- 88]
MIL-101(Cr)- SO₃H	Cr	monosodium 2- sulfoterephthalic acid (Na-SO₃H-BDC)	Cr <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> O[(O <sub>2</sub> C) -C <sub>6</sub> H <sub>3</sub> (SO <sub>3</sub> H)- (CO <sub>2</sub> )] <sub>2</sub> [(O <sub>2</sub> C)- C <sub>6</sub> H <sub>3</sub> (SO <sub>3</sub> )- (CO <sub>2</sub> )]}·nH <sub>2</sub> O (n ≈ 38)	~2.0	1800- 2000	12-16		[89- 91]
MIL-160	AI	2,5-furandicarboxylic acid (FDC)	[AI(OH)(FDC)]	0.398	1070	5	► 3 <b></b> 	[92, 93]
MIL-53 (AI)	AI	BDC	[AI(OH)(BDC)]x	0.65	1294	8	~	[94- 96]
MIL-53-NH <sub>2</sub>	AI	2-NH <sub>2</sub> - benzenedicarboxylic acid (NH <sub>2</sub> -BDC)	AI(OH)[H <sub>2</sub> N-BDC]	0.37	940	~3.4 Å ×16.0 Å or ~8.5 Å ×12.0 Å		[87, 97, 98]
MOF-5 (Zn)	Zn	BDC	Zn <sub>4</sub> O(BDC) <sub>3</sub>	1.4	3800	12		[99, 100]
MOF-801	Zr	fumaric acid	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (fumar ate) <sub>6</sub>	0.38	963	3.5	**	[101 - 103]
MOF-808	Zr	BTC and formic acid	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BTC) <sub>2</sub> (HCOO) <sub>6</sub>	0.84	2060	14	*	[104 - 106]
NH <sub>2</sub> -MIL-125	Ti	2- aminoterephthalate (bdc-NH2)	Ti <sub>8</sub> O <sub>8</sub> (OH)₄(bdc- NH₂)6	0.47	1160	5	000	[87, 107]
Ni <sub>2</sub> (L-asp) <sub>2</sub> (bipy)	Ni	L-aspartic acid and 4,4'-bipyridine (L-asp and bipy)	Ni <sub>2</sub> (L-asp) <sub>2</sub> (bipy)	N/A	247 (CO <sub>2</sub> )	3.8 Å × 4.7 Å		[108 , 109]

SIM-1(ZIF-94)	Zn	4,5- imidazolecarboxaldeh vde	Zn(4-methyl-5- imidazolcarboxald ehyde)2	0.19	471	2.6		[110 - 112]
Sm-DOBDC	Sm	2,5-dihydroxy-1,4- benzenedicarboxylate	Sm <sub>6</sub> (OH) <sub>8</sub> (DOBD C) <sub>6</sub>	0.263	520	N/A		[113 ,
UiO-66	Zr	BDC	$Zr_6O_4(OH)_4(BDC)_6$	0.36	970	6	187841 180841	[115 ,
	_			0.50	1000	0.00	an an an	116]
UIO-66-(OH)2	∠r	2,5- Dihydroxyterephthalic acid (DOBDC)	C) <sub>6</sub>	0.56	1230	3.93		[117 ]
UiO-66-F <sub>4</sub>	Zr	tetrafluorobenzene- 1,4-dicarboxylic acid	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC- F <sub>4</sub> ) <sub>6</sub>	0.24	640	4.6	×	[118 ,
UiO-66-NH <sub>2</sub>	Zr	(H2BDC-F4) 2-amino-1,4- benzenedicarboxylic	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC- NH <sub>2</sub> ) <sub>6</sub>	0.48	1073	7.5	Ж	[120 -
UiO-66-OH	Zr	acid (H <sub>2</sub> BDC-NH <sub>2</sub> ) 2-Hydroxyterephthalic acid (H <sub>2</sub> BDC-OH)	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC- OH) <sub>6</sub>	0.45	1210	7.5	Alexan	122] [120
							A COL	, 121, 1221
UiO-67	Zr	biphenyldicarboxylic acid (BPDC)	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BPDC) <sub>6</sub>	0.91	1998	8		[123] [116 ,
UiO-67-bpydc	Zr	2,2'-bipyridine-5,5'- dicarboxylic acid	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (bpydc	1.061	2306	N/A	4.	124] [125 -
	Ca	(H <sub>2</sub> bpydc)		0.665	1045	4 5		127]
211-07	0	(Hmim)	CO(1111111)2	0.005	1245	4.5	¥\$¥	-
ZIF-68	Zn	2-benzimidazolate and 2-nitroimidazolate	Zn(blm)(nlm)	0.552	1557	7.5	٢	130] [131 ,
ZIF-7	Zn	(blm and nlm) Benzimidazole (H-	Zn(bIM) <sub>2</sub>	0.207	380	3	25	132] [133
	_						182	, 134]
ZIF-71	Zn	4,5-dichloroimidazole (dclm)	Zn(dclm) <sub>2</sub>	0.452	1007	4.8	E.	[134 ,
ZIF-8	Zn	2-Methylimidazole (Hmim)	Zn(mim) <sub>2</sub>	0.554	1344	3.4	**	135] [134 -
7IE-90	Zn	imidazolate-2-	$Z_{n}(ICA)_{n}$	0 561	1360	2.86		136] [134
211-30	211	carboxyaldehyde (ICA)		0.001	1300	2.00		, 135]
ZIF-L	Zn	2-methylimidazole	Zn(mim)₂⋅(Hmim)₁	0.02	18	3.4 and	10.00 ×	[136
		(111111)	/2•(1120)3/2			7.0 Å ×	$\Delta \sim \Delta$	- 138]
Zn(BDC)(TED)0.5	Zn	Benzenedicarboxylate	Zn(BDC)(TED)0.5	0.65	1794	ວ.3 A 4.8 Å ×	<b>ಭಂಭಂಭಾ</b> © © © ©	[139
		(BDC) and triethylenediamine (TED)				3.2 A and 7.5 × 7.5 Å	क्रा-क्रा-क्रा-क्रा क्रा-क्रा-क्रा-क्रा प्र-क्रा-क्रा-क्रा प्र-क्रा-क्रा-क्रा क्रा-क्रा-क्रा-क्रा	, 140]

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Two strategies exist for MOF utilization in pervaporation membranes (Figure 2): (i) as a pure MOF-based crystalline membrane, and (ii) as a particulate filler embedded in polymer matrix to form MOF-based mixed matrix membranes. However, the design and preparation of a superior MOF-based membrane remains an ultimate research goal intertwined with both synthetic aspects and properties of MOFs as well as processing and optimisation of the MOF-based membranes.



Figure 2 Examples of MOF-based membranes. Adapted with permission from Ref.[141, 142]

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208 Although the developments of MOF-based membranes are quite promising, MOF-based 209 membranes for pervaporation were not applied until 2011 [38, 143]. Since then, the research 210 interest in MOF-based pervaporation membranes has only intensified. Up to now, there have 211 been some reviews dealing with MOFs that are focusing on different aspects such as MOF 212 synthesis, post-synthetic modification of MOFs, MOF-based membranes, MOF-based membranes applied in gas separation, MOF-based membranes applied in liquid separation, etc 213 214 [31, 144-154]. However, these reviews have hardly summarized the applications of MOF-based 215 membranes in pervaporation, while the rapid advancements in the field of MOF synthesis and 216 manufacturing will have a pronounced effect on the growth in their applications for pervaporation 217 membranes. In this review, the current design strategies of pervaporation membranes containing MOFs are first comprehensively discussed. Then, pervaporation separations using MOF-based 218 219 membranes which encompass evaluation ways of pervaporation process and membrane 220 performance as well as the development of MOF-based membranes in pervaporation are 221 surveyed. In addition, performances of pervaporation process using MOF-based membranes for the separation of some typical mixtures are analysed, providing theoretical basis for large-scale 222 223 production and industrialization of MOF-based membranes. Finally, some perspectives of MOF-224 based membranes in pervaporation are presented.

# 225 2. Design strategies of MOF-based membranes used in 226 pervaporation

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#### 228 2.1. Pure MOF-based membranes

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A pure MOF-based membrane consists of a pure MOF layer deposited on a porous substrate that 230 provides mechanical support and allows the penetration of liquid molecules with minimal 231 232 resistance. For pure MOF-based membranes in pervaporation, the main preparation methods are 233 in-situ growth and secondary growth mechanisms, as shown in Figure 3. Further examples are 234 included in Error! Reference source not found.. This limited number of membrane preparation 235 methods together with their technical complexity further hinders their wide application in preparing pervaporation membranes. Therefore, recent research efforts have been directed to the 236 237 development of the new synthetic strategies to yield pure MOF-based membranes with good performance for pervaporation. For example, one of the methods is referred to as the contra-238 diffusion approach that was first extended to fabricate ZIF-71 hollow fibre membranes for 239 pervaporation[155]. 240

Membrane type	Substrate	Seeding method	Synthetic method for pure MOF- based membrane	Application	Ref.
Dehydration via	a pervaporation				
UiO-66	Yttria-stabilized zirconia hollow fibre	N/A	In situ growth	Dehydration of i-butanol, furfural and tetrahydrofuran	[156]
MIL-53	a-Al <sub>2</sub> O <sub>3</sub> support	Reactive	Secondary growth	Dehydration of ethyl acetate	[157]
CAU-10-H	α-Al <sub>2</sub> O <sub>3</sub> disc	Thermal	Secondary growth	Dehydration of ethanol	[158]
ZIF-8	Polyimide substrate	Covalent- assisted	Secondary growth	Dehydration of isopropanol	[159]
Sm-DOBDC	Al <sub>2</sub> O <sub>3</sub> ceramic hollow fibre	In-situ	Secondary growth	Dehydration of alcohol	[113]
Substituted Imidazolate Material 1 (SIM-1)	N/A	N/A	Pressing and chemical cross- linking	Dehydration of ethanol	[160]
ŽIF-8	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> support	Dip-coating	Secondary growth	Dehydration of 2-methylimidazole (Hmim)	[161]
Ni <sub>2</sub> (L- asp) <sub>2</sub> (bipy)	SiO <sub>2</sub> disc	Wet rubbing	Secondary growth	Dehydration of ethanol	[162]
Recovery or re	moval of organics vi	a pervaporation			
UiO-66	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> tube	N/A	In-situ growth	Recovery or removal methanol, ethanol, and acetone	[163]
ZIF-71	α-Al₂O₃ hollow fibre	N/A	Contra-Diffusion	Recovery of ethanol	[155]
Ni₂(L- asp)₂(bipy)	SiO <sub>2</sub> disc	Wet rubbing	Secondary growth	Recovery or removal of ethanol	[162]

#### 241 Table 3 Brief overview of pure MOF-based membranes in pervaporation

ZIF-71	ZnO support	Reactive	Secondary growth	Recovery or removal of ethanol and methanol	[164]					
Separation of organic-organic mixtures via pervaporation										
UiO-66-NH <sub>2</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> tube	N/A	In-situ growth	Desulfurization of model gasoline (n-octane containing thiophene)	[45]					
MOF-5 (Zn)	α-Al <sub>2</sub> O <sub>3</sub> support	Dip-coating	Secondary growth	Separation of xylene isomers	[165]					
ZIF-71	ZnO support	Reactive	Secondary growth	Separation of dimethyl carbonate (DMC)–methanol mixtures	[164]					
MIL-160	α-Al <sub>2</sub> O <sub>3</sub> disk	N/A	In-situ growth	Separation of xylene isomers	[166]					
UiO-66 tubular	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> support	dip-coating	Secondary growth	Separation of methanol/methyl tert- butyl ether (MTBE)	[167]					
MOF-5	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> support	dip-coating	Secondary growth	Separation of toluene/1,3,5- triisopropylbenzene (TIPB) and o- xylene/TIPB	[168]					
Ni2(L- asp)2(bipy)	Nickel net substrate	N/A	In situ growth	Chiral separation of (R, S)-2-methyl- 2,4-pentanediol	[169]					
ZIF-8	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> disc	Dip-coating	Secondary growth	Separation of n-hexane/benzene and n-hexane/mesitylene	[170]					
Pure component	pervaporation									
ZIF-8	α-Al <sub>2</sub> O <sub>3</sub> support	Dip-coating	Secondary growth	Pure water pervaporation	[161]					
ZIF-68	Zinc oxide support	Reactive	Secondary growth	Pure p-xylene pervaporation	[171]					
ZIF-90	poly(amide– imide) hollow fibre	Dip-coating	Secondary growth	Pervaporation of cyclohexane, benzene, and n-hexane	[172]					
MOF-5	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> disk	Dip-coating	Secondary growth	Pervaporation of p-xylene, o-xylene, 1,3,5-triisopropylbenzene (TIPB), 1,3-Di-tert-butylbenzene (DTBB) and 2-Dicyclohexylphosphino-2'-(N, N-dimethylamino) biphenyl (DCPD)	[143]					



Figure 3 Schematic illustrations of synthesis for pure MOF-based membranes: (a) in-situ growth, (b) secondary growth and (c) contra-diffusion synthesis. Schematic illustrations of applications of pure MOF-based membranes in pervaporation. Reprinted with permission from Ref. [155, 162, 169]

#### 243 2.1.1. In situ growth

244 In-situ growth is the fabrication of membranes by the growth of pure MOFs membranes on 245 substrates immersed in solutions of metal salt / organic ligand, as illustrated by Figure 3a. The whole process consists of two steps: nucleation and crystal growth. The generalised method is to 246 247 induce crystal nucleation on the support surface under conditions and facilitate the growth of MOF crystal on nucleation sites which results in surface coverage with a polycrystalline film. However, 248 249 it is difficult to achieve sufficient density of nucleation sites on unmodified substrates. To solve 250 this difficulty and at the same time strengthen the adhesion MOFs layers and substrates, 251 supporting substrates are modified. A modification of the substrate surface is sometimes crucial 252 to form defect-free MOF membranes. In-situ growth can be further classified into two routes: in-253 situ growth on unmodified support and in-situ growth on modified support.

254 In-situ growth on unmodified support usually involves immersing the supports without any modifications in the growth solutions. During the entire process, the MOF crystals almost 255 256 simultaneously nucleate, grow and intergrow on the substrate [173]. For in-situ growth on 257 unmodified supports, Miyamoto et al. adopted an in-situ growth method to create a UiO-66 membrane on Al<sub>2</sub>O<sub>3</sub> support[163]. A porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> tube was soaked into the mother solution of 258 UiO-66, and the solution was heated to 393 K for 24 h. Highly intergrown UiO-66 membranes 259 260 were finally prepared on alumina support by varying the amount of the solvent, N,N dimethylformamide. As more and more pure-MOFs membranes have been prepared, a 261 262 phenomenon, the absence of strong interfacial bonding between pure MOFs layers with native 263 supports, has gradually been noted. To address this issue, Liu et al. demonstrated the in-situ 264 growth of UiO-66 (zirconia) layers on prestructured yttria-stabilized zirconia (YSZ) hollow 265 fibres[156]. YSZ hollow fibres were deployed as substrates due to their merits, including high 266 packing density, low transport resistance, easy scale-up, good mechanical strength, and 267 outstanding chemical and thermal stability. The other function of YSZ hollow fibres is that they 268 could be chemically modified by the 1,4-benzenedicarboxylate (BDC) ligands during the 269 fabrication of MOF membrane, thus enhancing the adhesion of the MOF layer to the substrate 270 greatly. Another method called 'single metal source' was developed to enhance the Interfacial 271 adhesion between pure MOF membranes and supports by Kang and co-workers[169]. In this 272 scenario, the support played dual roles in the preparation process, one is acting as the only nickel 273 source participating in the synthesis reaction and the other is acting as a substrate to support the 274 as-synthesized MOF membrane. The nickel net was placed horizontally in an autoclave filled with

a ligand solution under conditions. The MOF crystals first grew around the wires of the nickel netand then intergrew over time, finally generating a thin and crack-free MOF layer.

277 For in-situ synthesis growth on the support, the poor interaction between MOF membranes and supports is a common challenge, modifications on supports have been suggested to be an 278 279 effective strategy to increase the heterogeneous nucleation between MOF crystals and substrates. 280 Zhang group reported the growth of defect-free UiO-66-NH<sub>2</sub> membranes on tubular α-alumina 281 substrates that were modified by coating a thin layer of sacrificial zirconia (ZrO<sub>2</sub>) sol. The resulting 282 UiO-66-NH<sub>2</sub> layers on modified supports exhibited excellent separation performance. These ZrO<sub>2</sub> 283 layer has an important role in promoting the synthesis of UiO-66-NH<sub>2</sub> membrane since ZrO<sub>2</sub> can 284 be utilized as fillers to modify the support and creates a graded layer of finer pore size suitable 285 for the growth of UiO-66-NH<sub>2</sub> membrane, but also provides nucleation and anchoring sites for the 286 deposition and growth of UiO-66-NH<sub>2</sub> membrane by being utilized as the secondary metal source for the preparation of the UiO-66-NH<sub>2</sub> structure. Wu et. al prepared continuous polycrystalline 287 MIL-160 membranes on polydopamine (PDA) modified α-Al<sub>2</sub>O<sub>3</sub> disks[166]. Firstly, they covered 288 289 the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disks with polydopamine (PDA) layer twice. Subsequently, the substrates with the 50 ~ 200 nm thickness of PDA layers were dried at 60 °C. PDA can be used as highly efficient 290 291 molecular linker to attract and anchor MIL-160 building blocks onto the support surface for the 292 formation of a homogeneous PDA layer, thus promoting the nucleation and growth of MIL-160 membranes. Highly crystalline MIL-160 membranes were finally synthesized on the modified 293 294 substrate as a promising candidate for the separation of xylene isomers by pervaporation.

#### 295 2.1.2. Secondary growth

Secondary growth or seeded-secondary growth refers to an approach that involves the seeding 296 297 of crystal nucleus on the support, where pure MOF layer grows substrate-independently. 298 Compared to in-situ growth for polycrystalline MOF membrane fabrication, the crystal nucleation 299 and growth steps of secondary growth can be independently manipulated. This is favourable to 300 obtain the dense and continuous membrane that is thinner and less defective[174]. In addition, 301 the final thickness of the MOF membrane is relatively easy to control by controlling the thickness of the seed crystal layer[175]. Moreover, the seeded growth method can systematically control 302 303 the MOF membrane orientation, which can be achieved either by the Van der Drift competitive 304 growth theory [138, 176, 177] or pre-deposition of oriented MOF seed layers [175, 178]. Nowadays, 305 there are several seeding techniques for the preparation of pure MOF-based membranes used in 306 pervaporation including rubbing[162], dip-coating[172], covalent-assisted seeding[159], reactive

307 seeding[157] and thermal seeding[158], which can be categorized into two classes: physical 308 seeding and chemical seeding. As a result, secondary growth can be further classified into 309 secondary growth-substrates with physically attached seeds and secondary growth-substrates 310 with chemically attached seeds. Wang's group deployed wet-rubbed Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy powders to 311 synthesize Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy membranes on porous SiO<sub>2</sub> discs using a seeded solvothermal growth 312 [162]. In this report, the seeded support was immersed into the mother solution of Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy at 150 °C for 24 h, forming a continuously polycrystalline Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy membrane on the support 313 314 surface. Diestel et. al also reported on the preparation of continuous ZIF-8 membranes[170]. The seeds were first attached to asymmetric  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> microfiltration disc membranes by dip-coating 315 and dried. Then, the seed support was placed vertically in the autoclave filled with a secondary 316 317 solution. Subsequently, the autoclave was heated under certain under certain conditions, finally producing a continuous ZIF-8 membrane with a thickness of about 15 µm. 318

319 For improving further interaction between pure MOF layers and supports, a lot of chemically 320 seeding techniques are developed to anchor crystal seeds on porous supports. A new seeding 321 method, "thermal seeding", was reported to chemically deposit MOF seeds on porous  $\alpha$ -alumina 322 substrates[158]. The so-called "thermal seeding" is that the solution containing CAU-10-H 323 crystals was dropped on hot porous  $\alpha$ -alumina support. Once the seeded support was cooled 324 down to the room temperature, the resulting seeded support was placed in the autoclave, into 325 which the solution containing CAU-10-H precursors was then filled. Under appropriate synthesis 326 conditions, the continuous CAU-10-H membrane without cracks and fractures grew on the 327 chemically seeding support.

328 Like the in-situ growth method, the seeding step can be carried out by in-situ growth synthesis. A 329 facile reactive seeding (RS) was developed to synthesize pure MOF membranes on porous 330 supports. In this process, porous supports not only played a supporting role but also served as 331 inorganic source reacting with organic ligands to deposit a seeding layer. For example, Hu et al. 332 demonstrated the pure MIL-53 membrane was synthesized on the alumina support modified through RS in seeded growth [157]. First,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support was used as inorganic precursor to 333 334 react with 1.4-benzenedicarboxylic acid ( $H_2BDC$ ) under hydrothermal conditions, which led to 335 grow a seed layer on the aluminium support. Next, the alumina support was placed vertically in 336 the autoclave with a mother solution of MIL-53, and then the autoclave was heated under appropriate circumstances for 12 hours, obtaining a uniform, thin and well-intergrown MIL-53 layer 337 on the aluminium support surface. In 2019, a covalent-assisted seeding method has been 338 339 introduced to prepared ZIF-8 /PI membranes[159]. To form strong interaction between the seed

340 layer and polymeric substrate, the imidazole-2-carbaldehyde (ICA) molecules were first 341 introduced onto the polyimide (PI) substrate cross-linked ethylenediamine (EDA) through the 342 imine condensation reaction, which offered the nucleation sites for the of ZIF-8 seed crystals. By 343 the covalent-assisted seeding method, a uniform seed layer was firmly deposited to the PI matrix 344 by covalent bonds.

#### 345 2.1.3. Contra-Diffusion

In the contra-diffusion synthesis, two precursor solutions are isolated by a porous substrate, two 346 precursor molecules diffuse in the opposite direction through the porous channels existing in the 347 substrate. Crystallization takes place on the substrate when two precursor molecules meet with 348 each other, finally forming the pure MOF layer. This method is beneficial to fabricate the defect-349 350 free MOF films because MOF precursors diffuse preferentially through the defect sites of the membranes compared to the already formed layers. Moreover, owing to two-separate precursor 351 352 solutions, this method can reduce the bulk MOF formation and the usage of the reactants for 353 MOFs, thereby producing the MOF films with the uniform thickness. For example, Jin et al. 354 reported that the ZIF-71 membrane was formed on the ceramic hollow fibre support using the 355 modified contra-diffusion method[155]. Two precursor solutions were placed on each side of the 356 hollow fibre, and the metal ions and the organic ligands met and reacted on the support interface. 357 In addition, an extended glass tube was connected vertically to the lumen of the ceramic hollow 358 fibre for maintaining an adequate supply of nutrients for coordination reaction. The as-prepared 359 ZIF-71 hollow fibre membrane was applied for the pervaporation separation of organic solutions, 360 exhibiting excellent ethanol recovery performance.

#### 361 2.2. MOF-based mixed matrix membranes

362

363 MOF-based mixed matrix membranes (MOF-based MMMs) are membranes in which the MOF is 364 added into the polymer casting solutions as micro- or nanoparticles. MOF-based MMMs 365 consisting of easily processable polymers have been pursued by many researchers since the first 366 report in 2004[179]. As we can see from Table 4, various strategies of the preparation of MOF-367 based MMMs used in pervaporation are surveyed (Figure 4-6). Up to date, researchers have 368 already developed a variety of synthesis methods including room temperature[180, 181], solvothermal 369 [182-185], microwave-assisted[186-189], sonochemical[190-192], 370 electrochemical[193-195], and mechanochemical synthesis[196-198]. However, room 371 temperature and solvothermal methods are the only two choices that have been used for the synthesis of MOFs in pervaporation. Post-synthetic modification (PSM) has also gradually 372

- attracted attention in pervaporation for endowing the MOF with new functionalities[199]. As for
  the synthesis of MOF-based MMMs, blending is the most used method in pervaporation. Besides
  these methods, there are some new approaches to improve the performance of MMMs in
  pervaporation, such as chemical cross-linking [86], in-situ synthesis [107], etc.
- 377

MOF	Polymer matrix	Synthetic method for MOF-based MMMs	Synthetic method for MOF	Application	Ref.
Dehydration via pervapora	tion	_			
ZIF-8	PI (Matrimid® 5218)	Blending	Room temperature	Dehydration of ethanol	[200]
ZIF-8	PBI	Blending	Room temperature	Dehydration of ethanol, isopropapol (IPA) and p-butapol	[201]
ZIF-8	PBI	Blending	Room temperature	Dehydration of methanol, ethanol and n-butanol	[202]
ZIF-90	PI (P84)	Blending	Room temperature	Dehydration of isopropanol	[203]
ZIF-7	CS	Blending	Solvothermal synthesis	Dehydration of ethanol	[204]
NH2-UiO-66	PEtI	Blending	Solvothermal synthesis	Dehydration of acetic acid	[205]
ZIF-8	PVA	Blending	Room temperature	Dehydration of ethanol	[206]
UiO-66, UiO-66-OH, UiO-66-(OH) <sub>2</sub> and UiO-67	PVA	Blending	Solvothermal synthesis	Dehydration of ethanol	[207]
NH <sub>2</sub> -MIL-125(Ti)	SA	Blending	Solvothermal synthesis	Dehydration of acetic acid	[208]
ZIF-8	CS	Blending	Room temperature	Dehydration of Isopropanol	[209]
ZIF-8*	PVA	Blending	Solvothermal synthesis	Dehydration of Isopropanol	[210]
[AI(OH)(MBA)] (CYCU-7) and [AI(OH)(SBA)]	CS	Blending	Solvothermal synthesis	Dehydration of ethanol	[74]
MOF-801	CS	Blending	Solvothermal synthesis	Dehydration of ethanol	[211]
UiO-66	PI (6FDA-HAB/DABA)	Blending	Solvothermal synthesis	Dehydration of ethanol,	[212]
SO <sub>3</sub> H-MIL-101(Cr)*	PVA	Blending	Solvothermal synthesis	Dehydration of ethylene glycol	[213]
UiO-66-NH₂, UiO-66 and UiO-66-F₄	PI (6FDA-HAB/DABA)	Blending	Solvothermal synthesis and room temperature	Dehydration of methanol, ethanol and isopropanol	[214]
HKUST-1	PI (Matrimid® 5218)	Blending	Room temperature	Dehydration of ethanol	[215]
DUT-5 (AI)	CS	Blending	Solvothermal synthesis	Dehydration of ethanol	[216]
ZIF-L and ZIF-8	SA	Blending	Room temperature	Dehydration of ethanol	[217]
UiO-66-NH2**	PDMS	Chemical cross-linking	Solvothermal synthesis	Dehydration of ethanol	[218]
UiO-66-NH <sub>2</sub>	CTA and PEI (Ultem® 1010)	Blending	Solvothermal synthesis	Dehydration of ethanol	[219]

#### 378 Table 4 Brief Overview of MOF-based MMMs in Pervaporation

EuBTB	SA	Blending	Solvothermal synthesis	Dehydration of ethanol	[81]
MIL-53(AI) and	PVA	Blending	Solvothermal synthesis	Dehydration of ethanol	[220]
MIL-53(AI)-NH <sub>2</sub> ** ZIF-8	PVA	Blending	Room temperature	Dehydration of isopropanol	[221]
Recovery or removal of org	ganics via pervaporation				
ZIF-71	PDMS	Blending	Room temperature	Recovery of ethanol	[222]
and ZIF-8 ZIF-71	PDMS	Blending	Room temperature	Recovery of ethanol	[223]
ZIF-71	PDMS	Blending	Room temperature	Recovery of methanol, ethanol, isopropanol and	[224]
ZIF-8 and ZIF-7	PMPS	Blending	Room temperature	Recovery of i-butanol, ethanol, n-Propanol, n-Butanol and n-Pentanol	[38]
ZIF-8	PDMS	Blending	Room temperature	Recovery or removal of n-butanol	[225]
ZIF-71	PDMS	Blending	Room temperature	Removal of ethanol and n-butanol	[226]
MIL-53	PDMS	Blending	Solvothermal synthesis	Recovery of ethanol	[227]
ZIF-71	PDMS	Blending	Room temperature	Recovery of ethanol and n- butanol	[228]
ZIF-71	PEBA	Blending	Room temperature	Recovery of n-butanol	[229]
ZIF-8	PDMS	In situ synthesis	N/A	Recovery of ethanol	[37]
ZIF-8	PDMS	Blending	Room temperature	Recovery or removal of ethanol and p-butanol	[230]
ZIF-8	PMPS	Plugging— Filling	Room temperature	Recovery of furfural	[231]
MAF-6	PEBA	Blending	Room temperature	Recovery of ethanol	[232]
ZIF-8	PDMS	Blending	Room temperature	Recovery or removal of n-butanol	[233]
ZIF-71***	PDMS	Blending	Room temperature	Recovery of ethanol and n- butanol	[234]
ZIF-L	PDMS	Blending	Room temperature	Recovery of ethanol, n-propanol or	[235]
ZIF-90**	PDMS	Blending	Room temperature	Recovery of ethanol	[236]
ZIF-8	PDMS	In-situ synthesis	Room temperature	Recovery of n-butanol	[237]
ZIF-8	PDMS	Blending	N/A	Recovery or removal of ethanol	[238]
ZIF-8	PDMS	Blending	Room temperature	Volatile aroma components of	[239]
ZIF-8	PDMS	Blending	Room temperature	Recovery of ethanol	[240]
ZIF-8	PEBA	Blending (Vacuum- assisted assembly and	Room temperature	Recovery of biobutanol	[241]
ZIF-67	PI (P84)	immersion) Blending	Room temperature	Recovery of ethanol	[128]

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ZIF-90**	PDMS	Blending	Solvothermal synthesis	Recovery of ethanol	[242]				
MAF-6	PDMS	Blending	Room temperature	Recovery of ethanol	[243]				
Zn(BDC)(TED) <sub>0.5</sub>	PEBA	Blending	Solvothermal synthesis	Recovery of n-butanol	[244]				
Separation of organic-organic mixtures via pervaporation									
HKUST-1	PEBA	Blending	Room temperature	Gasoline desulfurization	[245]				
Co-formate	PEBA	Blending (dynamic assisted assembly)	Room temperature	Separation of aromatic/aliphatic hydrocarbon mixtures	[246]				
MOF-808	PDMS	Blending	Solvothermal synthesis	Separation of ethyl acetate/ethanol, ethyl acetate/isopropanol, and ethyl tert-butyl ether/ethanol	[106]				
HKUST-1	PDMS	Blending	Room temperature	Thiophene from model gasoline	[247]				
MIL-101	PDMS	Blending	Solvothermal synthesis	Desulfurization of model gasoline	[248]				
HKUST-1	PVA	Blending	Solvothermal synthesis	Toluene/n-heptane mixtures	[249]				
CPO-27	PDMS	Blending	Solvothermal synthesis	Desulfurization of model gasoline	[250]				
UiO-67-bpydc	PDMS	Blending	Solvothermal synthesis	Desulfurization of model gasoline	[46]				
MIL-53(AI)-SO <sub>3</sub> H**	SPES-C	Blending	Solvothermal synthesis	Separation of methanol and	[251]				
[Cu2(bdc)2(bpy)]n	PES-C	Blending	Room temperature	Separation of methanol/methyl tert-butyl ether mixture	[252]				
* Post-synthetic polymerisation									

Covalent post-synthetic modification
 \*\* Post-synthetic ligand exchange

379

#### 380 **2.2.1. Synthesis of MOFs used in pervaporation**

As indicated above, room temperature and solvothermal methods are the main strategies employed to synthesis MOFs particles in pervaporation. These two methods as well as postsynthetic modification (PSM) are described in this section.

#### 384 *Room-temperature synthesis*

385 The room-temperature method is a conventional method for the synthesis of MOFs by mixing 386 directly starting materials under more sustainable conditions, most of which does not need any external energy supply to initiate the nucleation and growth of MOFs. Many MOFs reported so far 387 388 are synthesized by room-temperature method, such as NU-100[253], MOF-Fe/AgOTf-1, MOF-389 Co/AqSbF<sub>6</sub>-1,MOF-Fe/AqOTf-1[254]. This method is sometimes preferable because it can solve 390 some problems associated with heating, such as thermally sensitive starting materials for the 391 preparation of MOFs[255]. In addition, room-temperature synthesis is beneficial to meet the needs 392 of MOFs for large-scale industrial production[180]. However, compared to other well-known 393 methods, the major disadvantage of room-temperature synthesis is its time-consuming (hours to

394 weeks) nature. In view of the above disadvantage, Yan and colleagues introduced a rapid room-395 temperature synthesis method to prepare bulk quantity of thermally stable and highly porous 396 MOF-5 nanocrystals, in which the pH of a mixed solution of metal and ligand changes suddenly and the precipitation occurs owing to the addition of amines to the reaction solution[256]. Wiebcke 397 398 and co-workers reported rapid room-temperature synthesis of a prototype zeolitic imidazolate 399 framework (ZIF) material, ZIF-8 in the form of powders or stable colloidal dispersions with a 400 narrow size distribution without any auxiliary stabilizing agent or activated operation could be obtained[257]. However, this method relied on adding excess 2-methylimidazole (Hmim) to the 401 402 zinc source. Good results could be achieved when using Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Hmin and methanol with 403 a molar ratio of about 1:8:700. A simple methodology to synthesize bimetallic Co-Zn based zeolitic 404 imidazolate frameworks in water at room temperature was demonstrated by Singh and coworkers[258]. By tuning the molar ratios of Co and Zn precursors, bimetallic CoZn-ZIF-8 405 frameworks with varying Co: Zn were obtained. It was found that incorporation of Co<sup>2+</sup> into the 406 407 Zn-ZIF-8 framework resulted in an increase in surface area of up to 40% and an increase in pore volume of up to 33% without structural damage or alteration compared to Zn-ZIF-8. 408





410 Figure 4 Schematic diagrams for MOF synthesis: (a) room temperature synthesis and (b) solvothermal synthesis.

For the improvement of the space-time yield (STY) of the hierarchically porous MOF (HP-MOF) and the reduction of energy consumption. Duan *et al.* also developed a different strategy for roomtemperature synthesis of MOFs[261]. In which surfactants were used as the template and zinc oxide (ZnO) was deployed as an accelerant. The as- synthesized HP-MOF had multimodal

<sup>411</sup> Reprinted with permission from Ref. [259, 260]

<sup>412</sup> 

hierarchical porous structures and excellent thermal stability. In addition, the synthesis time was
 significantly shortened to 11 minutes, and the maximum HP-MOFs STY was as high as 2575 kg
 m<sup>-3</sup> d<sup>-1</sup>. Furthermore, other surfactants were also able to be utilized as templates to quickly
 prepare diverse stable HP-MOFs via room temperature synthesis, and the porosity of HP-MOFs
 could be easily adjusted by controlling the type of templates.

#### 422 Solvothermal synthesis

423 In solvothermal synthesis, organic ligands and metal salt precursors are generally dissolved or 424 dispersed at a certain ratio in solvents including dimethyl formamide[262, 263], diethyl 425 formamide[264, 265], acetonitrile[266, 267], glycol[268, 269], acetone [270, 271], ethanol[272, 426 273], methanol[274, 275] etc, then loaded in closed container under autogenous pressure via electrical heating, as shown in Figure 3b. Water is also often used as a solvent, and its 427 428 corresponding reaction is called hydrothermal reaction[276, 277]. Mixtures of solvents have been 429 used to avoid the problem the different solubility of precursors and tune the polarity or pH of the 430 reactant solution. According to the reaction requirements, the solvothermal reaction can be 431 carried out in different temperature ranges. The reaction temperature between 100-260 °C is 432 usually higher than the boiling point of the solvent. Under such temperature conditions, a relatively 433 high pressure can be obtained in the sealed reaction vessels, which promotes the solubility of the 434 reactants and accelerates the reaction, thereby promoting the nucleation and growth of MOF 435 crystals. The solvothermal synthesis has the advantages of simple operation, low equipment 436 requirements, relatively short reaction time, and high-quality MOF crystals, which make it the most 437 commonly used method among many MOFs synthesis methods. High-throughput solvothermal 438 synthesis is a powerful tool to accelerate the discovery of new MOF structures and optimize synthetic schemes [278, 279]. However, it is difficult to control the reaction process because the 439 440 solvothermal synthesis is performed in a closed container with relatively high temperature and 441 pressure. Since two representative MOFs, HKUST-1[280] and MOF-5[281], were prepared by solvothermal synthesis in 1999, a large number of MOFs such as MOF-2, Fe-MOF-74[182], ZIF-442 78[282], UiO-66[283] have been synthesized by this method. 443

Since the properties of materials are profoundly affected by their specific morphology, there is an urgent need to synthesize MOFs with controllable morphology [284-286]. Herein, Guo and coworkers used solvothermal synthesis by modulating the concentration of the precursors to synthesize NH<sub>2</sub>-MIL-125(Ti)[286]. By varying the total solvent volumes, NH<sub>2</sub>-MIL-125 (Ti) crystals with four different morphologies were produced, which were circular plate, tetragonal plate, truncated bipyramid and octahedron. It was found that the light response of NH<sub>2</sub>-MIL-125 (Ti) 450 crystal was deeply affected by their morphology, the absorption edges of different morphologies 451 lied between 480 nm and 533 nm with the band gaps of 2.6 to 2.3 eV. When synthesizing the 452 same MOF, different laboratory might use different solvent conditions. To investigate the solvent 453 effect to the formation of Ni-BTC (BTC = 1,3,5-benzene tricarboxylate), Israr et al. synthesized 454 Ni-BTC via solvothermal synthesis using different solvent mixtures of water/N,Ndimethylformamide (DMF), water/ethanol, and water/ethanol/DMF with or without a variety of 455 456 bases[287]. The results showed that Ni-BTC crystals with different BET surface areas as well as 457 different XRD patterns were produced under different solvent conditions, obtaining Ni-BTC 458 crystals with a maximum BET surface area of 850 m<sup>2</sup>/g when NH<sub>4</sub>OH was used as a base and 459 water/DMF was used as the solvent. Recently, Chen and colleagues have successfully explored 460 using "one-pot" solvothermal method to synthesized a heterometallic MOF In/Gd-CBDA (CBDA: 461 5.5'-(carbonylbis(azanediyl))-diisophthalic acid ) based on monofunctional linker CBDA[288]. 462 Because CBDA has a non-centrosymmetric geometry of tetra-carboxylic acid structure. Under 463 different coordination environments, carboxylic groups can recognize the predicted different 464 metals, thereby generating tetra-nuclear  $In_4O_2(COO)_4$  and tri-nuclear  $Gd_3O(COO)_6$  clusters.

465 466

#### 2.2.2. Post-synthetic modification (PSM)

466

#### 467 Covalent post-synthetic modification (Covalent PSM)

468 Covalent PSM is the most thoroughly investigated approach for post-synthetic modifications of 469 MOFs. This approach relies on the use of a reagent to form new covalent bonds with reactive functional groups on the organic linkers of MOFs, imparting an array of new functionalities into 470 471 MOFs. These organic functional groups mainly include amines, carboxylic acids, and azides, 472 reacting respectively with carbonyl, amine, and alkyne groups on the organic linkers[289]. Up to 473 now, a number of researchers have already investigated various kinds of covalent PSM reactions, 474 including amide coupling [290-293], imine condensation [294-298], urea and cyanates 475 formation[299-301], N-alkylation[302, 303], click reactions, bromination[292, 304], reduction[295, 476 305], et cetera. The covalent PSM of MOFs was first reported for enantioselective separation and 477 catalysis by Kim et al. in 2000, in which CH<sub>3</sub>I and (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>I) reacted with free pyridyl groups of 478 the MOF (D-POST-1) to form the covalent bonds [302]. In 2007, Cohen and his co-worker 479 demonstrated a MOF (IRMOF-3-AM1) containing methyl amide substituents by the reaction of 480 amino groups within IRMOF-3 with acetic anhydride, which is the first detailed example of 481 Covalent PSM[290]. In 2018, Zhu and Yan showed that UiO-66-NH<sub>2</sub> can be modified at the free 482 amine groups with salicylaldehyde by covalent PSM[306]. UiO-66-NH<sub>2</sub> is an amino derivative of UiO-66, in which Zr<sub>6</sub>-cluster SBU makes UiO-66-NH<sub>2</sub> highly resistant to many solvents (such as
ethanol, water, benzene). When treated with salicylic-aldehyde in ethanol with gentle heating,
UiO-66-NH<sub>2</sub> can be converted to the corresponding the Schiff base grafted UiO-66-NH<sub>2</sub>,
designated as UiO-66-NH<sub>2</sub>-SA, with imine formation via a Schiff-base reaction.

487



488

489 Figure 5 Schematic diagram for post-synthetic modification to MOF: (a) covalent post-synthetic modification, (b) post-490 synthetic polymerisation and (c) post-synthetic ligand exchange. Reprinted with permission from Ref. [307-309]

491

492

#### 493 *Post-synthetic polymerisation (PSP)*

Post-synthetic polymerization (PSP) of MOFs is a useful method that can make the metal-organic 494 framework (MOF) interact with the polymer components very closely, thereby directly 495 496 transforming MOFs into polymer materials. This method, bridging the gap between polymer and 497 MOFs, endows MOFs with the flexible and durable characteristics from polymer components. The 498 methods of post-synthetic polymerization for MOFs are mainly categorized in two schemes: (1) 499 polymerisation of functionalized organic ligands in MOFs with organic monomers, (2) 500 polymerisation of functionalized organic ligands adhering to MOFs with organic monomers. Sada 501 et al. reported a fascinating study[310]. The azide-tagged MOF (AzM) with two azide groups 502 ("clickable" group) in the organic ligand was firstly prepared, and then cubic AzM was treated with 503 the external alkynes. That resulted in the in situ click reaction between azide groups within the 504 MOF and various alkynes. Based on this study, they used "clickable" groups throughout the MOF 505 lattice and reactants with more than one reactive site in the nanopores of AzM to react, obtaining 506 a cross-linked MOF [311]. It was reported that novel elastically stretchable and compressible 507 nanocomposite hydrogels (MIL-101-MAAm/PAAm) with high MOF content (20 - 60wt.%) was 508 fabricated by combining polymer hydrogel networks with MIL-101[312]. The polymerizable 509 methacrylamide groups (MAAm) were first incorporated into MIL-101, generating MIL-101-MAAm, 510 and then the resulting MIL-101-MAAm nanoparticles were copolymerized with acrylamide (AAm) 511 monomers in solutions to prepare the MOF-laden hydrogels. Such MOF-laden hydrogels 512 overcame the limitations of the poor structural or functional adjustability and the loading of fillers 513 during the combination of conventional nanocomposite hydrogels with common nanofillers. Due 514 to the distinctive gelation mechanism and microstructure, this type of MOF-laden hydrogels can 515 not only withstand 500% tensile strain or 90% compressive strain without breaking, but also 516 recover guickly after unloading. In addition, they showed excellent resistance to freezing at -25°C.

517

#### 518 Post-synthetic ligand exchange (PSLE)

519 Some MOFs are difficult to prepared through direct synthesis. Given this situation, post-synthetic 520 ligand exchange has been developed. The generalized methodology of PSLE is that the MOF 521 with the desired structure is first synthesized, and then the existing ligands within the as-522 synthesized MOF are replaced with alternative components.

523 Post-synthetic ligand exchange, also known as solvent-assisted linker exchange or bridging-linker 524 replacement, conceptually involves a heterogeneous reaction that occurs at the solid-solution 525 interface. In which the free linkers from the solution are incorporated into the parent MOF crystals, 526 producing a new MOF crystal with the topology of the parent MOF. Interestingly, post-synthetic 527 ligand exchange can also procced in a solid-to-solid way. For example, when a mixture of UiO-528 66-Br and UiO-66-NH<sub>2</sub> was suspended in water, ligand exchange occurred in more than 50% of 529 the particles, and a new MOF containing both bdc-Br (2-bromo-1,4-benzendicarboxylic acid) and 530 bdc-NH<sub>2</sub> (2-amino-1,4-benzendicarboxylic acid) was formed without losing the connection and 531 crystalline state [313]. Similar to trans-metalation, post-synthetic ligand exchange also involves 532 the complete or partial exchange to the ligands within MOFs[314]. Up to now, there are three 533 main types of linkers that have been deployed for post-synthetic ligand exchange, namely, 534 dipyridyl, imidazolate and carboxylate linker. The first study of ligand-exchange reactions in MOF chemistry was reported by Choe et. al[315]. They soaked the porphyrin-based MOF (PPF-20) in 535 536 which the paddle-wheel porphyrin layers are pillared by dpni (N,N'-di-4-537 pyridylnaphthalenetetracarboxydiimide) into a solution of 4,4'-bipyridine (bpy) as the replacement 538 linker for 2 h, obtaining isostructural PPF-4 with 97% transformation. That involves a decrease of 539 the interlayer distance from 21.2 to 12.8 Å, corresponding to the shorter length of the bpy linker. 540 Imidazolate exchange was achieved by Hupp, Farha and co-workers. In this process, they used 2-methylimidazolate (mim) under solvothermal conditions to exchange the linkers of the MOF 541 542  $(Cd(eim)_2, (eim = 2-ethylimidazolate)), obtaining a new MOF (CdIF-9) with high yield in a crystal-$ 543 to-crystal transformation. In addition to the above-mentioned exchange examples of bipyridine 544 and imidazolate, carboxylate exchange has been also demonstrated. Rosi and co-workers used 545 bio-MOF-100 which is a mesoporous material containing metal-adeninate tetrahedral building blocks connected through trimeric "bundles" of 4,4'-biphenyldicarboxylate (bpdc<sup>2-</sup>) as the scaffold 546 for ligand exchange[316]. In their study, bpdc<sup>2-</sup> within bio-MOF-100 was replaced with 2-547 azidobiphenyldicarboxylic acid, generating  $N_3$ -bio-MOF-100 with the isostructure to bio-MOF-100. 548 549 Another report of ligand exchange is incorporating thermally unstable metal complexes into the 550 UiO-67 at ambient temperature. The UiO-67 (Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BPDC)<sub>6</sub>) composed of Zr (IV)-based 551 SBUs and the 4,4'-biphenyl dicarboxylic acid (BPDC) ligands was suspended in aqueous solution 552 containing tris-carbonyl-chloro(5,5'-dicarboxyl-2,2'-bipyridine) rhenium(I) (Re complex) for a 553 period of time, generating Re-based UiO-67. It has dual function not only as the photosensitizer,

but also as the catalyst for photochemical reduction of CO<sub>2</sub>. In addition, Re-based UiO-67 containing 30% Re-based ligands showed stronger activity than UiO-67 with 100% Re-based ligands[317]. The post-synthetic ligand exchange was suggested a widespread phenomenon by the examples of imidazolate and carboxylate exchange. Because metal-imidazolate bonds and metal-carboxylate both are exceptionally strong unlike metal-dipyridyl bonds, MOFs containing metal-imidazolate bonds or metal-carboxylate bonds have been reported to have good stability.

#### 560 2.2.3. Synthesis of MOF-based MMMs

561

562 Three main methods have been reported for the synthesis of MOF-based MMMs, i.e., blending 563 method, chemical cross-linking and in situ synthesis methods, which are briefly described below. 564 Figure 5 shows main steps involved in each method.

#### 565 Blending method

566 Blending method is a typical method for MOF-based MMMs formation. There are three main 567 manufacturing routes for preparing MOF-based MMM on a laboratory scale: (1) dispersion of 568 MOF particles in the solvent before polymer addition, (2) dissolution of polymer in the solvent 569 before adding MOF particles to polymer solution, (3) dissolution of the polymer in the solvent and 570 disperse the filler particles in the solvent, then mix the two suspensions[318]. The mixture can be 571 made into a membrane by doctor blading[228], dip- or spin-coating[219, 227], vacuum or pressure-assisted assembly[241, 246], etc. on the substrate, and the MOF-based MMMs are 572 573 obtained by a curing or drying process to completely evaporate the solvent. The entire process can lead to free-standing membranes delaminated from the nonporous substrate (e.g., silica 574 575 wafers)[319] or asymmetric MMMs typically consisting of a selective layer on a mechanically 576 robust porous support [320]. Compared to the Pure MOF-based membranes, MOF-based MMMs 577 have greater functionality per unit weight (or volume). Since MOF-based MMMs use prefabricated 578 MOF particles, their advantage is that they are able to use a variety of MOF and MOF mixtures 579 without having to consider the original MOF synthesis conditions[321].



580

581 Figure 6 Schematic diagram the preparation of MOF-based MMMs: (a) blending, (b) chemical cross-linking 582 and (c) in situ synthesis methods. Reprinted with permission from Refs. [37, 206, 218]

583

Coronas et al. used as-synthesized ZIF-8 crystals as filler, and polyimide (PI) Matrimid® 5218 as 584 585 the polymer matrix, to produce ZIF-8-PI mixed matrix membranes by the solution-blending casting process[200]. During the process, ZIF-8 powders were first dispersed evenly in the solvent and 586 then PI were added into the dispersion containing ZIF-8 particles. To promote compatibilization 587 of the MOF particles with the polymer, MOF particles were "primed" with the matrix polymer by 588 589 adding a portion of matrix polymer first into the mixture containing MOF particles and then stirring 590 the mixture[229]. This step continued to be repeated until the required total amount of the polymer 591 was added. After mixing, the MOF/polymer solution was cast on a substrate by a flat membrane 592 casting equipment. In 2019, Lin et al. used the path B to make 3D aluminum MOF (DUT-5) based 593 MMMs[216]. In the process of fabricating the membrane, the chitosan solution was first prepared 594 by mixing chitosan with 2 wt.% acetic acid and then DUT-5 particles were distributed into the 595 chitosan solution. The final MMMs were obtained by casting the mixture solution. The resulting 596 MMMs were deployed to separate ethanol/water binary mixture by pervaporation. Shi et al. 597 reported polybenzimidazole (PBI)/ZIF-8 mixed matrix membranes by blending-casting[202]. The casting solution was obtained by dissolving PBI into 1-Methyl-2-pyrrolidinone (NMP) and 598 599 dispersing ZIF-8 nanoparticles into NMP, then mixing two solutions. After casting the combined 600 solution into a casting ring placed on a silica wafer, the solvent in the freshly cast membranes 601 needed to be cooled down before drying, and the free-standing membranes were removed from

the silica wafer and finally annealed in a vacuum oven. The as-formed membranes wereinvestigated for dehydrating water from alcohols by pervaporation.

#### 604 *Chemical cross-linking synthesis*

The dispersion of MOFs into polymer matrix by blending method endows the MOF-based MMMs 605 606 with the superior flexibility of polymers and the porous characteristics of MOFs. However, the 607 desired properties and performance of MOF-based MMMs are still hampered by poor 608 compatibility between MOF particles and the polymer matrix as well as aggregation of MOF particles[322, 323]. Alternatively, small molecules and polymer chains can block the pores of the 609 610 MOF particles, which can cause clogging of the molecular sieves [324, 325]. Despite the progress 611 made in recent years, the lack of homogeneity at the molecular level has always been a challenge 612 for most MOF-based MMMs. To solve the above problems and access MOF-based membranes 613 with good dispersibility and dense uniform structure, the chemical cross-linking of MOFs bearing 614 polymerizable groups and monomers has been developed by Zhang and colleagues[326]. MOF-615 based MMMs were fabricated using UiO-66-NH<sub>2</sub> where methacrylamide groups were covalently 616 grafted on the surface of UiO-66-NH<sub>2</sub> using post-synthetic polymerisation strategy. The modified 617 UiO-66-NH-Met photopolymerized with butyl methacrylate (BMA) through covalent bonds in the 618 presence of the photoinitiator phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide under UV light. 619 Using the same concept, Wang et al. synthesized UiO-66-MOF-based MMMs by covalent 620 polymerization of the glycidyloxypropyltrimethoxysilane (TMS)-modified UiO-66-NH-TMS and Si hydroxy groups from PDMS[218]. MMMs with high loading of UiO-66-TMS (up to 50 wt.%) can 621 retain good membrane-forming ability, mechanical properties, and pervaporation selectivity, while 622 623 MMMs filled with pristine UiO-66-NH<sub>2</sub> compromised membrane selectivity and mechanical 624 strength even at a lower loading of 10 wt.%.

625

#### 626 In-situ synthesis

For the same purpose as the chemical cross-linking method, in-situ synthesis has been developed to address two major challenges along with blending method, such as the limitation of the particle content, and the performance declined created by nonselective interfacial voids between polymer matrix and inorganic fillers[35, 327]. In-situ synthesis has been inspired by the interfacial polymerization and proved to be a facile and efficient strategy to prepare defect-free MOF-based MMMs[37]. First, inorganic precursors and organic precursors are dispersed in two solutions (generally aqueous phase and organic phase), and then polymer is dissolved in at least one phase. Subsequently, two solutions are contacted with each other on the substrate surface. After that, inorganic precursors and organic precursors meet and react to generate MOF particles in the polymer matrix. In such a way, the formation of MOF particles within polymer matrix is controlled precisely, it favours the dispersion of the MOF fillers with polymer bulk and the compatibility between the MOF fillers and polymer matrix.

639 Mao et. al first reported that such in-situ synthesis route was exploited in the preparation of MOF-640 based MMMs for pervaporation[37]. ZIF-8/PDMS MMMs with 1 µm thick active layer were used 641 for ethanol permselective pervaporation and broke the trade-off effect of polymer in pervaporation membranes. Derived from the same design strategy, in-situ growth of the MOF and 642 polymerization of the polymer were combined to prepare ZIF-8/PDMS MMMs with excellent 643 644 continuity and integrity by Qin group[237]. In the membrane preparation process, solution A containing PDMS and tetraethyl orthosilicate (TEOS) and solution B containing PDMS and 645 dibutyltin dilaurate (DBTDL) were firstly deposited on the PVDF support to generate PDMS layer. 646 647 Then, solution C (PDMS/TEOS/Zn<sup>2+</sup>) and solution D (PDMS/ DBTDL /2-methylimidazole) were coated on the PDMS layer in turn. During this process, ZIF-8 crystallization and PDMS 648 649 polymerization started simultaneously. A ZIF-8/PDMS layer with passable diffusion channels was 650 finally obtained. The resulting ZIF-8 based MMMs combining both the compactness of PDMS and 651 diffusion of ZIF-8 exhibited high-efficiency performance for recovery of n-butanol from agueous 652 solutions.

653

#### 654 **2.3. Other methods**

In addition to the above strategies for synthesizing MOF-based membranes in pervaporation,
some novel synthetic strategies of MOF-based membranes in pervaporation have been explored,
such as pressing and chemical cross-linking method and plugging–filling method.

Pressing and chemical cross-linking method reported by Marti *et al.* is a relatively new route to make free-standing pure MOF-based membranes without the need for a polymeric binder or support[160]. In this report, the synthesized MOF particles were pressed into a wafer by external force, and then modified with ethylenediamine (EDA) vapor to form a free-standing membrane.

With regards to the plugging-filling method, it is targeted at improving the dispersion of MOF particles at high filler content within polymer matrix and the membrane endurance. Liu et. al prepared ZIF-8/silicone MMMs on hierarchically ordered stainless-steel-mesh (HOSSM) using the plugging-filling method[231]. In this process, ZIF-8 nanoparticles were first plugged into the holes with average pore sizes of 6.5 μm in the top layer of HOSSM consisting of a top layer, an
intermediate layer and a bottom layer, and then the spaces between the fillers and mesh wires
were filled with PMPS.

669

## 670 3. Pervaporation separations employing MOF-based 671 membranes

672

# 3.1. Evaluation approaches of pervaporation process and membrane performance

The mass transfer through the pervaporation membrane involves three sequential steps: sorption 676 677 of molecules into the membrane, transport through the active layer of the membrane, and 678 desorption and evaporation of molecules. The pervaporation process performance is highly 679 dependent on the intrinsic properties of the membranes and operating conditions (pressure, feed 680 temperature and feed composition) [328]. The mass transfer in pervaporation can be evaluated 681 in two ways: (i) determining the transmembrane flux and the separation factor or enrichment factor (process performance); and (ii) calculating the permeance or permeability, and the selectivity 682 683 (membrane performance). The former approach is based on experimental results when the membrane is tested under specific pressure, specific feed temperature and composition. Thus, 684 685 this approach is regarded as the evaluation of the whole pervaporation process. The latter relies 686 on mathematic models to calculate the main mass transfer coefficient for the description of the 687 mass transfer through the membrane and figuring out the permeance of the membrane to the targeted compound. By the second approach, we can know if the selected membrane is a good 688 689 choice for the separation of the specific liquid mixture. Therefore the second approach should be considered for the evaluation of membranes utilized in the pervaporation process[329]. 690

The flux J (g/m<sup>2</sup>·h) can be expressed as follows [330]:

$$692 J = \frac{Q}{t \times A} (1)$$

693 in which A is the membrane effective area (m<sup>2</sup>), *t* is the permeate collecting time (h) and Q is the 694 weight of permeate (g).

695 Selectivity can be expressed by separation factor  $\beta_{ij}$  and enrichment factor  $\beta_{\rho/f}$ . Separation factor 696  $\beta_{ij}$  is mainly used for a specific binary mixture [331, 332].

32

$$697 \qquad \beta_{i/j} = \frac{y_i/y_j}{x_i/x_j} \tag{2}$$

698 where *x* and *y* are weight fraction of components, the subscript indicates the components *i* and *j* 699 in the permeate  $(y_i, y_j)$  and feed  $(x_i, x_j)$  solutions, respectively.

The enrichment factor  $\beta_{p/f}$  is mostly utilized as an index of the pervaporation desulfurization [250, 333].

$$\beta_{p/f} = \frac{c_p}{c_f} \tag{3}$$

in the equation (3),  $C_{\rho}$  (µg/g) and  $C_{f}$  (µg/g) are the sulfur content in the feed and permeate, respectively.

Given that both permeability or permeance and selectivity can be used to evaluate the intrinsic membrane properties, normalizing the transmembrane flux to driving force for each component is essential to calculate the permeability ( $P_i$ ) or the permeance ( $P_i/l$ ). Permeability is most commonly expressed as Barrers (1 Barrer = 1 × 10<sup>-10</sup> cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg). (1 m<sup>3</sup> m/m<sup>2</sup> s kPa = 1.33 × 10<sup>14</sup> Barrer). Permeance is most commonly reported as gas permeation units (GPU) (1 GPU =1 × 10<sup>-6</sup> cm<sup>3</sup>(STP)/cm<sup>2</sup> s cm Hg), (1 m<sup>3</sup> m/m<sup>2</sup> s kPa = 1.33 × 10<sup>8</sup> GPU).[37, 328, 334, 335].

712 
$$P_i / l = \frac{J_i}{x_i \cdot \gamma_i \cdot p_i^{sat} - y_i p^p}$$
(4)

713 Driving force = 
$$x_i \cdot \gamma_i \cdot p_i^{sat} - y_i p^p$$
 (5)

Wherein *l* is the thickness of membrane active layer (m),  $J_i$  (g/m<sup>2</sup>·h),  $\gamma_i$ , and  $p_i^{sat}$  are the permeation flux, the activity coefficient, and the saturated vapor pressure of component *i*, respectively,  $x_i$  and  $y_i$  are the mole fractions of component *i* in feed and permeate, respectively,  $p^p$  is the total pressure at the permeate side.

The membrane selectivity is defined as the ratio of the permeabilities or permeances of components i and j through the membrane.

720 
$$\alpha_{i/j} = \frac{P_i/l}{P_j/l} = \frac{P_i}{P_j}$$
(6)

721

722

#### **3.2. Performance of pure MOF-based membranes utilized in pervaporation**

724

Due to the low mechanical strength of pure MOF-based membranes and possible defects within them, many reports on pure MOF-based membranes in pervaporation paid attention to the fabrication of pure MOF-based membranes with the stability and no defects. Figure 7 shows the schematic illustrations of applications of pure MOF-based membranes in pervaporation.

729 To the best of our knowledge, Hu et al. were the first to apply pure MOF membranes in pervaporation in 2011 [157]. The MIL-53 membranes were prepared on alumina porous supports 730 731 via a facile reactive seeding method. In the pervaporation dehydration of the water- ethyl acetate 732 mixtures (7 wt.% water), the water concentration of the permeate increased to 99 wt.% with the 733 flux of 454 g/(m<sup>2</sup>·h) at 60 °C. In this method, the alumina support does not only provide mechanical 734 strength for the MOF layer, but also acts as an inorganic precursor of the MOF reacting with the 735 organic precursor to grow a seeding layer for secondary growth of the MOF membrane. Using the same concept, an integrated ZIF-71 membrane was formed on a porous ZnO substrate for 736 737 the first time and showed obvious separation capacity for both ethanol (with the flux of 322.18  $g/(m^2 \cdot h)$  and separation factor of 6.07) and methanol (with the flux of 394.64  $g/(m^2 \cdot h)$  and 738 separation factor of 21.38) from water in the separation of 5 wt.% ethanol-water and methanol-739 740 water at 25 °C via pervaporation [164]. Due to uniform microporous structure and good thermal 741 stability of MOF-5, Zhao et al. chose MOF-5 to make continuous and crack-free membranes by 742 secondary growth synthesis, and used a series of organic compounds to examine the MOF-5 743 membrane quality in single-liquid pervaporation system [143]. MOF-5 membranes are not stable 744 upon contact with humid air because the polar water molecule can replace partially the organic 745 ligands thus leading to hydrolysis of Zn atoms from the zinc-oxygen tetrahedra [256, 336].



Figure 7 Schematic illustrations of applications of pure MOF-based membranes in pervaporation: (a) separating water from organics, (b) separation of organic-organic mixtures and (c) recovery of ethanol from aqueous solutions. Reprinted with permission from Ref. [45, 156, 163].

746 Nevertheless, only limited number of reports concerning the sustained stability of MOF 747 membrane after exposure to organic solvents exist with Lin and Kasik as pioneers in this field in 2014 [165]. The seeded growth method allowed the formation of a high-guality MOF-5 membrane 748 749 with a thickness of about 10 µm by deploying ball-milled MOF-5 as seed crystals. After the 750 synthetic MOF-5 membrane was run for 16 hours, the p-xylene flux decreased and stabilized at 751 about 70% of the original value of the fresh membrane in the p-xylene pervaporation test. That 752 showed that the MOF-5 membrane is quite stable in organic solvent and can be applied in the separation of liquid organic streams. Jin et al. utilized the ZIF-71 membrane prepared by contra-753 754 diffusion to recover ethanol from ethanol-water solvents [155]. To remove the high resistance of 755 the ZnO disk supports [164], the ceramic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> hollow fibres were deployed as supports to 756 fabricate ZIF-71 hollow fibre membranes. Notably, the flux and separation factor of the ZIF-71 757 membrane for pervaporation recovery of ethanol at 25 °C were 2601 g/(m<sup>2</sup>·h) and 6.88, respectively. However, the selectivity of this pure ZIF-71 membrane is less than 1 and thus it is 758 759 not appropriate for separating the target compound.

Another MOF having considerable chemical stability is UiO-66, which owes its strong hydrophilic adsorption properties to a large number of hydroxyl groups [104, 337, 338]. Wellintergrown UiO-66 membranes, fabricated on pre-structured yttria-stabilized zirconia hollow fibres using solvothermal synthesis, were used to dehydrate i-butanol, furfural, and tetrahydrofuran, ensuring the flux of up to ca. 6000 g/(m<sup>2</sup>·h) and the separation factor of more 765 than 45,000 for separating water from these three 3 different binary mixtures[156]. This work 766 confirmed excellent molecular sieving of UiO-66. Alternatively, Miyamoto et al. reported for the 767 first time an UiO-66 membrane without defects deposited on an Al<sub>2</sub>O<sub>3</sub> substrate by an in situ 768 solvothermal method with acetic acid as a coordination modulator [163]. The UiO-66 membrane 769 was also used for recovery of methanol, ethanol and acetone in mixtures with water in 770 pervaporation tests. It also demonstrated its highly stable pervaporation performance in an 771 ethanol/water mixture with a separation factor of approximately 4.3 and a flux of 1280 g/( $m^2 \cdot h$ ) 772 because of higher driving forces of the organic compound. However, the estimated selectivity is 773 0.35, which shows it is a water-selective membrane. Clearly, reporting selectivity values would 774 show the real membrane performance. In addition to the above two applications of UiO-66 family, UiO-66-NH<sub>2</sub> tubular membranes were also synthesized to desulfurize model gasoline via 775 776 pervaporation [45]. In this research, a "zirconia-induced" strategy was developed to make UiO-777 66-NH<sub>2</sub> membranes continuous and stable. When applied in pervaporation desulfurization of n-778 octane model gasoline containing 1312 ppm thiophene under 40 °C, the UiO-66-NH<sub>2</sub> membrane 779 exhibited excellent performance with a flux of 2160  $g/(m^2 \cdot h)$  and an enrichment factor of 17.86 780 along with high reproducibility.

781 ZIF-8 also draws much attention for its chemical and thermal stability[339, 340]. The first 782 liquid separation experiments with polycrystalline ZIF-8 membranes were made by pervaporation in 2012 [170]. The molecular sieving effect of ZIF-8 membranes was evaluated by the 783 784 pervaporation separation of the two liquid mixtures of n-hexane/benzene and nhexane/mesitylene. The results revealed that there was no distinct cut-off existing for 785 786 hydrocarbons with critical diameters larger than the crystallographic pore size of ZIF-8. Recently, 787 a high-quality ZIF-8 layer with imidazole-2-carboxaldehyde (ICA) as the covalent agent was 788 deposited on polyimide (PI) substrate via a novel covalent-assisted seeding method [159]. ZIF-789 8/PI composite membrane synthesized with ICA covalent-assisted seeding method displayed 790 better pervaporation performance for dehydration of isopropanol compared to ethylenediamine-791 crosslinked PI membrane and ZIF-8/PI membrane fabricated without covalent-assisted seeding 792 method.

MOFs based on rare earth (RE) cations have gradually attracted attention because of theirs high water stability and rich functionality [341-344]. In addition, RE-based MOFs have less missing-ligand defects and lower bond energies of RE-O within RE-MOFs, it is highly likely to form continuous and defect-free polycrystalline RE-MOF membranes [114, 345-349]. Given the advantages of the above RE-MOFs, Zhao and colleagues used a series of RE-metal ions (RE =
Sm, Y, Dy, Er, and Gd) to react with 2,5-dihydroxy-1,4-benzenedicarboxylate (DOBDC) for the fabrication of corresponding RE-based MOF membranes in the presence of 2-fluorobenzoic acid (2-FBA) as the modulator and structure directing agent [113]. The defect-free polycrystalline REbased MOF membranes constructed on alumina hollow fibres by secondary method were used for the dehydration of 5 wt.% water/ethanol mixture at 49.85 °C, showing outstanding performance of a total flux of 786.4 ± 33.7 g/(m<sup>2</sup>·h) and a 99.8 ± 0.2 wt.% water concentration in the permeate with a high separation factor of ca. 9500.

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# 3.3. Performance of MOF-based mixed matrix membranes utilized in pervaporation

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While research on pure MOF-based membranes mainly focuses on the advances in the synthesis methods (as described in section 3.2), research on MOF-based mixed matrix membranes (MMM) is more oriented towards the application and the evaluation of the separation performance of selected membranes. For this reason, section 3.3 includes the application of MOF-based MMM in the typical fields covered by pervaporation: (1) dehydration of organic solvents; (2) the removal or recovery of organic compounds from aqueous solutions; (3) organicorganic mixtures separation.

816

## 817 **3.3.1. Dehydration of organic solvents**

818 Pervaporation MMM with MOFs crystals facilitate the dehydration of organic solvents (e.g., ethanol, isopropanol, acetic acid, etc.) relying on the molecular sieving effect achieved by defined 819 820 architecture of MOF aperture. Shi et al. was one of the first to disperse the ZIF-8 nano-particles 821 into the polybenzimidazole (PBI) matrix for the preparation of MMMs for the alcohol dehydration 822 [201]. We can see from Table 1 and Table 2, ZIF-8 have the appropriate window size to separate water and alcohols. When ZIF-8-based MMMs with 33.7 wt.% loading were utilized for the 823 dehydration of n-butanol and isopropanol, the water permeability increased four times without 824 considerable decrease in selectivity. The same group investigated the sorption, diffusion, dry- and 825 826 wet-state characteristics of PBI and PBI/ZIF-8 nano-composite membranes by positron 827 annihilation lifetime spectroscopy (PALS). It confirmed that the high permeability of PBI/ZIF-8 membrane in the pervaporation dehydration of alcohols was attributed to the high relative 828 829 fractional free volume generated by the large cavities of the filler [202]. ZIF-7 microparticles with size of 1-2 µm were successfully added to chitosan (CS) polymer for the separation of water/ 830

831 ethanol mixtures in pervaporation setup [204]. The separation efficiency of MMMs with 5 wt.% 832 ZIF-7 loading displayed 19 times higher than that of pure CS membranes and a lower flux due to 833 the rigidified cross-linking between the zinc atoms within ZIF-7 and -NH<sub>2</sub> of the CS polymer. Considering the high hydrophilicity of HKUST-1, Coronas and co-workers prepared polyimide 834 835 based MMMs for the pervaporation separation of water/ethanol mixtures by incorporation of 20-836 40 wt.% loading HKUST-1 particles into commercial polyimide Matrimid® 5218 [215]. The water flux increased from 240 g/(m<sup>2</sup>·h) of bare polyimide membrane to 430 g/(m<sup>2</sup>·h) of 40 wt.% 837  $Cu_3(BTC)_2$  based MMM, while the separation factor (>200) did not change significantly. 838

In acetic acid dehydration application, the permeability and selectivity of the NH<sub>2</sub>-MIL-125(Ti)/ 839 840 sodium alginate MMMs with the loading of 6 wt.% NH<sub>2</sub>-MIL-125(Ti) nanoparticles increased 83.80% 841 and 425.93%, respectively, compared to the pristine sodium alginate membrane [208]. Wang et al. employed an acid stable Zr-MOF NH<sub>2</sub>-UiO-66 as the filler to prepare NH<sub>2</sub>-UiO-66/PEI 842 (poly(ethyleneimine)) MMMs deposited on NaA zeolite tubular substrate through dip-coating 843 844 method for the pervaporation separation of acetic acid/water mixtures [205]. The resulting composite membranes displayed comparable performance with the separation factor of 356 and 845 846 the flux of 212 g/( $m^2 \cdot h$ ) in the dehydration of 95 wt.% acetic acid solution at 60 °C. In another 847 report for dehydration of 90 wt.% ethanol solution at 25 °C, Vinu et al. found that 2.5 wt.% defects-848 rich [AI(OH)(MBA)] (CYCU-7, MBA = diphenylmethane-4,4'-dicarboxylate anion) @ chitosan 849 MMMs showed higher flux of 665 g/( $m^2 \cdot h$ ) and 2.5 wt.% [Al(OH)(SBA)] (CAU-11, SBA = 4,4'-850 sulfonyldibenzoate anion) @chitosan MMMs with higher crystallinity exhibited a higher separation 851 factor of 1139 [74].

Although the above studies have successfully introduced MOF crystals into the polymer matrix, 852 853 the fabrication of defect-free MMMs is still very challenging [223, 350]. A drying-free and water-854 based mixing process has been developed to prepare MMMs based on poly (vinyl alcohol) (PVA) polymer with up to 39 wt.% loading ZIF-8 particles [351]. The high-quality PVA/ZIF-8 MMM (39 855 856 wt.%) made via this approach showed no particle agglomeration or phase separation resulted in 857 three times increase in permeability and nearly nine times increase in separation factor compared to pristine PVA for ethanol pervaporation dehydration. Beyond the method described above, a 858 859 thin and uniform polydopamine (PD) layer was coated on the surface of the filler, a sulfonic acid-860 functionalized SO<sub>3</sub>H-MIL-101-Cr, to form MMMs relied on a hydrophilic polymer poly(vinyl alcohol) 861 (PVA) [213]. The amine groups in PD formed hydrogen bonds with the hydroxyl in PVA polymer, 862 enhancing the compatibility between the filler and polymer matrix. The obtained SO<sub>3</sub>H-MIL-101-Cr@PD-PVA MMM with the loading of 30 wt.% was then utilized for the dehydration of 90 wt.% 863

ethylene glycol (EG) water solution at 69,85 °C. This process displayed a stable performance with water permeability of  $3.26 \times 10^{15}$  Barrer, water flux of 540 g/(m<sup>2</sup>·h), selectivity of 68.1, and separation factor of 2864.

867 Polyethylene glycol (PEG) with different chain lengths (480 Da and 5 kDa) was grafted on the 868 surface of ZIF-8 nanoparticles applying the so-called Graftfast reaction to enhance its 869 hydrophilicity [210]. A series of colloidal composite solutions of PEG-modified ZIF-8 nanoparticles 870 by mixing PEG-grafted ZIF-8 (i.e., PEG-g-ZIF-8) nanoparticles with different amounts of 871 polyethylene (PVA) exhibited their long-term colloidal stability. The very highly stable colloidal solutions of PEG-g-ZIF-8/PVA with PEG chains of 5 kDa were used to cast dense and supported 872 873 MMMs without interfacial defects. In the dehydration of isopropanol (IPA) by pervaporation, the 874 permeation flux of the supported MMM (i.e., 91  $q/(m^2 \cdot h)$ ) was increased by 10 times when 875 compared to that of the pure PVA membrane, and the separation factor was approx. 7300. More 876 recently, a covalent cross-linking strategy was deployed to enhance the interfacial compatibility 877 between UiO-66 particles and polydimethylsiloxane (PDMS) to achieve fine dispersion of MOF 878 particles at high loading in the polymer matrix [218]. In this method, (TMS) was first used to modify 879 UiO-66-NH<sub>2</sub>, generating UiO-66-TMS and then UiO-66-TMS with the content of up to 50 wt.% 880 were incorporated into the PDMS. Prepared UiO-66-TMS/PDMS MMMs formed robust 881 membranes with enhanced mechanical stability when compared to the pristine UiO-66-NH<sub>2</sub> MMMs, due to the covalent reaction between the siloxane groups on UiO-66-TMS and Si hydroxy 882 883 groups from PDMS, and the flux of UiO-66-TMS/PDMS MMMs (50 wt.% loading) was 3.6 times improved with the selectivity retained compared PDMS pristine membranes in the dehydration of 884 885 aqueous ethanol solution.

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### **3.3.2. Removal or recovery of organic compounds**

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889 MOFs can be used not only to dehydrate organic solutions, but also to remove or recover organics 890 from aqueous solutions. In the dehydration of organic solvents using MOF-based membranes, 891 the molecular sieve effect of MOFs is used for the exclusion of certain components of a liquid 892 mixture based upon size/shape. In addition to this property, MOFs show stronger adsorption affinities to certain compound in liquid mixtures. By exploiting the difference in adsorption affinities, 893 894 MOFs can be applied to remove or recover organics from aqueous solutions. Up to now, the application of MOF-based MMMs for the removal or recovery of dilute organic compounds is 895 896 mainly about alcohol separation from aqueous solutions or from fermentation broths.

897 An organophilic pervaporation MMMs containing ZIF-8 particles were first applied for the 898 preferential permeation of bio-alcohols from fermentation broths in 2011 [320]. ZIF-8 899 nanoparticles, incorporated in silicone rubber (polymethylphenylsiloxane, PMPS), formed preferential pathways for adsorption of bio-alcohols due to their superhydrophobicity, in which, to 900 a large extent determined the overall selectivity of organophilic pervaporation. Another 901 hydrophobic ZIF-71 was introduced into polyether-block-amides (PEBA) mixed matrix 902 903 membranes for recovery of bio-butanol solution [229]. Since ZIF-8 and ZIF-71 have ideal 904 hydrophobicity, they have been found to be very suitable for separating butanol/propanol from 905 water.

906 Contrary to butanol, ethanol has similar physical and chemical properties as water, making it difficult to separate from ethanol/water mixtures by ZIF-8 and ZIF-71 [227, 352]. Zhang et al. 907 908 dispersed MIL-53 into PDMS by the sonication-enhanced dip-coating method relying on the 909 hydrophobic surface and ethanol-affinity channels of MIL-53 to form hybrid membranes for 910 pervaporation recovery of ethanol [227]. The hybrid membrane with 40 wt.% MIL-53 showed a 911 significant increase from 1667 to 5467  $q/(m^2 \cdot h)$  in the permeate flux while maintaining the 912 separation factor of 11.1 in comparison to pristine PDMS membrane. The estimated selectivity of 913 this hybrid membrane is 0.99, thus it is not selective to ethanol.

914 For MOF-based MMMs in pervaporation, the separation performance of the membrane is not only 915 affected by its constituent materials, but also by its structure and the membrane surface properties. 916 The more hydrophobic the membrane surface, the greater the repulsive force for water molecules 917 and thus more water molecules are retained during the recovery of organic compounds [225]. 918 Inspired by the superhydrophobic surface of the lotus leaf, a ZIF-8/PDMS nanohybrid membrane 919 was successfully designed and prepared by the deposition of self-assembled monolayers (SAMs) 920 formed from semi-fluorinated (SF) molecules with CF<sub>3</sub>- terminal groups onto the surface of the 921 ZIF-8/PDMS membrane. The as-prepared MMM exhibited 25.73% increase in the flux and 532.84% in separation factor in contrast with PDMS membrane in the pervaporation recovery of bio-alcohol 922 923 from 3 wt.% n-butanol solution at 60 °C [225]. In organic solvents dehydration, the agglomeration 924 of MOF particles in the polymer matrix limits the dehydration performance of the membrane. 925 Similarly, the aggregation of MOF particles in the MMMs limits further improvement of alcohol 926 separation performance. For the defects elimination, polysulfone (PS) support membrane was 927 repeatedly immersed in a dilute ZIF-8/PDMS solution followed by in a concentrated PDMS 928 solution to form a homogeneous, nano-disperse ZIF-8/PDMS membrane [233]. In this work, the 929 nascent ZIF-8 suspension was directly distributed into a PDMS solution without drying for the

930 improvement of ZIF-8 nanoscale dispersion and thus avoiding aggregation and redispersion of 931 ZIF-8 particles using ZIF-8 powders. In contrast to the powder-dispersed ZIF-8/PDMS hybrid 932 membrane, the suspension-dispersed ZIF-8/PDMS membrane performed better in the separation 933 of 5.0 wt.% aqueous n-butanol solution at 80 °C with a separation factor of 52.81 and flux of 934 2800.5 g/(m<sup>2</sup>·h). Free-standing PDMS MMMs with 40 wt.% ZIF-71 loading were prepared by 935 condensation-curing and had an a maximum ethanol/water selectivity of 0.81±0.04 (separation 936 factor of 12.5±0.3 for 2 wt.% ethanol feed) and maximum 1-butnaol/water selectivity of 5.64±0.15 (separation factor of 69.9±1.8 for 2 wt.% 1-butanol feed) [228]. The size of ZIF-71 particles played 937 938 an important role in ZIF-71/PDMS composite membrane performance for pervaporation removal 939 of ethanol and 1-butanol from water [226]. The ethanol permeability and the 1-butanol permeability of the membranes with micron-sized ZIF-71 particles exhibited 1.83 times and 1.32 940 941 times increase, respectively, compared to the membranes with smaller particles. Meanwhile, the ethanol/water selectivity and the 1-butanol/water selectivity also increased from  $0.67 \pm 0.07$  to 942 943  $0.82 \pm 0.10$  and from  $4.03 \pm 0.20$  to  $5.09 \pm 0.94$ , respectively as the particle sizes increased. Mao and co-workers inspired by the interfacial polymerization [327] implemented a method to fabricate 944 in-situ ZIF-8-based mixed matrix layer with ca. 1 µm thickness without particle agglomeration on 945 946 a support membrane [37]. PDMS was utilized as polymer matrix, which adjusted the nucleation 947 of ZIF-8 precursors to in-situ form ZIF-8 nanocrystals. During the recovery of ethanol from 948 aqueous solution via pervaporation, the resulting MMMs showed simultaneous enhancement 949 both of permeation flux and separation factor, revealing the desired reverse trade-off effect. When deployed in the separation of 5.0 wt.% ethanol solutions at 40 °C, a comparable separation factor 950 951 of 12.1 and a relatively high permeation flux of 1778 g/(m<sup>2</sup>·h) were achieved. The estimated 952 selectivity of MMMs is 1.07, thus it is selective to ethanol. Two-dimensional zeolitic imidazolate framework-L (ZIF-L) nanosheets were introduced into PDMS matrix to explore their unique leaf-953 954 like morphology and brick-and-mortar architecture to prepare MMMs for the pervaporation 955 separation of alcohols (ethanol, n-propanol or n-butanol) from aqueous streams [235]. Obtained 956 MMMs showed outstanding pervaporation separation performance and mechanical properties in 957 the presence of ZIF-L nanosheets within PDMS matrix. The separation factor and the permeation flux attained to 57.6 and 402 g/(m<sup>2</sup>·h), respectively, when the resultant membrane was deployed 958 959 in separating 1.0 wt.% n-butanol aqueous solution at 40 °C.

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### 962 **3.3.3. Separation of organic-organic mixtures**

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964 MOF-based pervaporation membranes are also applied in refining and petrochemical industries 965 for the separation of organic-organic mixtures, such as methyl tert-butyl ether (MTBE)/methanol 966 (MeOH), toluene/n-heptane, desulfurization of gasoline (removing thiophene from alkane 967 solutions), etc., [21, 245, 249, 353]. Although some MOF-based nano-hybrid membranes have 968 been prepared and used in the pervaporation, the relevant research reports on hybrid membranes 969 using MOFs in pervaporation separation of organic-organic mixtures are scarce. To the best of 970 our knowledge, the first study on the pervaporation separation of organic-organic mixtures using 971 MOF-based MMMs was reported by Yu and colleagues [248]. Submicron MIL-101 (Cr) particles were introduced into PDMS for the preparation of MOF-based hybrid layers deposited on 972 973 polyvinylidene fluoride (PVDF) supports.

974 Separation performance of composite polymer membranes from PDMS can be further improved 975 by incorporation of MIL-101 particles. When the hybrid membrane with a weight ratio of MIL-101 976 to PDMS of 6% was used in desulfurization of model gasoline with n-octane as the bulk of feed 977 and thiophene as the sulphur-containing impurity, the optimal performance with a flux of 5200 978  $g/(m^2 \cdot h)$  and an enrichment factor of 5.6 was achieved. Alternative strategy to improve the 979 pervaporative desulfurization of model gasoline was developed by the incorporation of submicron-980 sized CuBTC particles into PDMS matrix to prepare MMMs. The hybrid membrane with the weight 981 ratio of normal CuBTC to PDMS of 8% showed the optimal performance, and the permeation flux 982 and enrichment factor attained to 194200 g µm/(m<sup>2</sup>·h) (100% higher than PDMS control 983 membrane) and 5.2 (75% higher than PDMS control membrane), respectively [247]. In these two 984 studies, the non-selective voids at the interface between PDMS and the fillers were reduced by 985 using the submicrometer fillers. Their permeability was also enhanced due to the channels of the 986 fillers distributed into PDMS as well as the additional free volume at the interface between polymer 987 matrix and the fillers formed by the interruption of chain packing of PDMS.

The MOF-based hybrid membrane for the pervaporation separation of aromatic/aliphatic mixtures was initially reported in 2015[249]. Poly-(vinyl alcohol) (PVA) blend membranes were prepared with the nano-sized Cu<sub>3</sub>(BTC)<sub>2</sub> (BTC=benzene-1,3,5-tricarboxylate) particles dispersed uniformly in PVA solution. Subsequently, the Cu<sub>3</sub>(BTC)<sub>2</sub>/PVA solution was assembled onto silane agent modified tubular ceramic substrate to form Cu<sub>3</sub>(BTC)<sub>2</sub>/PVA hybrid membranes by a pressuredriven assembly method. The permeation flux and separation factor of the resulting hybrid membranes were simultaneously increased in contrast with pure PVA membrane, when

995 separating toluene/n-heptane (50/50 wt.%) mixture at 40 °C. The improved separation 996 performance (the permeation flux of 133  $q/(m^2 \cdot h)$  and the separation factor of 17.9) of the hybrid 997 membranes was ascribed to the enhanced affinity between incorporated Cu<sub>3</sub>(BTC)<sub>2</sub> particles and 998 toluene. Subsequently, similar method was used to fabricate Co(II)-formate (Co(HCOO)<sub>2</sub>/PEBA 999 (poly(ether-block-amide)) hybrid membranes on the outer surface of tubular ceramic substrate for separating toluene/n-heptane mixtures [246]. The hybrid membrane exhibited robust 1000 pervaporation performance with the permeate flux of 771  $g/(m^2 \cdot h)$  and separation factor of 5.1 for 1001 1002 the separation of 10 wt.% toluene/n-heptane mixtures at 40 °C owing to the enhanced affinity 1003 between the fillers incorporated in hybrid membranes and toluene.

1004 Beside conventional ones, MOFs with various metal atoms, such as Ni, Cu (II), Ag, etc. were 1005 successfully implemented in MMMs for pervaporation applications. Han et al. fabricated CPO-27-1006 Ni MOF filled PDMS MMMs to improve the performance of the gasoline desulfurization via 1007 pervaporation [250]. The MMM with 6.0 wt.% loading had the optimal pervaporation performance 1008 with a flux of  $5.920 \text{ g/(m^2 \cdot h)}$  and an enrichment factor of 4.05, increased by 68.7% and 23.7%compared with pristine PDMS membrane respectively. Song et al. studied the PDMS containing 1009 1010 Cu(II) loaded UiO-67-bpydc (bpydc refers to 2,2'-bipyridine-5,5'-dicarboxylic acid) facilitated 1011 transport for removing thiophene from model gasoline [46]. In comparison to pristine PDMS 1012 membrane, the hybrid membrane showed that the flux of 8.100  $g/(m^2 \cdot h)$  and enrichment factor 1013 of 4.2 increased by 74% and 10%, respectively, when the mass ratio of UiO-67b to PDMS was 1014 4% and the molar ratio of Cu(II) to bpydc ligand was 38.6%. Post-synthetic MIL-53(AI)-1015 SO<sub>3</sub>H/sulfonated polyarylethersulfone with cardo (SPES-C) membranes with 15 wt% loading were used for the pervaporation separation of methanol (15 wt.%)/methyl tert-butyl ether (MTBE) 1016 mixture at 40 °C, and a permeation flux of 368  $q/(m^2 \cdot h)$  and a separation factor of 1990 were 1017 1018 achieved [251]. The reason is that the agglomeration of nano-scale MIL-53(AI)-SO<sub>3</sub>H particles 1019 was inhibited by the introduced sulfonic groups that preferentially adsorbed methanol over MTBE 1020 and, thus, no obvious interfacial defects were observed. This result contributed to considerable improvement in the membrane hydrophilicity, swelling behaviour as well as free volume 1021 1022 parameters. Recently, a kind of hetero-structured laminates by in-situ growth of aminefunctionalized zirconium-based metal-organic frameworks (UiO) on graphene oxide (GO) 1023 1024 nanosheets, UGO were constructed and then utilized as supports for immobilization of Ag<sup>+</sup> by 1025 Zhang and co-workers [354]. The resulting Ag<sup>+</sup>@UGO were introduced into poly (ether-block-1026 amide) (PEBA) matrix for the preparation of hybrid membranes on porous polysulfone (PSf) 1027 ultrafiltration membranes. In pervaporation desulfurization, the prepared hybrid membrane

showed good permeation characteristics for thiophene, the permeation flux and the enrichment factor attained to 23,400 g/( $m^2 \cdot h$ ) and 7.12, respectively.

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# 3.4 Performance analysis of pervaporation process using MOF-based membranes

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Although the newly synthesised MOFs are effectively utilized in MOF-based pervaporation membranes to improve the performance of conventional processes, not all applications of MOFbased membranes outperform the polymeric membranes. MOF-based membranes have been demonstrated to have an enhanced performance to pervaporation process in contrast with polymer membranes. Unfortunately, most of results are reported in terms of flux and separation factor instead of permeability (or permeance) and selectivity. Thus, Figures 8 to 10 and Table 5-7 are including the flux vs separation factor. Still some conclusions can be drawn:

1041 (1) Most experimental points of MOF-based membranes are located at higher positions in 1042 the figures that indicates that MOF-based membranes possess improved properties in 1043 pervaporation application. However, polymeric membranes are limited by the trade-off 1044 phenomenon as observed by Roberson [355] and Qi *et al.* [356].

1045



#### Figure 8 Separation performance of MOF-based and polymeric membranes in the dehydration of organic solutions

1046 (2) From Table 1, we see that the kinetic diameter of water molecules is much smaller than 1047 those of other organic molecules. In the pervaporation dehydration of organic solutions, MOFs 1048 are usually utilized as molecular sieve to separate efficiently mixtures by considering the kinetic 1049 diameter differences of the molecules. By choosing suitable MOFs with pore aperture diameter 1050 falling between the kinetic diameters of water molecules and organic molecules, MOF-based 1051 membranes with suitable loadings can simultaneously improve performance of both flux 1052 (permeance) and the separation factor (selectivity). Figure 8 depicts the performances of different 1053 types of membranes in pervaporation dehydration. The dehydration involves dehydrating from 1054 various aqueous organic solutions, aqueous ethanol solution, aqueous isopropanol solution and 1055 aqueous acetic acid solutions included, most membranes based on MOFs exhibited enhanced 1056 performances in contrast with polymeric membranes owing to the size or shape exclusion effects of MOFs to organic molecules. Even in MOF-based MMMs, the MOF choice is still the dominant 1057 1058 factor for pervaporation dehydration.

1059 MOFs can be used effectively to recover or remove organic compounds from aqueous (3) 1060 organic solutions, including the recovery or removal of ethanol, n-butanol and i-butanol. In this 1061 application, MOFs are usually utilized as the channels to make organic molecules pass through. 1062 However, we can see in Table 1 that the kinetic diameter of the water molecule is smaller than 1063 the kinetic diameters of all of alcohol molecules. If alcohol molecules can pass through the 1064 channels of MOFs, then water molecule can also pass through the channels of MOFs. Therefore, 1065 the molecular sieve effects of MOFs cannot be used, instead the preferential adsorption of the MOF to target molecules can be used. The MOF can serve as both a crystalline continuous 1066 1067 membrane material and the filler within MMMs with promising performance (Figure 9). In recovery 1068 or removal of organic compounds via pervaporation, inorganic membranes show greater fluxes 1069 and permeances at the cost of separation factor and selectivity compared to most polymeric 1070 membranes. That may stem from the similarity of the dipole moments between these organic 1071 components and water (as shown in Table 1) so that the difference in preferential adsorption 1072 between water and these organic molecules is minimum. However, MMMs exhibit good 1073 performances in fluxes with competitive separation factors in contrast to polymer membranes. It 1074 indicates that the polymer factor of MMMs plays an important role in the recovery or removal of 1075 organic compounds from their corresponding aqueous solutions. In addition, ZIF-8 due to the 1076 gate-opening effect and the superhydrophobicity[320] was frequently utilized as the fillers to 1077 combine with the hydrophobic polymer like PDMS for the fabrication of hydrophobic MMMs1078 utilized in the recovery or removal of organics from aqueous solutions.









MOF-based MMMs for recovery or removal of organics (i-butanol/water)
 Polymer membranes for recovery or removal of organics (i-butanol/water)

(c)













Figure 9 Separation performance of MOF-based and polymeric membranes in the recovery or removal of organic compounds

While much less represented in the separation of organic-organic mixtures via 1080 (4) pervaporation (i.e., separation MeOH, toluene and thiophene from MeOH/MTBE mixture, 1081 1082 toluene/n-heptane mixture and model gasoline solution containing thiophene), MOF-based 1083 membranes show strong potential and improved separation performance (Figure 10). The 1084 separation of MeOH/MTBE mixture using MOF-based membranes is mainly achieved by 1085 molecular sieving mechanism of the MOF and show enhanced permeances and selectivity. As 1086 for the separation of toluene/n-heptane and desulfurization of thiophene/alkane (n-heptane or n-1087 octane), preferential adsorption mechanism dominates the transport of toluene and thiophene, 1088 resulting in competitive performance with higher fluxes and moderate selectivity. UiO-66-NH<sub>2</sub> (Zr) 1089 tubular membranes (Figure 10c and f blue diamond dot) are superior in desulfurization of model gasoline, with a higher flux and the highest enrichment factor, due to a large difference in dipole 1090 1091 moments between thiophene and alkane, resulting in a preferential adsorption of thiophene over 1092 alkane. Furthermore, like other unsaturated molecules (aromatic components [357, 358], olefins 1093 [359-361], thiophene can form the chemical bond with transition metal ions (Zr, Fe, Mn, Co, Ni, 1094 Ag and Cu) through  $\pi$ -complexation reaction [45, 47, 362-364], thereby promoting further the 1095 migration of thiophene from model gasoline.



Figure 10 Separation performance of MOF-based and polymeric membranes in the separation of organic-organic mixtures

(5) Beside a great influence of membrane materials, the driving forces of components also play an important role in the pervaporation process performance. The driving force of the component is related to its vapor pressure, the component with higher vapor pressure will probably present a higher driving force for the pervaporation separation[329, 334, 365]. The driving force characteristics may not completely constant and can vary with the feed temperature and feed composition.

1102

1103 Table 5 Brief overview of MOF-based and polymeric membranes for the pervaporation dehydration of organic 1104 solutions

Polymer	MOF	Mixture	Feed compositi on (mass ratio)	T (°C)	Flux (g/m²h)	Water permeance (GPU)	Solvent permeance (GPU)	Separation factor (β <i>i/j</i> )	Selectiv ity (\u00e9water/s olvent)	Ref.
CS	ZIF-7	H <sub>2</sub> O/EtO H	10/90	25	322	N/A	N/A	2812	N/A	[204]
PVA	ZIF-8	H₂O/EtO H	20/80	25	486	N/A	N/A	4725	N/A	[351]
PVA	Zr-MOF	H₂O/EtO H	10/90	30	46.3	948.53	14.68	46.3	64.63	[207]
CS	AI-MOF	H <sub>2</sub> O/EtO	10/90	25	458	N/A	N/A	2741	N/A	[74]
CS	MOF-801	H <sub>2</sub> O/EtO	10/90	70	1937	6521.20	2.47	2156	2641.1	[211]
SA	ZIF-L	H <sub>2</sub> O/EtO	10/90	76	1218	3164.02	1.43	1840	2205.1	[217]
	ZIF-8				879	2264.38	2.9	678	812.48	
SA	EuBTB	H₂O/EtO H	10/90	76	1996	5112.48	3.72	1160	1374.6 4	[81]
CS	DUT-5	H₂O/EtO	10/90	25	378	N/A	N/A	3429	N/A	[216]
N/A	CAU-10-	H <sub>2</sub> O/EtO	10/90	40	397	5391.77	12.52	324	430.61	[158]
	Н	Н		65	493	1914.48	10.63	148	180.09	
N/A	Ni₂(I- asp)₂bipy	H <sub>2</sub> O/EtO H	50/50	30	28100	373279.57	1169.20	73.6	319.26	[162]
N/A	Sm-	H <sub>2</sub> O/EtO	5/95	49.8 5	786.4	N/A	N/A	> 9481	N/A	[113]
N/A	SIM-1	H₂O/EtO H	55.82/44. 18	25	460	10493.15	0.1589	>10000	>66036 24	[160]
PASAs	N/A	H₂O/EtO H	10/90	20	11.43	519.92	1.45	230.49	357.88	[366]
PAA and	N/A	H₂O/EtO H	5/95	40	140	33335.07	2.2952	1207	1453.0 8	[367]
a-PVA	N/A	H₂O/EtO H	15/85	60	263.89	1099.16	8.90	79.4	123.55	[368]
PI	N/A	H <sub>2</sub> O/EtO	10/90	42	240	N/A	N/A	260	N/A	[200]
PAA and PVA	N/A	H <sub>2</sub> O/EtO H	5/95	50	260	2902.97	47.08	50	61.66	[369]

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SC and PVA	N/A	H₂O/EtO H	10/90	60	~120 ~100 ~70	N/A N/A N/A	N/A N/A N/A	~90 ~105 ~190	N/A N/A N/A	[370]
MAC	N/A	H <sub>2</sub> O/EtO	10/90	60	300	1563.99	1.95	634	801.62	[371]
SA	N/A	H <sub>2</sub> O/EtO	5/95	50	95	1312.11	5.36	202	244.68	[372]
AA	N/A	H <sub>2</sub> O/EtO	5/95	50	172	2137.44	19.69	90	108.53	[372]
PVA	N/A	H <sub>2</sub> O/EtO	10/90	30	40	802.53	14.02	41	57.23	[207]
HVAcN-4	N/A	H <sub>2</sub> O/EtO	10/90	25	420	8280.84	429.02	13.5	19.30	[373]
PAA-g- PP	N/A	H <sub>2</sub> O/EtO	30/70	24	~200	~4492.65	~124.16	~11	~36.18	[374]
PI (P84)	ZIF-90	H <sub>2</sub> O/IPA	15/85	60	109	345.74	0.05	5668	6588.9 0	[203]
CS	ZIF-8	H <sub>2</sub> O/IPA	10/90	30	410	N/A	N/A	723	N/A	[209]
PVA	ZIF-8	H <sub>2</sub> O/IPA	12/88	25	91	2158.68	0.24	7326	8872.6 1	[210]
PBI	ZIF-8	H <sub>2</sub> O/IPA	15/85	60	103	N/A	N/A	1686	N/A	[201]
PVA	ZIF-8	H <sub>2</sub> O/IPA	10/90	30	868	19922.35	108.05	132	184.38	[221]
PVA	ZIF-8	H <sub>2</sub> O/IPA	10/90	30	952	21173.72	167.24	91	126.61	[221]
N/A	Sm-	H <sub>2</sub> O/IPA	5/95	24.8 5	305.5	N/A	N/A	1881	N/A	[113]
N/A	UiO-66	H <sub>2</sub> O/IPA	10/90	70	4620	9567.98	32.46	689	294.73	[156]
PEtI, PAA and	N/A	H <sub>2</sub> O/IPA	9/91	70	1800	4721.26	10.20	>495	>462.9 5	[375]
PI (P84)	N/A	H <sub>2</sub> O/IPA	15/85	60	883.5	2884.642	0.2280	10585	12653. 29	[376]
SA and	N/A	H <sub>2</sub> O/IPA	10/90	30	12.4	460.61	0.60	356	772.81	[377]
PTFE and PA	N/A	H <sub>2</sub> O/IPA	30/70	70	1910	3309.16	5.61	290	589.86	[378]
PVA and	N/A	H <sub>2</sub> O/IPA	10/90	30	29.2	1113.88	0.28	1791	3918.2 1	[379]
PDD-co-	N/A	H <sub>2</sub> O/IPA	1.3/98.7	22	50	N/A	N/A	500	N/A	[380]
PDD-co-	N/A	H <sub>2</sub> O/IPA	12.4/87.6	70	111	272.18	2.70	80	100.81	[380]
SA	N/A	H <sub>2</sub> O/IPA	10/90	30	67	1205.71	1.78	653	679.99	[381]
PVA	N/A	H <sub>2</sub> O/IPA	10/90	30	95	1551.65	19.35	77	80.17	[381]
CS	N/A	H <sub>2</sub> O/IPA	10/90	30	74	1325.58	2.61	488	508.17	[382]
PAI	N/A	H <sub>2</sub> O/IPA	15/85	60	6.8	22.16	0.006	2973	3553.8 4	[383]
PEI	N/A	H <sub>2</sub> O/IPA	15/85	60	7	22.63	0.03	585	699.21	[383]
s-PVA	N/A	H <sub>2</sub> O/IPA	10/90	40	35	508.71	0.61	3452	839.22	[384]
PEtl	NH2-UiO- 66	H <sub>2</sub> O/ acetic	5/95	60	212	1853.32	18.96	356	97.77	[205]
SA	NH <sub>2</sub> -MIL- 125(Ti)	H <sub>2</sub> O/ acetic	10/90	30	196.7	5166.40	60.40	328.1	85.54	[208]
SA, PVA and PEG	N/A	ACIO H <sub>2</sub> O/ acetic acid	10/90	30	23.9	1613.88	53.90	40	29.94	[385]

SA, PVA and PEG	N/A	H <sub>2</sub> O/ acetic acid	10/90	30	425	2190.05	167.71	21	13.06	[385]
SA, PVA and PEG	N/A	H <sub>2</sub> O/ acetic acid	10/90	30	739	2473.13	503.18	10.6	4.91	[385]
ALG-c- HDM	N/A	H <sub>2</sub> O/ acetic acid	15/85	70	262	728.48	12.16	161	59.92	[386]
PPSU	N/A	H <sub>2</sub> O/ acetic acid	5/95	50	280	1874.23	479.88	14.9	3.91	[387]
PVA and SA	N/A	H <sub>2</sub> O/ acetic acid	10/90	33	49	754.65	136.85	21.5	5.51	[388]
PEK-C and PVA	N/A	H₂O/ acetic acid	10/90	50	59.3	4097.36	221.82	492	18.47	[389]
PANI /SA	N/A	H <sub>2</sub> O/ acetic acid	2/98	30	40	N/A	N/A	1372	N/A	[390]
PANI/SA	N/A	H <sub>2</sub> O/ acetic acid	2/98	30	70	N/A	N/A	1102	N/A	[390]
PVA-m- MA	N/A	H <sub>2</sub> O/ acetic acid	10/90	40	48	714.75	3.87	670	184.47	[391]
SA and PP	N/A	H <sub>2</sub> O/ acetic acid	20/80	50	653	4041.12	17.08	631	236.59	[392]

1106Table 6 Brief overview of MOF-based and polymeric membranes for the pervaporation recovery or removal organic1107molecules from three aqueous solutions

Polymer	MOF	Mixture	Feed compos ition(m ass ratio)	Т (°С)	Flux (g/m²h)	Solvent permeance (GPU)	Water permeance (GPU)	Separation factor ( $\beta_{i/j}$ )	Selectiv ity (ɑ <sub>solvent/</sub> <sub>water</sub> )	Ref.
PMPS	ZIF-8	i- BuOH/H₂O	3/97	80	8600	5765.00	~4056.42	34.9	~1.45	[320]
PMPS	ZIF-8	i- BuOH/H₂O	1/99	80	6400	6454.00	~4447.59	40.1	~1.48	[320]
PMPS	ZIF-7	i- BuOH/H₂O	3/97	80	6100	3961.00	~2974.56	32.7	~1.35	[320]
PUR	N/A	i- BuOH/H₂O	1/99	50	80	N/A	N/A	9.2	N/A	[393]
PEBA	N/A	i- BuOH/H <sub>2</sub> O	1/99	50	240	N/A	N/A	23.2	N/A	[393]
PDMS	N/A	i- BuOH/H <sub>2</sub> O	1/99	50	70	N/A	N/A	40	N/A	[393]
PERVAP 4060	N/A	i- BuOH/H2O	1/99	40	724	1870.08	4095.52	14.9	0.46	[394]
PDMS	N/A	i- BuOH/H2O	1/99	40	542	2147.38	2825.38	24.5	0.76	[394]
PDMS	ZIF-8	n- BuOH/H2O	3/97	60	1459	5763.20	1215.63	58.4	4.74	[225]
PDMS and PTES	ZIF-8	n- BuOH/H <sub>2</sub> O	3/97	60	1339	5976.76	863.83	84.8	6.92	[225]

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PDMS and	ZIF-8	n- BuOH/H₂O	1/99	60	1041	8807.35	1235.83	95.2	7.13	[225]
PEBA	ZIF-7- NH₂	n- BuOH/H₂O	5/95	40	2320.26	19355.00	7698.75	18.8	2.51	[395]
PDMS	ZIF-8	n- BuOH/H2O	1/99	80	1097	2338.01	645.43	65.9	3.62	[233]
PDMS	ZIF-8	n- BuOH/H2O	5/95	80	2800.5	2614.22	731.68	52.81	3.57	[233]
PDMS	ZIF-8	n- BuOH/H₂O	5/95	50	1879.9	10137.86	2216.39	42.5	4.57	[233]
PDMS	ZIF-8	n- BuOH/H2O	5/95	40	1358.8	14293.93	3121.53	34.2	4.58	[233]
PDMS	ZIF-8	n- BuOH/H2O	1/99	80	4846.2	11708.26	2603.12	81.6	4.50	[396]
PDMS	ZIF-L	n- BuOH/H2O	1/99	40	402	12534.09	1646.80	57.7	7.61	[235]
PDMS	ZIF-8	n- BuOH/H2O	1.5/98. 5	55	2046.3	12844.70	3672.45	42.4	3.50	[237]
PDMS	ZIF-8	n- BuOH/H2O	5/95	60	1743	4254.88	1593.13	30.0	2.67	[397]
PDMS	ZIF-8	n- BuOH/HaO	1.5/98. 5	55	1039.04	7615.71	1652.41	56	4.61	[398]
PDMS	N/A	n- BuOH/HaO	2/98	37	132	2399.59	599.19	32	4.00	[399]
PTMSP	N/A	n-	1/99	25	60	11243.38	618.66	52	18.17	[400]
PTMSP	N/A	n- BuOH/HaO	1/99	70	999	3923.27	874.58	70	4.49	[400]
PTMSP	N/A	n- BuOH/HaO	6/94	25	436	28574.68	1371.44	61	20.84	[400]
PTMSP	N/A	n- BuOH/HaO	6/94	70	2097	2905.08	874.03	41	3.32	[400]
PIM- 1and PDMS	N/A	n- BuOH/H2O	1/99	60	1425.3	N/A	N/A	30.7	N/A	[401]
PDMS	N/A	n- BuOU/UaO	1/99	60	628.4	N/A	N/A	22.9	N/A	[401]
PDMS	N/A	n- BuOH/H2O	~1.5/9	37	158.2	N/A	N/A	17.3	N/A	[402]
PDMS	N/A	n- BuOH/HaO	1.5/98. 5	55	670.18	4374.63	1194.80	43.72	3.66	[403]
PDMS	N/A	n- BuOH/HaO	-1/99	30	52.8	2477.12-	408.60-	42	6.06-	[404]
PDMS	N/A	n- BuOH/HaO	1/99	40	300	4383.24	1495.29	26.8	2.93	[405]
PTFE	N/A	n- BuOH/HaO	1.25/	50	805	N/A	N/A	~9.9	N/A	[406]
PUR	N/A	n- BuOH/HaO	1/99	50	88	N/A	N/A	9	N/A	[393]
PEBA	N/A	n- BuOH/HaO	5/95	23	65.3	1718.55	964.52	8.2	1.78	[407]
PDMS	N/A	n- BuOH/HaO	1/99	70	2210	6655.78	2264.68	46	2.94	[408]
PDMS	MIL-53	EtOH/H <sub>2</sub> O	5/95	70	5467	5174.64	5220.29	11.1	0.99	[227]
PDMS	ZIF-8	EtOH/H <sub>2</sub> O	5/95	40	1778	7645.17	7145.11	12.1	1.07	[37]
PEBA	MAF-6	EtOH/H <sub>2</sub> O	5/95	60	4446	4063.75	8212.53	5.6	0.49	[232]
PDMS	ZIF-L	EtOH/H <sub>2</sub> O	5/95	40	575	2524.16	2280.85	12.5	1.11	[235]
PDMS	ZIF-L	EtOH/H <sub>2</sub> O	5/95	40	567	2716.25	2119.00	14.4	1.28	[235]
PDMS	ZIF-91	EtOH/H <sub>2</sub> O	5/95	55	846	1947.09	1384.93	15.8	1.41	[236]

PDMS	ZIF-8	EtOH/H <sub>2</sub> O	5/95	60	847	1084.85	1372.38	8.9	0.79	[238]
PDMS	ZIF-8	EtOH/H <sub>2</sub> O	5/95	60	1229	1691.49	1922.14	9.9	0.88	[397]
PDMS	ZIF-8	EtOH/H <sub>2</sub> O	~4/96	30	1148.24	N/A	N/A	7.29	N/A	[239]
PDMS	ZIF-67	EtOH/H <sub>2</sub> O	6/94	40	2780	N/A	N/A	15.4	N/A	[128]
PDMS	MAF-6	EtOH/H <sub>2</sub> O	5/95	40	1200	5867.15	4417.36	14.9	1.33	[243]
N/A	UiO-66	EtOH/H <sub>2</sub> O	10/90	50	1490	N/A	N/A	4.9	N/A	[163]
N/A	UiO-66	EtOH/H <sub>2</sub> O	10/90	70	3150	N/A	N/A	4.8	N/A	[163]
N/A	ZIF-71	EtOH/H <sub>2</sub> O	5/95	25	2601	17619.83	29951.78	6.88	0.59	[155]
N/A	ZIF-71	EtOH/H <sub>2</sub> O	5/95	25	322.18	1980.52	3833.32	6.07	0.52	[164]
PDMS	N/A	EtOH/H <sub>2</sub> O	5/95	70	1667	1210.05	1808.32	7.5	0.67	[227]
ddPDMS	N/A	EtOH/H <sub>2</sub> O	5/95	60	3275	3718.09	5588.00	7.5	0.67	[409]
PDMS	N/A	EtOH/H <sub>2</sub> O	10/90	40	130	364.76	433.83	8.6	0.84	[410]
and PUU	ΝΙ/Δ		10/00	40	560	NI/A	NI/A	10.6	ΝΙ/Δ	[/11]
			10/90	40 60	160	132.04	242 74	5.5	0.54	[+11] [/12]
and PS			10/30	00	100	152.04	242.74	0.0	0.54	[412]
PDMS	N/A	EtOH/H <sub>2</sub> O	5/95	40	1300	4386.44	5896.50	8.5	0.74	[413]
PDMS	N/A	EtOH/H <sub>2</sub> O	5/95	55	496	444.17	1224.56	4.1	0.36	[236]
PDMS	N/A	EtOH/H <sub>2</sub> O	5/95	40	500.7	1636.99	2242.67	8.3	0.73	[414]
PPMS	N/A	EtOH/H <sub>2</sub> O	5/95	40	450.1	1603.59	1937.51	9.4	0.83	[414]
PDMS	N/A	EtOH/H <sub>2</sub> O	8/92	50	265	398.29	659.87	6.4	0.60	[415]
and PSU PDMS	N/A	EtOH/H <sub>2</sub> O	4.7/95.	31	420	1618.64	4468.46	4.78	0.36	[416]
DDMC	ΝΙ/Δ		3	25	150	NI/A	NI/A	10.0	ΝΙ/Δ	[447]
PDIVIS	IN/A		4/90	25 40	100	N/A	N/A	10.0	N/A	[417]
PDIVIS	IN/A		10/90 E/05	40	201	502.57	107.03	4.0	0.43	[410] [410]
PDIVIS	IN/A		5/95 1/00	40	202	1202 44	1203.00	0.0	0.00	[410] [410]
PDIVIS	IN/A		1/99	40	232	1302.41	1427.70	11.3	0.91	[410]
PDMS, PSU and	N/A	EIOH/H2O	8/92	25	4500	27281.94	43850.97	0.8	0.62	[419]
PHS	NI/A		5/05	60	152.2	803 03	600 74	15	1 24	[420]
	N/A		5/95	40	402.2 1120.6	4571 95	5754 97	0.2	0.70	[420] [424]
PDIVI3	IN/A		0/90	40	1139.0	4371.03	5754.67	9.0	0.79	[421]

1109Table 7 Brief overview of MOF-based and polymeric membranes for the pervaporation separation of three organic-<br/>organic mixtures

Polymer	MOF	Mixture (mass ratio, i/j (p/f))	Feed compos ition	Т (°С)	Flux (g/m²h)	i (p) permeance (GPU)	j (f) permeance (GPU)	Separation factor β <sub>i/j</sub> (enrichmen t factor β <sub>p/t</sub> )/	[Selecti vity (α <sub>i/j</sub> )]	Ref.
SPES-C	Sulfonate d MIL- 53(AI)	MeOH/ MTBE	15/85	40	368	493.61	0.23	1990	2193.1 7	[251]
SPES-C	[Cu <sub>2</sub> (bdc) <sub>2</sub> (bpy)] <sub>n</sub>	MeOH/ MTBE	15/85	40	288	386.23	0.19	1870	2060.9 2	[252]
N/A	UiO-66	MeOH/ MTBE	5/95	40	1210	2733.36	6.92	597	395.06	[167]
N/A	UiO-66	MeOH/ MTBE	15/85	40	1920	2423.83	15.35	147	157.90	[167]

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CA and PVP	N/A	MeOH/ MTBE	20/80	40	430	510.93	0.94	411	541.06	[422]
PVA and SFA	N/A	MeOH/ MTBE	20/80	50	36.9	27.46	0.02	1230	1514.4 0	[423]
PI (Matrimid ® 5218)	N/A	MeOH/ MTBE	14.3/85 .7	45	73.03	60.54	2.83	21.16	21.40	[424]
PI (Matrimid ® 5218)	N/A	MeOH/ MTBE	14.3/85 .7	25	39.57	79.18	4.21	16.66	18.83	[424]
PLA	N/A	MeOH/	15/85	30	~620	~627.68	~107.90	~5	~5.82	[425]
PVA	N/A	MeOH/	30/70	45	~900	~727.33	~16.02	~25	~45.41	[426]
PEEK- WC	N/A	MeOH/ MTBF	15/85	40	~68	~58.08	~5.31	~10	~10.94	[427]
PVA and SEA	N/A	MeOH/ MTBE	20/80	30	12.79	24.48	0.008	2095	2921.9 0	[423]
AAm and HEMA	N/A	MeOH/ MTBE	0.53/99 .47	30	18.48 9.9	283.03 199.44	2.05 0.68	243 511.7	138.10 295.10	[428]
PEBA	Co(HCO	toluene/	10/90	40	771	2758.23	389.67	5.1	7.08	[246]
PVA	O)₂ HKUST-1	n-Heptane toluene/	50/50	40	133.3	276.72	9.29	17.9	29.79	[249]
PVA	N/A	n-Heptane toluene/	50/50	40	14	27.41	1.87	8.9	14.65	[249]
pmPAN	N/A	n-Heptane toluene/	20.6/79	80	690	396.97	44.43	7.3	8.94	[429]
PAN, PEMA	N/A	toluene/ n-Heptane	.4 20/80	85	5130	1875.68	422.46	3.63	4.44	[430]
PEMA PAN.	N/A	toluene/	40/60	85	6580	1682.66	517.19	2.46	3.25	[430]
PEMA and mm-	,, .	n-Heptane							0.20	[]
PEMA HBP	N/A	toluene/	50/50	40	63	107.20	13.64	5.1	7.86	[431]
HBP	N/A	n-Heptane toluene/	10/90	40	25	122.19	9.12	10.1	13.40	[431]
PBLG	N/A	toluene/	3/97	20	28	N/A	N/A	29.5	N/A	[432]
PBLG	N/A	toluene/	50/50	40	280	N/A	N/A	3.8	N/A	[432]
PBLG and PAI-	N/A	toluene/ n-Heptane	3/97	20	0.9	N/A	N/A	88	N/A	[433]
PBLG and PAI- S	N/A	toluene/ n-Heptane	50/50	40	2.5	N/A	N/A	3.7	N/A	[433]
PEBA	HKUST-1	Thiophene/	0.13/99 87	40	4400	6178.43	7969.53	6.0 (α <sub>p/f</sub> )	0.78	[245]
PEBA	HKUST-1	Thiophene/	0.13/99 87	70	16450	4772.30	7595.13	4.04 (α <sub>p/f</sub> )	0.63	[245]
PDMS	HKUST-1	Thiophene/	.07 0.13/99 87	40	~6936	~8376.48	~12577.38	5.2 (α <sub>p/f</sub> )	~0.67	[247]
PDMS	CPO-27-	Thiophene/	0.02/99	45	5920	N/A	N/A	4.05 (α <sub>p/f</sub> )	N/A	[250]
PDMS	MIL-101 (Cr)	Thiophene/ n-octane	.90 0.05/99 .95	30	5200	10855.58	16531.45	5.6 (α <sub>p/f</sub> )	0.66	[248]

PDMS	Cu(II) Ioaded UiO-67- bpydc	Thiophene/ n-octane	0.13/99 .87	40	8100	7826.36	14709.29	4.2 (α <sub>p/f</sub> )	0.53	[46]
PEBA	NH <sub>2</sub> -UiO- 66	Thiophene/ n-octane	0.05/99 .95	60	23400	17894.00	16568.52	7.12 (α <sub>p/f</sub> )	1.08	[354]
N/A	UiO-66- NH2	Thiophene/ n-octane	0.13/99 .87	40	2160	~21000	~4000	17.96 (α <sub>p/f</sub> )	~5.8	[45]
PDMS	N/A	Thiophene/ n-octane	0.40/99	31	~1040	~1670.37	~3349.86	~4.4 (\alpha_p/f)	~0.50	[434]
PDMS	N/A	Thiophene/ n-heptane	~0.014 6/99.98 6	80	~800	~348.95	~117.24	~7.6 (ɑ <sub>p/f</sub> )	~2.98	[435]
PEG	N/A	Thiophene/ n-heptane	0.12/99 .88	84.8 5	3330	552.59	422.19	3.31 (α <sub>p/f</sub> )	1.31	[436]
PI	N/A	Thiophene/ n-heptane	0.12/99 .88	84.8 5	120	7.46	15.25	1.26 (α <sub>p/f</sub> )	0.49	[436]
PUR	N/A	Thiophene/ n-heptane	0.12/99	84.8 5	10810	806.65	1373.57	1.51 (α <sub>p/f</sub> )	0.59	[436]
PUR and PEG	N/A	Thiophene/ n-heptane	0.20/99	65	~510	~381.16	~130.07	7.1 (α <sub>p/f</sub> )	~2.93	[437]
PDMS	N/A	Thiophene/ n-octane	0.364/9 9.636	30	1500	2858.96	5148.47	4.9 (α <sub>p/f</sub> )	0.56	[438]

## **4. Conclusions and future perspectives**

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1114 Owing to the high aspect ratios and capacities, molecular sieving effect and/or preferential 1115 adsorption of MOF crystals, more attentions have been paid to the development of novel MOF-1116 based membranes with enhanced pervaporation performance for liquid mixtures over the past 1117 decade. Compared with pure MOF-based membranes, MOF-based MMMs are more popular in 1118 the field of pervaporation. Both the pure MOF-based membranes and MMMs for pervaporation 1119 show significant potential for future applications, but the applications of these two types of 1120 membranes in pervaporation are still in the early stage. Performance analysis of the available 1121 literature shows that for specific liquid mixtures, pervaporation performance may be beneficial 1122 from a more deliberate selection of MOF with suitable functionalities on the basis of the properties of the liquid mixtures (kinetic diameter, dipole moment and polarizability) rather than universal 1123 selection of several well-known MOFs (such as ZIF-8, UiO-66 and ZIF-71) in such a wide range 1124 1125 of applications. More studies on synthetic strategies of MOF-based membranes in pervaporation 1126 are required, considering the only several production methods of reported MOF-based 1127 pervaporative membranes. In addition, obtaining high-performance pure MOF membranes have always been a challenge as a result of complex MOF nucleation and growth processes. In this 1128 regard, we can consider repeated growth to reduce the defects of pure MOF membranes. Various 1129 parameters should also be considered in the manufacture of pure MOF membranes, including 1130

1131 the surface properties of the substrate and the crystallization behaviour of the MOF crystal. 1132 Therefore, it may be necessary to combine different methods (such as surface modification of the 1133 substrate, repeated growth and post-modification of pure MOF membranes) to obtain pure MOF 1134 membranes with less defects. As for MOF-based MMMs, this kind of membranes combines the 1135 ease of polymer processing and the high selectivity and permeability of MOF crystals. In pervaporation, polymer matrixes and the fillers have a synergistic effect on the separation of liquid 1136 1137 mixtures. MOF particles as the fillers utilized in pervaporation are mostly prepared using room temperature synthesis and solvothermal synthesis. Although MOF synthesis routes have not yet 1138 1139 reached the ability to fine-tune the adsorption interactions in MOFs, exploring other MOF 1140 synthesis routes other than room temperature synthesis and solvothermal synthesis can provide 1141 more topological structure options for the pervaporation separation of liquid mixtures[44]. In terms 1142 of adjusting the adsorption capacity of the MOF, post-synthetic modification (PSM) is a potential 1143 strategy, and PSM can also improve the interactions between polymer matrixes and the fillers. 1144 Furthermore, polymer choice is a key factor, because polymer matrixes of MOF-based MMMs play a role in pervaporation, especially for applications utilizing preferential adsorption mechanism. 1145 Besides, the incompatibility and non-uniform dispersion of the MOF and its loading capacity within 1146 1147 polymer matrixes are important issues, we can address such issues from three directions: (1) 1148 reduce the size of MOF particles, thereby improving their interaction with the polymer phase, (2) 1149 endow the MOF new functionalities through post-modification methods to form hydrogen bonds 1150 with polymer matrixes, (3) chemically induce the covalent cross-linking of MOF crystals and polymer matrixes. Last but not least, evaluation of the driving forces of target compounds is 1151 1152 necessary when pervaporation as an appropriate technique is utilized to separate the mixtures. 1153 As for the future development of MOF-based membranes, in addition to high stability and high 1154 separation performance, low cost and scalability are also needed so that MOF-based membranes can be widely used in industry. 1155

In summary, although the pervaporation application of MOF-based membranes is still in an early stage of development, current research shows promising results. We believe that with relentless efforts in the investigations of MOFs and their corresponding membranes, the industrial application of MOF-based pervaporation membranes will be witnessed in the near future.

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