

## Supporting Information

### **Metal–organic framework membranes: from fabrication to application in gas separation.**

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<i>l</i> - Thickness (m)	<i>T</i> -Temperature (K)	<i>P</i> -Pressure (bar)
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**Table S1.** Comparison of permeation properties of pure MOFs membranes reported in the literature for sorption-driven reverse selective CO<sub>2</sub>/H<sub>2</sub> separation. (the data plotted for the reported polymers in Figure 71, b in the article is taken from the <https://membrane-australasia.org/polymer-gas-separation-membranes/>)

MOF	Support, Method	Permeance (mol/(m <sup>2</sup> *s*Pa))		Permeation (Barrer)		H <sub>2</sub> /CO <sub>2</sub>	l (m)	T (K)	P (bar)	Ref.
		H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub>					
[Ni <sub>2</sub> (L-aspartic acid) <sub>2</sub> (1,2-bis(4-pyridyl)ethylene))]·(Guest)	Nickel meshes	1.02X10 <sup>-6</sup>	4.52X10 <sup>-8</sup>	6.09X10 <sup>+4</sup>	2.70X10 <sup>+3</sup>	22.6	2.0X10 <sup>-5</sup>	298	1	[1]
ZIF-22	APTES-functionalized Ti <sub>2</sub> O	1.70X10 <sup>-7</sup>	2.00X10 <sup>-8</sup>	2.03X10 <sup>+4</sup>	2.39X10 <sup>+3</sup>	8.5	4.0X10 <sup>-5</sup>	323	1	[2]
ZIF-90	APTES-functionalized Al <sub>2</sub> O <sub>3</sub>	2.50X10 <sup>-7</sup>	3.48X10 <sup>-8</sup>	1.49X10 <sup>+4</sup>	2.08X10 <sup>+3</sup>	7.2	2.0X10 <sup>-5</sup>	473	1	[3]
ZIF-7	Al <sub>2</sub> O <sub>3</sub> , seeding	4.55X10 <sup>-8</sup>	3.50X10 <sup>-9</sup>	2.72X10 <sup>+2</sup>	2.09X10 <sup>+1</sup>	13.0	2.0X10 <sup>-6</sup>	493	1	[4]
ZIF-69	Al <sub>2</sub> O <sub>3</sub>	6.70X10 <sup>-8</sup>	2.55X10 <sup>-8</sup>	1.00X10 <sup>+4</sup>	3.81X10 <sup>+3</sup>	2.6	5.0X10 <sup>-5</sup>	298	1	[5]
HKUST-1	Al <sub>2</sub> O <sub>3</sub> , seeding	7.48X10 <sup>-7</sup>	1.48X10 <sup>-7</sup>	5.59X10 <sup>+4</sup>	1.11X10 <sup>+4</sup>	5.1	2.5X10 <sup>-5</sup>	298	1	[6]
NH <sub>2</sub> -MIL-53(Al)	glass frit, seeding	2.67X10 <sup>-6</sup>	9.80X10 <sup>-8</sup>	1.20X10 <sup>+5</sup>	4.39X10 <sup>+3</sup>	27.3	1.5X10 <sup>-5</sup>	288	1	[7]
ZIF-8	Al <sub>2</sub> O <sub>3</sub> hollow fiber, seeding	4.32X10 <sup>-7</sup>	1.22X10 <sup>-7</sup>	2.58X10 <sup>+3</sup>	7.29X10 <sup>+2</sup>	3.5	2.0X10 <sup>-6</sup>	298	1	[8]
JUC-150 [Ni <sub>2</sub> (L-aspartic acid) <sub>2</sub> (pyrazine)]	Nickel meshes	1.83X10 <sup>-7</sup>	4.60X10 <sup>-9</sup>	1.91X10 <sup>+4</sup>	4.81X10 <sup>+2</sup>	39.8	3.5X10 <sup>-5</sup>	298	1	[9]
JUC-150 [Ni <sub>2</sub> (L-aspartic acid) <sub>2</sub> (bipy)]		1.82X10 <sup>-6</sup>	1.65X10 <sup>-7</sup>	2.45X10 <sup>+5</sup>	2.22X10 <sup>+4</sup>	11.0	4.5X10 <sup>-5</sup>	298	1	
ZIF-100	polydopamine modified Al <sub>2</sub> O <sub>3</sub>	6.30X10 <sup>-8</sup>	8.10 X10 <sup>-10</sup>	1.88X10 <sup>+3</sup>	2.42X10 <sup>+1</sup>	77.8	1.0X10 <sup>-5</sup>	298	1	[10]
Amine-modified Mg-MOF-74/CPO-27-Mg	MgO seeds, Al <sub>2</sub> O <sub>3</sub>	8.20X10 <sup>-8</sup>	2.90X10 <sup>-9</sup>	2.45X10 <sup>+3</sup>	8.66X10 <sup>+1</sup>	28.3	1.0X10 <sup>-5</sup>	298	1	[11]
Mg-MOF-74/CPO-27-Mg		1.24X10 <sup>-7</sup>	1.10X10 <sup>-8</sup>	3.70X10 <sup>+3</sup>	3.29X10 <sup>+2</sup>	11.3	1.0X10 <sup>-5</sup>	298	1	

ZIF-8	1H,1H,2H,2H-perfluoroalkyltriethoxysilanes modified Al <sub>2</sub> O <sub>3</sub>	2.66X10 <sup>-7</sup>	1.55X10 <sup>-8</sup>	1.59X10 <sup>+4</sup>	9.26X10 <sup>+2</sup>	17.2	2.0X10 <sup>-5</sup>	473	1	[12]
ZIF-67	porous Al <sub>2</sub> O <sub>3</sub> tube, from Cobalt carbonate	5.70X10 <sup>-7</sup>	1.30X10 <sup>-7</sup>	2.89X10 <sup>+3</sup>	6.60X10 <sup>+2</sup>	4.4	1.7X10 <sup>-6</sup>	323	1	[13]
2D sheet Zn <sub>2</sub> (benzimidazole) <sub>4</sub>	porous Al <sub>2</sub> O <sub>3</sub> tube, from GO coated ZnO	1.50X10 <sup>-7</sup>	1.42X10 <sup>-9</sup>	8.96X10 <sup>+1</sup>	8.45X10 <sup>-1</sup>	106.0	2.0X10 <sup>-7</sup>	423	1	[14]
2D sheet Zn <sub>2</sub> (benzimidazole) <sub>4</sub>	porous Al <sub>2</sub> O <sub>3</sub> tube, from ZnO	2.10X10 <sup>-7</sup>	3.94X10 <sup>-9</sup>	3.14X10 <sup>+1</sup>	5.88X10 <sup>-1</sup>	53.3	5.0X10 <sup>-8</sup>	323,473	1	[15]
ZIF-8	reduced GO-modified PVDF hollow fibe. con-diffusion	6.79X10 <sup>-7</sup>	2.72X10 <sup>-8</sup>	3.04X10 <sup>+2</sup>	1.22X10 <sup>+1</sup>	25.0	1.5X10 <sup>-7</sup>	298	1	[16]
ZIF-8-on-ZIF-67	Al <sub>2</sub> O <sub>3</sub> , LbL	1.20X10 <sup>-8</sup>	9.00E-10	1.29X10 <sup>+1</sup>	9.68X10 <sup>-1</sup>	13.3	3.6X10 <sup>-7</sup>	298	1	[17]
ZIF-8/2D g-C <sub>3</sub> N <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub> , spin LbL	6.70X10 <sup>-8</sup>	1.60X10 <sup>-9</sup>	4.80X10 <sup>+1</sup>	1.15X10 <sup>+0</sup>	41.9	2.4X10 <sup>-7</sup>	298	1	[18]
ZIF-8	polyacrylonitrile, PAN, electrophoretic nuclei assembly	9.90X10 <sup>-8</sup>	1.36X10 <sup>-8</sup>	1.48X10 <sup>+2</sup>	2.03X10 <sup>+1</sup>	7.3	5.0X10 <sup>-7</sup>	298	1	[19]
2D sheet Zn <sub>2</sub> (benzimidazole) <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	6.51X10 <sup>-7</sup>	5.20X10 <sup>-9</sup>	1.94X10 <sup>+1</sup>	1.55X10 <sup>-1</sup>	125.2	1.0X10 <sup>-8</sup>	293	1	[20]
2D sheet Zn <sub>2</sub> (benzimidazole) <sub>4</sub>		9.00X10 <sup>-7</sup>	5.42X10 <sup>-9</sup>	2.69X10 <sup>+1</sup>	1.62X10 <sup>-1</sup>	166.0	1.0X10 <sup>-8</sup>	393	1	
CAU-10-H (Al, 1,3-benzene dicarboxylic acid)	Al <sub>2</sub> O <sub>3</sub>	3.80X10 <sup>-9</sup>	3.62E-10	6.81X10 <sup>+1</sup>	6.49X10 <sup>+0</sup>	10.5	6.0X10 <sup>-6</sup>	473	2	[21]
ZIF-9	APTES-functionalized Al <sub>2</sub> O <sub>3</sub>	7.43X10 <sup>-6</sup>	5.00X10 <sup>-7</sup>	1.11X10 <sup>+6</sup>	7.47X10 <sup>+4</sup>	14.9	5.0X10 <sup>-5</sup>	298	1	[22]
COF-300	SiO <sub>2</sub> disk			1.10X10 <sup>+5</sup>	1.83X10 <sup>+4</sup>	6.0	4.5X10 <sup>-5</sup>	298	1	[23]
Zn <sub>2</sub> (bdc) <sub>2</sub> (dabco)				2.80X10 <sup>+5</sup>	4.00X10 <sup>+4</sup>	7.0	1.2X10 <sup>-4</sup>	298	1	
ZIF-8				1.20X10 <sup>+5</sup>	1.32X10 <sup>+4</sup>	9.1	6.0X10 <sup>-5</sup>	298	1	
(COF-300)-(Zn <sub>2</sub> (bdc) <sub>2</sub> (dabco))				1.30X10 <sup>+5</sup>	1.03X10 <sup>+4</sup>	12.6	9.7X10 <sup>-5</sup>	298	1	
(COF-300)-(ZIF-8)				1.10X10 <sup>+5</sup>	8.15X10 <sup>+3</sup>	13.5	1.0X10 <sup>-4</sup>	298	1	

NH <sub>2</sub> -MIL-125	Al <sub>2</sub> O <sub>3</sub>			4.25X10+3	5.20X10+2	8.2	2.0X10-6	298	1	[24]
CuBTC/MIL-100	polydopamine modified PVDF hollow fiber, converted CuBTC	8.80X10-8	1.13X10-9	5.26X10+3	6.77X10+1	77.6	2.0X10-5	298	2	[25]
CuBTC/MIL-100		1.05X10-7	1.18X10-9	6.27X10+3	7.05X10+1	89.0	2.0X10-5	358	2	
MIL-96(Al)	Al <sub>2</sub> O <sub>3</sub> , toluene seeding	5.30X10-7	6.09X10-8	1.11X10+4	1.27X10+3	8.7	7.0X10-6	298	1	[26]
MIL-96(Al)	Al <sub>2</sub> O <sub>3</sub> , DMF seeding	3.80X10-7	5.76X10-8	2.27X10+3	3.44X10+2	6.6	2.0X10-6	298	1	
ZIF-8	APTES, Titania- functionalized PVDF hollow fiber	2.01X10-5	2.86X10-6	6.00X10+4	8.53X10+3	7.0	1.0X10-6	293	1	[27]
ZIF-8	Al <sub>2</sub> O <sub>3</sub>	1.40X10-8	1.87X10-9	9.20X10+0	1.23X10+0	7.5	2.2X10-7	298	1	[28]
NH <sub>2</sub> -MIL-53	ammoniated PVDF hollow fibe	5.42X10-6	1.78X10-7	1.30X10+5	4.26X10+3	30.4	8.0X10-6	298	1	[29]
ZIF-7-NH <sub>2</sub> coated PEBAX 1657	Al <sub>2</sub> O <sub>3</sub>	1.00X10-7	5.26X10-9	5.97X10+3	3.14X10+2	19.0	2.0X10-5	298	1	[30]
Zn <sub>2</sub> (bim) <sub>4</sub> nanosheets	Al <sub>2</sub> O <sub>3</sub>	1.20X10-6	1.35X10-8	3.58X10+0	4.03X10-2	89.0	1.0X10-9	298	1	[31]
MOF-5	Al <sub>2</sub> O <sub>3</sub>	4.70X10-6	1.05X10-6	3.51X10+5	7.84X10+4	4.5	2.5X10-5	298	1	[32]
MOF-5 oriented	graphite-coated Al <sub>2</sub> O <sub>3</sub>	8.30X10-7	2.10X10-7	9.92X10+4	2.51X10+4	4.0	4.0X10-5	298	1	[33]
HKUST-1	Al <sub>2</sub> O <sub>3</sub> hollow fiber, seeding	7.25X10-8	5.50X10-9	2.82X10+3	2.14X10+2	13.2	1.3X10-5	313	1	[34]
ZIF-8	Al <sub>2</sub> O <sub>3</sub>	6.04X10-8	1.33X10-8	7.22X10+3	1.59X10+3	4.5	4.0X10-5	298	1	[35]
ZIF-8	Al <sub>2</sub> O <sub>3</sub> , seeding	1.87X10-6	5.00X10-7	1.40X10+5	3.73X10+4	3.7	2.5X10-5	298	1	[36]
ZIF-8/GO	Al <sub>2</sub> O <sub>3</sub>	1.45X10-7	6.46X10-9	1.52X10+4	6.75X10+2	22.4	3.5X10-5	523	1	[37]
ZIF-7	Al <sub>2</sub> O <sub>3</sub> , polyethyleneimine assisted seeding	7.40X10-8	1.10X10-8	3.32X10+2	4.93X10+1	6.7	1.5X10-6	473	1	[38]
ZIF-95	APTES-functionalized Al <sub>2</sub> O <sub>3</sub>	2.46X10-6	7.04X10-8	2.20X10+5	6.31X10+3	34.9	3.0X10-5	298	1	[39]
MIL-53	Al <sub>2</sub> O <sub>3</sub> , seeding	4.90X10-7	1.10X10-7	1.17X10+4	2.63X10+3	4.5	8.0X10-6	298	1	[40]

Ni-MOF-74	Al <sub>2</sub> O <sub>3</sub> , seeding	0.0000127	0.0000014	9.48X10+5	1.05X10+5	9.1	0.000025	298	1	[41]
ZIF-7-8	Al <sub>2</sub> O <sub>3</sub> , microwave	0.0000003	0.00000006	1.79X10+3	3.58X10+2	5.0	0.000002	298	1	[42]

**Table S2.** Comparison of permeation properties of pure MOFs membranes reported in the literature for diffusion-driven H<sub>2</sub>/CO<sub>2</sub> separation. (the data plotted for the reported polymers in Figure 71, a in the article is taken from the <https://membrane-australasia.org/polymer-gas-separation-membranes/>)

MOF	Support	Permeation (Barrer)		CO <sub>2</sub> /H <sub>2</sub>	Mix gas		l (m)	T (K)	P (bar)	Ref.
		H <sub>2</sub>	CO <sub>2</sub>		%/%	CO <sub>2</sub> /H <sub>2</sub>				
CAU-1	Al <sub>2</sub> O <sub>3</sub> hollow fiber, seeding	3.79X10+3	9.86X10+3	2.6			2.5X10-6	298	1	[43]
[Cu <sub>2</sub> (benzoate) <sub>4</sub> (pyrazine)] <sub>n</sub> [100] direction	single crystal	5.26X10-1	7.17X10-1	1.4	10/90	0.36	0.00016	298	1	[44]
		5.26X10-1	7.17X10-1		20/80	1.29	0.00016	298	1	
		5.26X10-1	7.17X10-1		70/30	2.19	0.00016	298	1	
		5.26X10-1	7.17X10-1		60/40	3.85	0.00016	298	1	
		5.26X10-1	7.17X10-1		50/50	4.08	0.00016	298	1	
		5.26X10-1	7.17X10-1		40/60	6.49	0.00016	298	1	
		5.26X10-1	7.17X10-1		30/70	14.17	0.00016	298	1	
		5.26X10-1	7.17X10-1		20/80	18.20	0.00016	298	1	
5.26X10-1	7.17X10-1	10/90	32.65	0.00016	298	1				
sod-ZMOF	Al <sub>2</sub> O <sub>3</sub>	35.8	94.1	2.6	70/30	5.20	0.00005	298	2	[45]
MOF-5	Al <sub>2</sub> O <sub>3</sub> , seeding	710.9	8154.1	4.5	20/80	1.25	0.000014	298	2.7	[46]
		710.9	8154.1		60/40	1.75	0.000014	298	2.7	
		710.9	8154.1		40/60	2.60	0.000014	298	2.7	
		710.9	8154.1		82/18	4.50	0.000014	298	2.7	
MOF-5,CO <sub>2</sub> treated		5266.7	23709.7	4.5	98/2	5781.00	0.000014	298	5	[47]

**Table S3.** Comparison of permeation properties of pure MOFs membranes reported in the literature for CO<sub>2</sub>/CH<sub>4</sub> separation. (the data plotted for the reported polymers in Figure 72, a in the article is taken from the <https://membrane-australasia.org/polymer-gas-separation-membranes/>)

MOF	Support, Method	Permeance (mol/(m <sup>2</sup> *s*Pa))		Permeation (Barrer)		CO <sub>2</sub> /CH <sub>4</sub>	l (m)	T (K)	P (bar)	Ref.
		CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>					
MOF-5	Al <sub>2</sub> O <sub>3</sub>	1.38X10 <sup>-7</sup>	0.00000015	5.75X10 <sup>+3</sup>	6.27X10 <sup>+3</sup>	1.1	0.000014	298	3	[48]
ZIF-8	Al <sub>2</sub> O <sub>3</sub>	2.41X10 <sup>-6</sup>	0.0000169	6.49X10 <sup>+4</sup>	4.54X10 <sup>+5</sup>	7.0	0.000009	295	1	[49]
Co <sub>3</sub> (HCOO) <sub>6</sub>	silicon wafer, seeding	4.1513X10 <sup>-7</sup>	0.00000225	1.49X10 <sup>+4</sup>	8.06X10 <sup>+4</sup>	5.4	0.000012	298	1	[50]
ZIF-69	Al <sub>2</sub> O <sub>3</sub> , seeding	8.6X10 <sup>-9</sup>	2.36X10 <sup>-8</sup>	1.03X10 <sup>+3</sup>	2.82X10 <sup>+3</sup>	2.7	0.00004	298	1	[51]
[Cu <sub>2</sub> (ndc) <sub>2</sub> (dabco)]	Al <sub>2</sub> O <sub>3</sub>	4X10 <sup>-9</sup>	1.4X10 <sup>-8</sup>	2.39X10 <sup>+2</sup>	8.36X10 <sup>+2</sup>	3.5	0.00002	298	1	[52]
Bio-MOF-1	stainless steel tube, seeding	0.00000046	0.00000119	2.06X10 <sup>+4</sup>	5.33X10 <sup>+4</sup>	2.6	0.000015	298	1.4	[53]
Bio-MOF-13	stainless steel tube, seeding	0.00000082	0.0000031	1.71X10 <sup>+4</sup>	6.48X10 <sup>+4</sup>	3.8	0.000007	298	1	[54]
Bio-MOF-14		0.00000118	0.00000416	4.58X10 <sup>+4</sup>	1.62X10 <sup>+5</sup>	3.5	0.000013	298	1	
ZIF-7-8	Al <sub>2</sub> O <sub>3</sub> , microwave	1.4X10 <sup>-8</sup>	0.00000006	8.36X10 <sup>+1</sup>	3.58X10 <sup>+2</sup>	4.3	0.000002	298	1	[42]
sod-ZMOF	Al <sub>2</sub> O <sub>3</sub>	1.8 X10 <sup>-10</sup>	6.3 X10 <sup>-10</sup>	2.69X10 <sup>+1</sup>	9.41X10 <sup>+1</sup>	3.5	0.00005	298	2	[45]
MIL-100(In)	Al <sub>2</sub> O <sub>3</sub>	2.4658X10 <sup>-7</sup>	0.0000009	3.68X10 <sup>+3</sup>	1.34X10 <sup>+4</sup>	3.7	0.000005	298	2	[55]
ZIF-8-ZnAl-NO <sub>3</sub> LDH composite membrane	Al <sub>2</sub> O <sub>3</sub>	7.5786 X10 <sup>-10</sup>	9.7763X10 <sup>-9</sup>	4.53X10 <sup>+1</sup>	5.84X10 <sup>+2</sup>	12.9	0.00002	363	1	[56]
CAU-1	Al <sub>2</sub> O <sub>3</sub> hollow fiber, seeding	8.9189X10 <sup>-8</sup>	0.00000132	6.66X10 <sup>+2</sup>	9.86X10 <sup>+3</sup>	14.8	0.0000025	298	1	[57]

**Table S4.** Comparison of permeation properties of pure MOFs membranes reported in the literature for CO<sub>2</sub>/N<sub>2</sub> separation. (the data plotted for the reported polymers in Figure 72, b in the article is taken from the <https://membrane-australasia.org/polymer-gas-separation-membranes/>)

MOF	Support, Method	Permeance (mol/(m <sup>2</sup> *s*Pa))		Permeation (Barrer)		CO <sub>2</sub> / N <sub>2</sub>	<i>l</i> (m)	<i>T</i> (K)	<i>P</i> (bar)	Ref.
		N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>					
MOF-5	Al <sub>2</sub> O <sub>3</sub>	1.82927X10-7	0.00000015	5.75X10+3	6.27X10+3	0.8	0.000014	298	3	[48]
ZIF-69	Al <sub>2</sub> O <sub>3</sub> , seeding	1.06X10-8	2.36X10-8	1.03X10+3	2.82X10+3	2.2	0.00004	298	1	[51]
ZIF-7-8	Al <sub>2</sub> O <sub>3</sub> , microwave	0.000000024	0.00000006	8.36X10+1	3.58X10+2	2.5	0.000002	298	1	[42]
sod-ZMOF	Al <sub>2</sub> O <sub>3</sub>	7.3 X10-11	6.3 X10-10	2.69X10+1	9.41X10+1	8.6	0.00005	298	2	[45]
MIL-100(In)	Al <sub>2</sub> O <sub>3</sub>	2.85714X10-7	0.0000009	3.68X10+3	1.34X10+4	3.2	0.000005	298	2	[55]
ZIF-8-ZnAl-NO <sub>3</sub> LDH composite membrane	Al <sub>2</sub> O <sub>3</sub>	2.44048X10-9	9.7763X10-9	4.53X10+1	5.84X10+2	4.0	0.00002	363	1	[56]
CAU-1	Al <sub>2</sub> O <sub>3</sub> hollow fiber, seeding	5.04X10-8	0.00000132	6.66X10+2	9.86X10+3	26.2	0.0000025	298	1	[43]

**Table S5.** Comparison of permeation properties of pure MOFs membranes reported in the literature for C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> separation. (the data plotted for the reported polymers in Figure 73, a in the article is taken from the [58])

MOF	Support, Method	Permeance (mol/(m <sup>2</sup> *s*Pa))		Permeation (Barrer)		C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>	<i>l</i> (m)	<i>T</i> (K)	<i>P</i> (bar)	Ref.
		C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>					
MOF-5	Al <sub>2</sub> O <sub>3</sub>	0.000000018	6.66667X10-9	1.34X10+3	4.98X10+2	2.7	0.000025	298	1	[59]

**Table S6.** Comparison of permeation properties of pure MOFs membranes reported in the literature for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation. (the data plotted for the reported polymers in Figure 73, b in the article is taken from the [60])

MOF	Support, Method	Permeance (mol/(m <sup>2</sup> *s*Pa))		Permeation (Barrer)		mix C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>	<i>l</i> (m)	<i>T</i> (K)	<i>P</i> (bar)	Ref.
		C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>					
ZIF-8	Al <sub>2</sub> O <sub>3</sub> , counter-diffusion	2.7799X10 <sup>-8</sup>	6.46488E-10	1.25X10 <sup>+2</sup>	2.90X10 <sup>+0</sup>	43.0	0.0000015	298	1	[61]
ZIF-8	Al <sub>2</sub> O <sub>3</sub>	8.09X10 <sup>-9</sup>	1.97317E-10	2.42X10 <sup>+2</sup>	5.89X10 <sup>+0</sup>	41.0	0.00001	298	1	[62]
ZIF-8	Al <sub>2</sub> O <sub>3</sub> , counter-diffusion	2.5X10 <sup>-9</sup>	4.23729E-11	5.97X10 <sup>+2</sup>	1.01X10 <sup>+1</sup>	59.0	0.00008	298	1	[63]
ZIF-8	Al <sub>2</sub> O <sub>3</sub> , secondary growth	0.000000011	3.66667E-10	8.21X10 <sup>+1</sup>	2.74X10 <sup>+0</sup>	30.0	0.0000025	298	1	[64]
ZIF-8	PAI hollow fiber, IMMP	1.4405X10 <sup>-8</sup>	9.47697E-11	3.49X10 <sup>+2</sup>	2.29X10 <sup>+0</sup>	152.0	0.0000081	298	1	[65]

**Table S7.** Comparison of permeation properties of pure MOFs membranes reported in the literature for C<sub>4</sub>H<sub>10</sub>/i-C<sub>4</sub>H<sub>10</sub> separation. (the data plotted for the reported polymers in Figure 73, c in the article is taken from the [66])

MOF	Support, Method	Permeation (Barrer)		C <sub>4</sub> H <sub>10</sub> /i-C <sub>4</sub> H <sub>10</sub>	<i>l</i> (m)	<i>T</i> (K)	<i>P</i> (bar)	Reference (DOI)
		C <sub>4</sub> H <sub>10</sub>	i-C <sub>4</sub> H <sub>10</sub>					
ZIF-90	carbon hollow fibers, fluidic processing technique	192	16	12	0.0000031	298	1	[67]

## References

1. Kang, Z.; Fan, L.; Wang, S.; Sun, D.; Xue, M.; Qiu, S. In situ confinement of free linkers within a stable mof membrane for highly improved gas separation properties. *CrystEngComm* **2017**, *19*, 1601-1606.
2. Huang, A.; Bux, H.; Steinbach, F.; Caro, J. Molecular-sieve membrane with hydrogen permselectivity: Zif-22 in Ita topology prepared with 3-aminopropyltriethoxysilane as covalent linker. *Angew. Chem. Int. Ed.* **2010**, *49*, 4958-4961.
3. Huang, A.; Dou, W.; Caro, J. Steam-stable zeolitic imidazolate framework zif-90 membrane with hydrogen selectivity through covalent functionalization. *J. Am. Chem. Soc.* **2010**, *132*, 15562-15564.
4. Li, Y.; Liang, F.; Bux, H.; Yang, W.; Caro, J. Zeolitic imidazolate framework zif-7 based molecular sieve membrane for hydrogen separation. *J. Memb. Sci.* **2010**, *354*, 48-54.
5. Liu, Y.; Hu, E.; Khan, E.A.; Lai, Z. Synthesis and characterization of zif-69 membranes and separation for co<sub>2</sub>/co mixture. *J. Memb. Sci.* **2010**, *353*, 36-40.
6. Nan, J.; Dong, X.; Wang, W.; Jin, W.; Xu, N. Step-by-step seeding procedure for preparing hkust-1 membrane on porous  $\alpha$ -alumina support. *Langmuir* **2011**, *27*, 4309-4312.
7. Zhang, F.; Zou, X.; Gao, X.; Fan, S.; Sun, F.; Ren, H.; Zhu, G. Hydrogen selective nh<sub>2</sub>-mil-53(al) mof membranes with high permeability. *Adv. Funct. Mater.* **2012**, *22*, 3583-3590.
8. Huang, K.; Dong, Z.; Li, Q.; Jin, W. Growth of a zif-8 membrane on the inner-surface of a ceramic hollow fiber via cycling precursors. *Chem. Commun.* **2013**, *49*, 10326-10328.
9. Kang, Z.; Xue, M.; Fan, L.; Huang, L.; Guo, L.; Wei, G.; Chen, B.; Qiu, S. Highly selective sieving of small gas molecules by using an ultra-microporous metal-organic framework membrane. *Energy Environ. Sci.* **2014**, *7*, 4053-4060.
10. Wang, N.; Liu, Y.; Qiao, Z.; Diestel, L.; Zhou, J.; Huang, A.; Caro, J. Polydopamine-based synthesis of a zeolite imidazolate framework zif-100 membrane with high h<sub>2</sub>/co<sub>2</sub> selectivity. *J. Mater. Chem. A* **2015**, *3*, 4722-4728.
11. Wang, N.; Mundstock, A.; Liu, Y.; Huang, A.; Caro, J. Amine-modified mg-mof-74/cpo-27-mg membrane with enhanced h<sub>2</sub>/co<sub>2</sub> separation. *Chemical Engineering Science* **2015**, *124*, 27-36.
12. Wu, X.; Liu, C.; Caro, J.; Huang, A. Facile synthesis of molecular sieve membranes following "like grows like" principle. *J. Memb. Sci.* **2018**, *559*, 1-7.
13. Nian, P.; Cao, Y.; Li, Y.; Zhang, X.; Wang, Y.; Liu, H.; Zhang, X. Preparation of a pure zif-67 membrane by self-conversion of cobalt carbonate hydroxide nanowires for h<sub>2</sub> separation. *CrystEngComm* **2018**, *20*, 2440-2448.
14. Li, Y.; Liu, H.; Wang, H.; Qiu, J.; Zhang, X. Go-guided direct growth of highly oriented metal-organic framework nanosheet membranes for h<sub>2</sub>/co<sub>2</sub> separation. *Chem. Sci.* **2018**, *9*, 4132-4141.
15. Li, Y.; Lin, L.; Tu, M.; Nian, P.; Howarth, A.J.; Farha, O.K.; Qiu, J.; Zhang, X. Growth of zno self-converted 2d nanosheet zeolitic imidazolate framework membranes by an ammonia-assisted strategy. *Nano Res.* **2018**, *11*, 1850-1860.
16. Li, W.; Shi, J.; Li, Z.; Wu, W.; Xia, Y.; Yu, Y.; Zhang, G. Hydrothermally reduced graphene oxide interfaces for synthesizing high-performance metal-organic framework hollow fiber membranes. *Adv. Mater. Interfaces* **2018**.

17. Knebel, A.; Wulfert-Holzmann, P.; Friebe, S.; Pavel, J.; Strauß, I.; Mundstock, A.; Steinbach, F.; Caro, J. Hierarchical nanostructures of metal-organic frameworks applied in gas separating zif-8-on-zif-67 membranes. *Chem. Eur. J.* **2018**, *24*, 5728-5733.
18. Hou, J.; Wei, Y.; Zhou, S.; Wang, Y.; Wang, H. Highly efficient  $\text{H}_2/\text{CO}_2$  separation via an ultrathin metal-organic framework membrane. *Chemical Engineering Science* **2018**, *182*, 180-188.
19. He, G.; Dakhchoune, M.; Zhao, J.; Huang, S.; Agrawal, K.V. Electrophoretic nuclei assembly for crystallization of high-performance membranes on unmodified supports. *Adv. Funct. Mater.* **2018**, *28*.
20. Peng, Y.; Li, Y.; Ban, Y.; Yang, W. Two-dimensional metal-organic framework nanosheets for membrane-based gas separation. *Angew. Chem. Int. Ed.* **2017**, *56*, 9757-9761.
21. Jin, H.; Wollbrink, A.; Yao, R.; Li, Y.; Caro, J.; Yang, W. A novel Cu-10-h mof membrane for hydrogen separation under hydrothermal conditions. *J. Memb. Sci.* **2016**, *513*, 40-46.
22. Huang, Y.; Liu, D.; Liu, Z.; Zhong, C. Synthesis of zeolitic imidazolate framework membrane using temperature-switching synthesis strategy for gas separation. *Ind. Eng. Chem. Res.* **2016**, *55*, 7164-7170.
23. Fu, J.; Das, S.; Xing, G.; Ben, T.; Valtchev, V.; Qiu, S. Fabrication of cof-mof composite membranes and their highly selective separation of  $\text{H}_2/\text{CO}_2$ . *J. Am. Chem. Soc.* **2016**, *138*, 7673-7680.
24. Friebe, S.; Mundstock, A.; Unruh, D.; Renz, F.; Caro, J.  $\text{NH}_2$ -mil-125 as membrane for carbon dioxide sequestration: Thin supported mof layers contra mixed-matrix-membranes. *J. Memb. Sci.* **2016**, *516*, 185-193.
25. Li, W.; Zhang, Y.; Zhang, C.; Meng, Q.; Xu, Z.; Su, P.; Li, Q.; Shen, C.; Fan, Z.; Qin, L., et al. Transformation of metal-organic frameworks for molecular sieving membranes. *Nat. Commun.* **2016**, *7*, 11315.
26. Knebel, A.; Friebe, S.; Bigall, N.C.; Benzaqui, M.; Serre, C.; Caro, J. Comparative study of mil-96(al) as continuous metal-organic frameworks layer and mixed-matrix membrane. *ACS Appl. Mater. Interfaces* **2016**, *8*, 7536-7544.
27. Hou, J.; Sutrisna, P.D.; Zhang, Y.; Chen, V. Formation of ultrathin, continuous metal-organic framework membranes on flexible polymer substrates. *Angew. Chem. Int. Ed.* **2016**, *55*, 3947-3951.
28. Liu, Y.; Peng, Y.; Wang, N.; Li, Y.; Pan, J.H.; Yang, W.; Caro, J. Significantly enhanced separation using zif-8 membranes by partial conversion of calcined layered double hydroxide precursors. *ChemSusChem* **2015**, *8*, 3582-3586.
29. Li, W.; Su, P.; Zhang, G.; Shen, C.; Meng, Q. Preparation of continuous  $\text{NH}_2$ -mil-53 membrane on ammoniated polyvinylidene fluoride hollow fiber for efficient  $\text{H}_2$  purification. *J. Memb. Sci.* **2015**, *495*, 384-391.
30. Chang, H.; Wang, Y.; Xiang, L.; Liu, D.; Wang, C.; Pan, Y. Improved  $\text{H}_2/\text{CO}_2$  separation performance on mixed-linker zif-7 polycrystalline membranes. *Chemical Engineering Science* **2018**, *192*, 85-93.
31. Peng, Y.; Li, Y.; Ban, Y.; Jin, H.; Jiao, W.; Liu, X.; Yang, W. Metal-organic framework nanosheets as building blocks for molecular sieving membranes. *Science* **2014**, *346*, 1356-1359.
32. Liu, Y.; Ng, Z.; Khan, E.A.; Jeong, H.-K.; Ching, C.-b.; Lai, Z. Synthesis of continuous mof-5 membranes on porous  $\alpha$ -alumina substrates. *Microporous Mesoporous Mater.* **2009**, *118*, 296-301.
33. Yoo, Y.; Lai, Z.; Jeong, H.K. Fabrication of mof-5 membranes using microwave-induced rapid seeding and solvothermal secondary growth. *Microporous Mesoporous Mater.* **2009**, *123*, 100-106.

34. Zhou, S.; Zou, X.; Sun, F.; Zhang, F.; Fan, S.; Zhao, H.; Schiestel, T.; Zhu, G. Challenging fabrication of hollow ceramic fiber supported  $\text{Cu}_3(\text{BTC})_2$  membrane for hydrogen separation. *J. Mater. Chem.* **2012**, *22*, 10322.
35. Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. *J. Am. Chem. Soc.* **2009**, *131*, 16000-16001.
36. Guerrero, V.V.; Yoo, Y.; McCarthy, M.C.; Jeong, H.K. HKUST-1 membranes on porous supports using secondary growth. *J. Mater. Chem.* **2010**, *20*, 3938-3943.
37. Huang, A.; Liu, Q.; Wang, N.; Zhu, Y.; Caro, J. Bicontinuous zeolitic imidazolate framework zif-8@GO membrane with enhanced hydrogen selectivity. *J. Am. Chem. Soc.* **2014**, *136*, 14686-14689.
38. Li, Y.-S.; Liang, F.-Y.; Bux, H.; Feldhoff, A.; Yang, W.-S.; Caro, J.R. Molecular sieve membrane: Supported metal-organic framework with high hydrogen selectivity. *Angew. Chem. Int. Ed.* **2010**, *122*, 558-561.
39. Huang, A.; Chen, Y.; Wang, N.; Hu, Z.; Jiang, J.; Caro, J. A highly permeable and selective zeolitic imidazolate framework zif-95 membrane for  $\text{H}_2/\text{CO}_2$  separation. *Chem. Commun.* **2012**, *48*, 10981-10983.
40. Hu, Y.; Dong, X.; Nan, J.; Jin, W.; Ren, X.; Xu, N.; Lee, Y.M. Metal-organic framework membranes fabricated via reactive seeding. *Chem. Commun.* **2011**, *47*, 737-739.
41. Lee, D.-J.; Li, Q.; Kim, H.; Lee, K. Preparation of Ni-MOF-74 membrane for  $\text{CO}_2$  separation by layer-by-layer seeding technique. *Microporous Mesoporous Mater.* **2012**, *163*, 169-177.
42. Hillman, F.; Brito, J.; Jeong, H.K. Rapid one-pot microwave synthesis of mixed-linker hybrid zeolitic-imidazolate framework membranes for tunable gas separations. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5586-5593.
43. Yin, H.; Wang, J.; Xie, Z.; Yang, J.; Bai, J.; Lu, J.; Zhang, Y.; Yin, D.; Lin, J.Y. A highly permeable and selective amino-functionalized MOF CAU-1 membrane for  $\text{CO}_2/\text{N}_2$  separation. *Chem. Commun.* **2014**, *50*, 3699-3701.
44. Takamizawa, S.; Takasaki, Y.; Miyake, R. Single-crystal membrane for anisotropic and efficient gas permeation. *J. Am. Chem. Soc.* **2010**, *132*, 2862-2863.
45. Al-Maythalony, B.A.; Shekhah, O.; Swaidan, R.; Belmabkhout, Y.; Pinnau, I.; Eddaoudi, M. Quest for anionic MOF membranes: Continuous SOD-ZMOF membrane with  $\text{CO}_2$  adsorption-driven selectivity. *J. Am. Chem. Soc.* **2015**, *137*, 1754-1757.
46. Zhao, Z.; Ma, X.; Kasik, A.; Li, Z.; Lin, Y.S. Gas separation properties of metal organic framework (MOF-5) membranes. *Ind. Eng. Chem. Res.* **2013**, *52*, 1102-1108.
47. Rui, Z.; James, J.B.; Lin, Y.S. Highly  $\text{CO}_2$  perm-selective metal-organic framework membranes through  $\text{CO}_2$  annealing post-treatment. *J. Memb. Sci.* **2018**, *555*, 97-104.
48. Rui, Z.; James, J.B.; Kasik, A.; Lin, Y.S. Metal-organic framework membrane process for high purity  $\text{CO}_2$  production. *AIChE J.* **2016**, *62*, 3836-3841.
49. Venna, S.R.; Carreon, M.A. Highly permeable zeolite imidazolate framework-8 membranes for  $\text{CO}_2/\text{CH}_4$  separation. *J. Am. Chem. Soc.* **2010**, *132*, 76-78.
50. Zou, X.; Zhang, F.; Thomas, S.; Zhu, G.; Valtchev, V.; Mintova, S.  $\text{Co}_3(\text{HCOO})_6$  microporous metal-organic framework membrane for separation of  $\text{CO}_2/\text{CH}_4$  mixtures. *Chemistry* **2011**, *17*, 12076-12083.

51. Liu, Y.; Zeng, G.; Pan, Y.; Lai, Z. Synthesis of highly c-oriented zif-69 membranes by secondary growth and their gas permeation properties. *J. Memb. Sci.* **2011**, *379*, 46-51.
52. Betard, A.; Bux, H.; Henke, S.; Zacher, D.; Caro, J.; Fischer, R.A. Fabrication of a co<sub>2</sub>-selective membrane by stepwise liquid-phase deposition of an alkylether functionalized pillared-layered metal-organic framework [cu<sub>2</sub>l<sub>2</sub>p](n) on a macroporous support. *Microporous Mesoporous Mater.* **2012**, *150*, 76-82.
53. Bohrman, J.A.; Carreon, M.A. Synthesis and co<sub>2</sub>/ch<sub>4</sub> separation performance of bio-mof-1 membranes. *Chem. Commun.* **2012**, *48*, 5130-5132.
54. Xie, Z.; Li, T.; Rosi, N.L.; Carreon, M.A. Alumina-supported cobalt-adeninate mof membranes for co<sub>2</sub>/ch<sub>4</sub> separation. *J. Mater. Chem. A* **2014**, *2*, 1239.
55. Dou, Z.; Cai, J.; Cui, Y.; Yu, J.; Xia, T.; Yang, Y.; Qian, G. Preparation and gas separation properties of metal-organic framework membranes. *Z. Anorg. Allg. Chem.* **2015**, *641*, 792-796.
56. Liu, Y.; Pan, J.H.; Wang, N.; Steinbach, F.; Liu, X.; Caro, J. Remarkably enhanced gas separation by partial self-conversion of a laminated membrane to metal-organic frameworks. *Angew. Chem. Int. Ed.* **2015**, *54*, 3028-3032.
57. Yin, H.; Wang, J.; Xie, Z.; Yang, J.; Bai, J.; Lu, J.; Zhang, Y.; Yin, D.; Lin, J.Y.S. A highly permeable and selective amino-functionalized mof cau-1 membrane for co<sub>2</sub>/n<sub>2</sub> separation. *Chem. Commun.* **2014**, *50*, 3699-3701.
58. Rungta, M.; Zhang, C.; Koros, W.J.; Xu, L. Membrane-based ethylene/ethane separation: The upper bound and beyond. *AIChE J.* **2013**, *59*, 3475-3489.
59. Bux, H.; Chmelik, C.; Krishna, R.; Caro, J. Ethene/ethane separation by the mof membrane zif-8: Molecular correlation of permeation, adsorption, diffusion. *J. Memb. Sci.* **2011**, *369*, 284-289.
60. Burns, R.L.; Koros, W.J. Defining the challenges for c<sub>3</sub>h<sub>6</sub>/c<sub>3</sub>h<sub>8</sub> separation using polymeric membranes. *J. Memb. Sci.* **2003**, *211*, 299-309.
61. Kwon, H.T.; Jeong, H.K. In situ synthesis of thin zeolitic-imidazolate framework zif-8 membranes exhibiting exceptionally high propylene/propane separation. *J. Am. Chem. Soc.* **2013**, *135*, 10763-10768.
62. Shah, M.N.; Gonzalez, M.A.; McCarthy, M.C.; Jeong, H.K. An unconventional rapid synthesis of high performance metal-organic framework membranes. *Langmuir* **2013**, *29*, 7896-7902.
63. Hara, N.; Yoshimune, M.; Negishi, H.; Haraya, K.; Hara, S.; Yamaguchi, T. Diffusive separation of propylene/propane with zif-8 membranes. *J. Memb. Sci.* **2014**, *450*, 215-223.
64. Liu, D.; Ma, X.; Xi, H.; Lin, Y.S. Gas transport properties and propylene/propane separation characteristics of zif-8 membranes. *J. Memb. Sci.* **2014**, *451*, 85-93.
65. Eum, K.; Ma, C.; Rownaghi, A.; Jones, C.W.; Nair, S. Zif-8 membranes via interfacial microfluidic processing in polymeric hollow fibers: Efficient propylene separation at elevated pressures. *ACS Appl. Mater. Interfaces* **2016**, *8*, 25337-25342.
66. Liu, G.; Chernikova, V.; Liu, Y.; Zhang, K.; Belmabkhout, Y.; Shekhah, O.; Zhang, C.; Yi, S.; Eddaoudi, M.; Koros, W.J. Mixed matrix formulations with mof molecular sieving for key energy-intensive separations. *Nat. Mater.* **2018**, *17*, 283-289.
67. Eum, K.; Ma, C.; Koh, D.-Y.; Rashidi, F.; Li, Z.; Jones, C.W.; Lively, R.P.; Nair, S. Zeolitic imidazolate framework membranes supported on macroporous carbon hollow fibers by fluidic processing techniques. *Adv. Mater. Interfaces* **2017**, *4*, 1700080-1700090.

