Supporting Information for

Ionic liquid enhancement of interface compatibility in mixed-linker ZIF-based mixed matrix membranes for advanced CO_2/CH_4 separation

Lili Gong [a,b], Zhili Cai [b], Qi Wu [b], Lu Liu [b], Can Wang [b], Linglong Shan [b], Xianghai Meng [a], Shuangjiang Luo [b,c*], Zhichang Liu [a*], Suojiang Zhang [b*]

[a] *State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering and Environment, China University of Petroleum, Beijing, 102249, China*
[b] *CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences (CAS), Beijing, 100190, China*
[c] *Dalian National Laboratory for Clean Energy, CAS, Dalian, 116023, China*

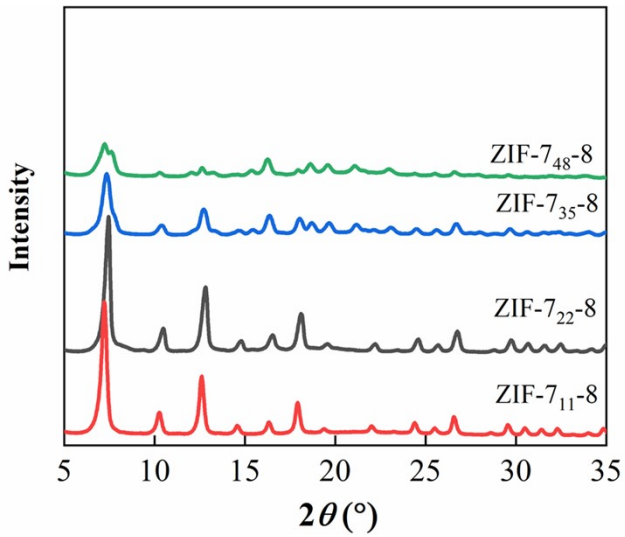

Fig. S1 The WAXD patterns of ZIF-7-8 nanoparticles

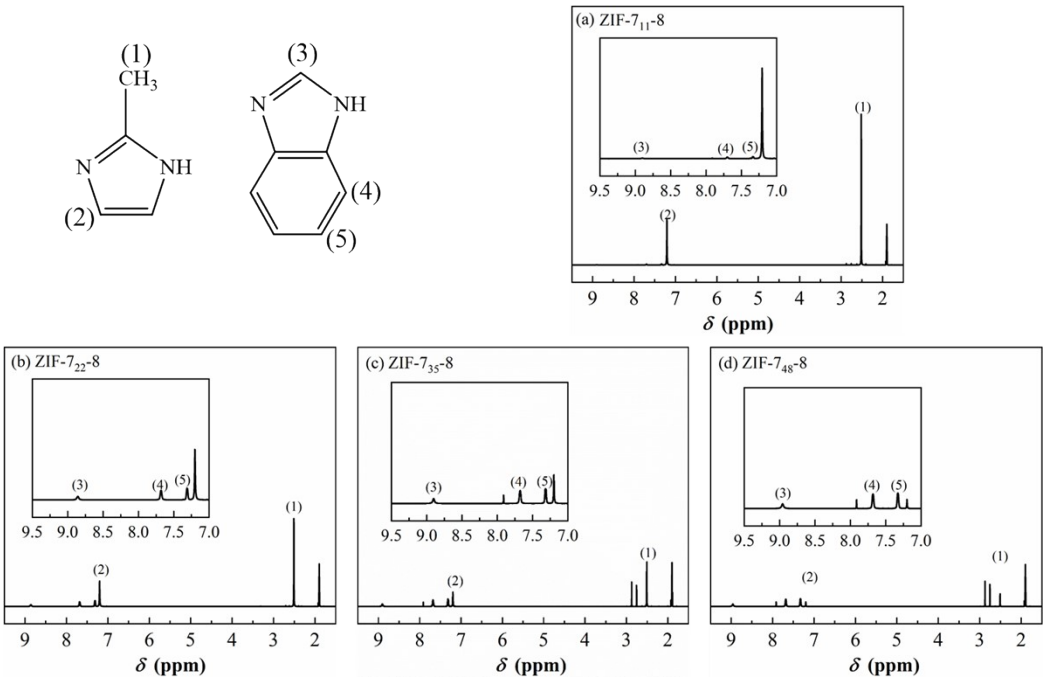

Fig. S2 Solution ^{1}H-NMR spectra of the mixed-linker ZIF-7-8 nanoparticle. Protons of mIm are observed at (1) 2.51 ppm and (2) 7.21 ppm; and protons of bIm are shown at (3) 8.90 ppm, (4) 7.71 ppm, and (5) 7.34 ppm. Deuterated acetic acid-d4 is used as the solvent.

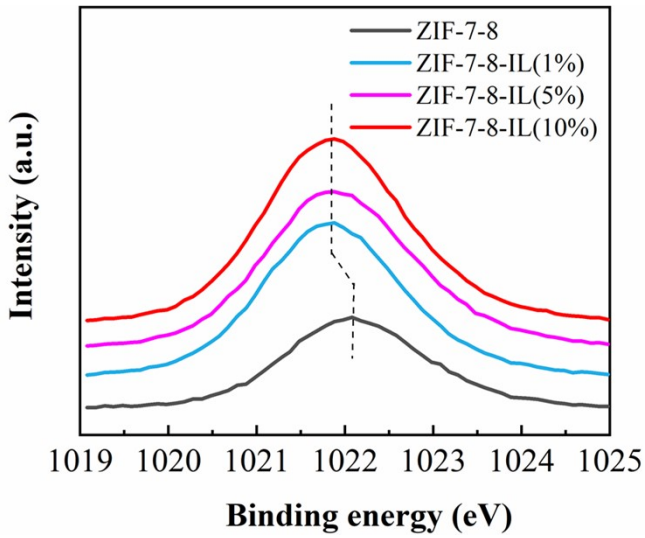

Fig. S3 Zn 2p3/2 XPS spectra of ZIF-7-8 and ZIF-7-8-IL.

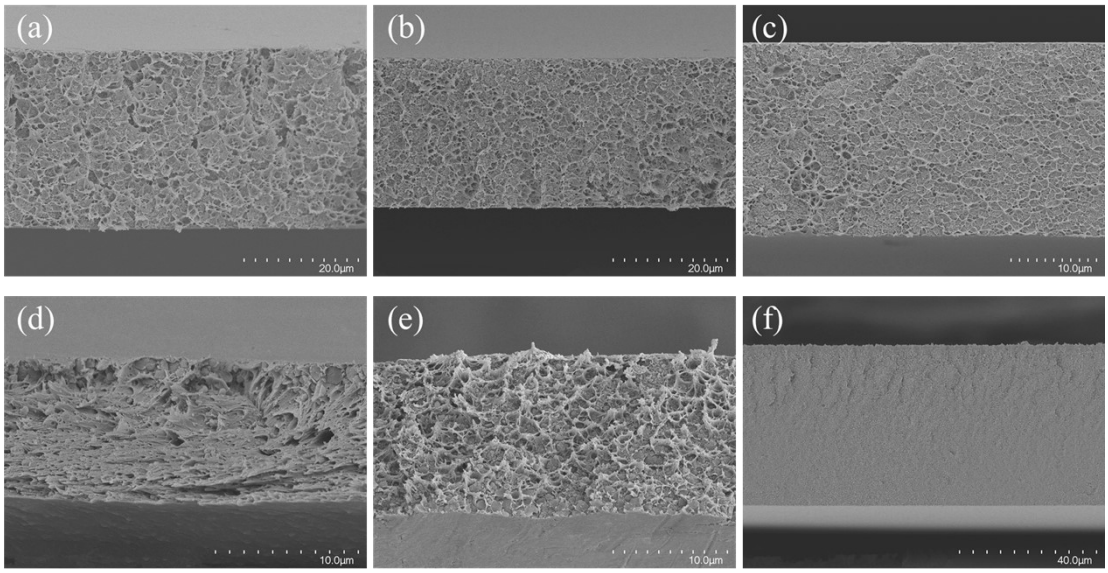

Fig. S4 SEM cross-section images of (a) 10%ZIF-7-8/PI, (b) 20%ZIF-7-8/PI, (c) 25%ZIF-7-8/PI, (d) 10%ZIF-7-8-IL (1%)/PI, (e) 20%ZIF-7-8-IL (10%)/PI, and (f) 25%ZIF-7-8-IL (10%)/PI

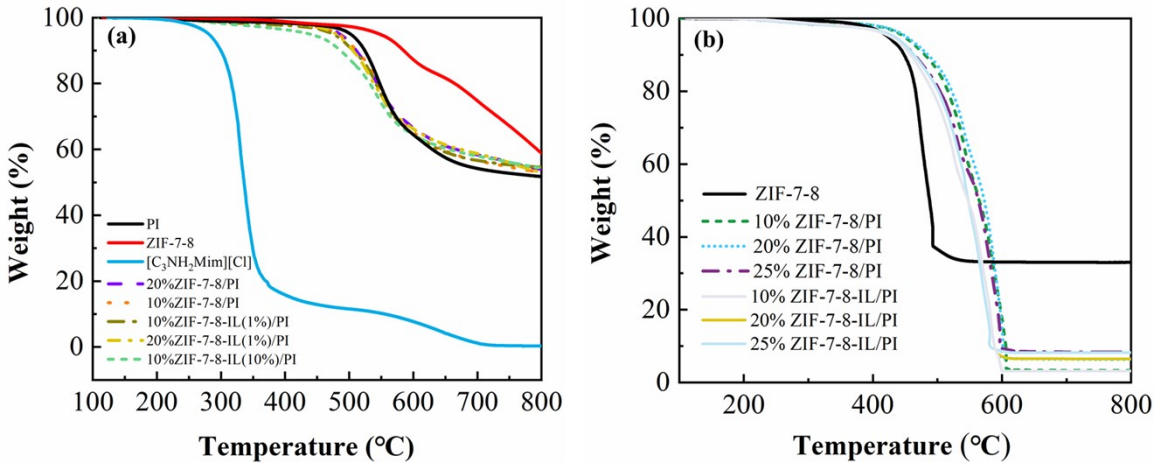

Fig. S5 TGA curves of ZIF-7-8 nanoparticles, [AEMim][Cl], and various membranes in the nitrogen (a) and air (b) atmosphere

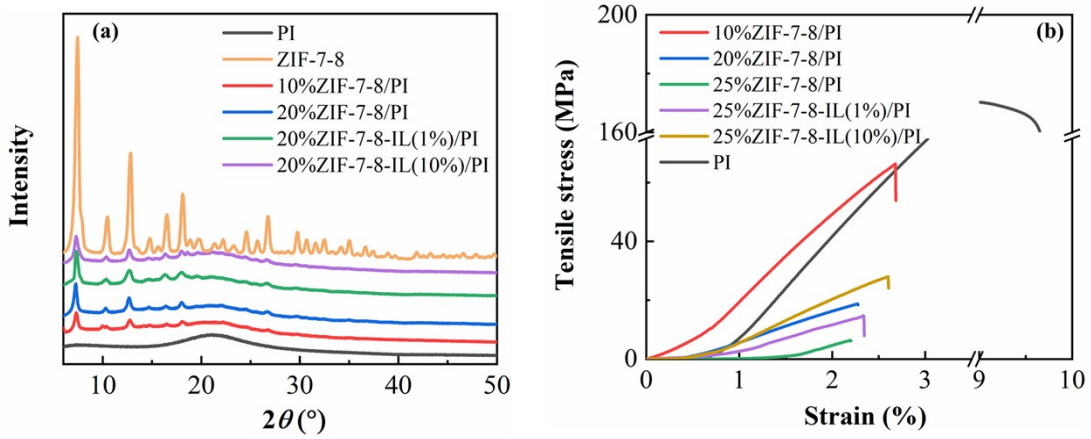

Fig.S6 (a) WAXD patterns and (b) tensile properties of pristine PI, ZIF-7-8/PI and ZIF-7-8-IL/PI MMMs

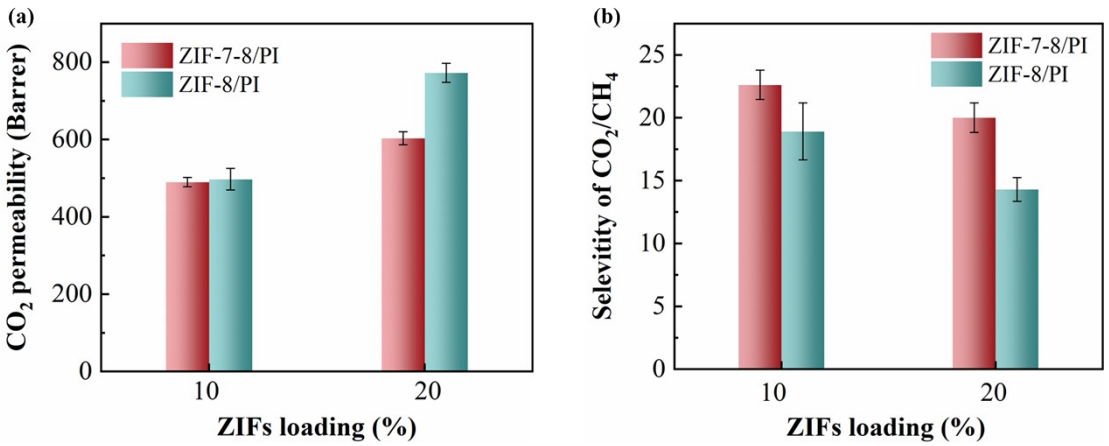

Fig. S7 Pure-gas (a) CO_2 permeabilities and (b) CO_2/CH_4 selectivities of ZIF-7-8/PI and ZIF-8/PI MMMs with different ZIFs mass loadings.

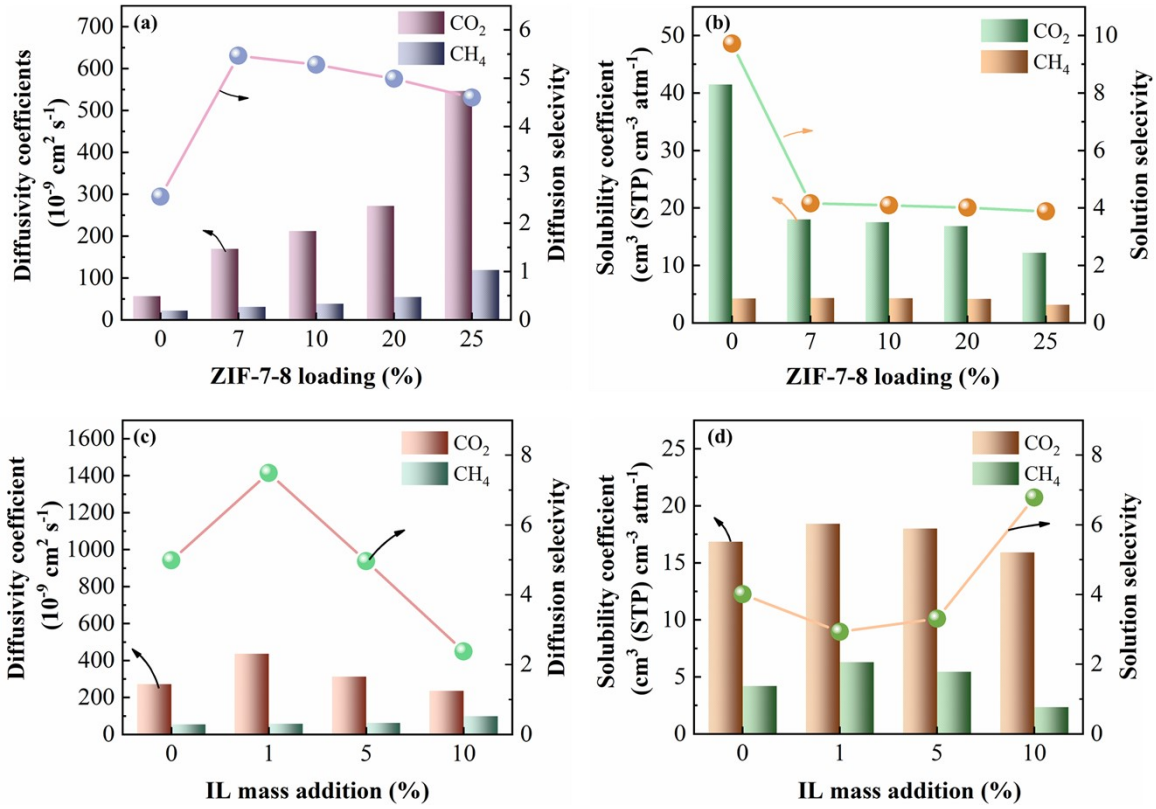

Fig. S8 Diffusivity coefficients (*D*), solubility coefficients (*S*) and their selectivities for (a), (b) ZIF-7-8/PI MMMs as a function of ZIF-7-8 mass loading, and (c), (d) 20%ZIF-7-8-IL/PI MMMs with different IL loadings.

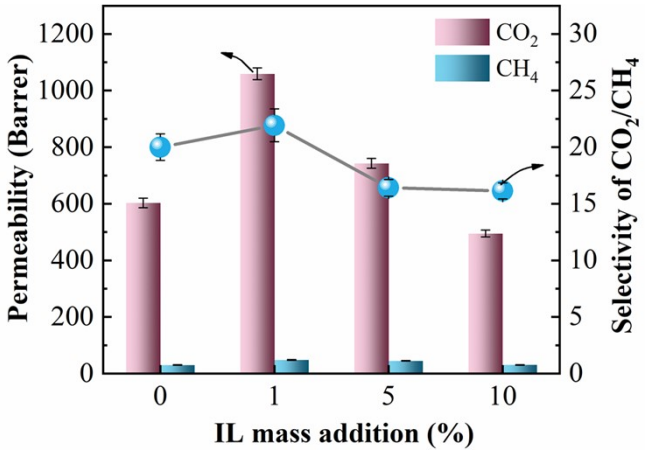

Fig. S9 Pure-gas separation properties of 20%ZIF-7-8-IL/PI MMMs as a function of IL mass loading.

Table S1 EXAFS fitting parameters at the Zn K-edge for various samples

Sample	Shell	*CN*[a]	*R*(Å)[b]	σ^2(Å^2)[c]	ΔE_0(eV)[d]	*R factor*
Zn foil	Zn-Zn1	6*	2.64±0.02	0.0093±0.0006	6.8±0.4	0.0006
	Zn-Zn2	6*	2.77±0.03	0.0084±0.0039	8.1±1.6	
ZnO	Zn-O	3.8±1.0	1.97±0.03	0.0030±0.0025	3.7±1.5	0.0157
	Zn-O-Zn	11.6±1.6	3.23±0.04	0.0039±0.0022	2.2±1.2	
ZnPc	Zn-N	3.8±0.8	1.98±0.02	0.0020±0.0019	3.6±1.8	0.0100
ZIF-7-8	**Zn-N**	**4.1±1.4**	**1.98±0.02**	**0.0033±0.0027**	**4.2±0.6**	**0.0102**
ZIF-7-8-IL (1%)	**Zn-N**	**4.5±0.7**	**1.99±0.02**	**0.0103±0.0026**	**5.2±0.8**	**0.0117**
ZIF-7-8-IL (10%)	**Zn-N**	**4.6±1.0**	**1.99±0.01**	**0.0041±0.0021**	**2.9±0.7**	**0.0121**

[a]*CN*, coordination number; [b]*R*, the distance between absorber and backscatter atoms; [c]σ^2, Debye-Waller factor to account for thermal and structural disorders; [d]ΔE_0, inner potential correction; *R* factor indicates the goodness of the fit. S_0^2 was fixed to 0.74, according to the experimental EXAFS fit of Zn foil by fixing CN as the known crystallographic value. FA reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; $CN > 0$; $\sigma^2 > 0$ Å^2; $|\Delta E_0| < 10$ eV; *R* factor < 0.02.

Table S2 BET surface areas, pore volumes and average pore width of ZIF-7-8 and ZIF-7-8-IL nanoparticles

	BET surface area/(m^2/g)	**Pore volume(V-t) /(m^3/g)**	**Average pore width/nm**
ZIF-8	1612	0.583	0.643
ZIF-7-8	1084	0.369	0.638
ZIF-7-8-IL (1%)	985	0.341	0.663
ZIF-7-8-IL (5%)	885	0.314	0.643
ZIF-7-8-IL (10%)	419	0.146	0.648

Table S3 The mechanical properties of the pristine PI membrane and MMMs

Membrane	Elastic modulus (MPa)	Breaking elongation strain (%)	Tensile break stress (MPa)	Tensile strength (MPa)
Pristine PI	3579.39	9.78	123.45	170.45
10%ZIF-7-8/PI	3141.87	2.68	53.89	66.32
20%ZIF-7-8/PI	1129.08	2.28	18.39	18.76
25%ZIF-7-8/PI	906.30	2.20	6.17	6.38
25%ZIF-7-8-IL(1%)/PI	1743.71	2.35	7.90	14.73
25%ZIF-7-8-IL(10%)/PI	2129.94	2.61	24.10	28.00

Table S4 Mixed-gas permeabilities and selectivities of 25%ZIF-7-8/PI and 25%ZIF-7-8-IL(1%)/PI MMMs using 50:50vol% CO_2:CH_4 feed at 35 °C.

Feed pressure/bar	25%ZIF-7-8/PI			25%ZIF-7-8-IL(1%)/PI		
	P_{CO2} (Barrer)	P_{CH4} (Barrer)	Selectivity	P_{CO2} (Barrer)	P_{CH4} (Barrer)	Selectivity
4	728	33	22	1166	49	24
8	640	32	20	1013	46	22
12	620	32	19	1066	55	21
16	568	30	19	1096	58	20
20	466	25	19	1167	63	19

Table S5 CO_2 permeabilities and CO_2/CH_4 selectivities of ZIF-7-8-IL/PI MMMs in this work and other reported MMMs

MOF-based filler	Polymer	Test condition	CO_2 permeability(Barrer)	CO_2/CH_4 selectivity	Ref.
0	6FDA-DAM-PI	35 °C, 2 bar	308	25	This work
10%ZIF-7-8			490	23	
20%ZIF-7-8			603	20	
25%ZIF-7-8			865	18	
10%ZIF-7-8-IL(1%)			879	25	
20%ZIF-7-8-IL(1%)			1060	22	
25%ZIF-7-8-IL(1%)			1206	21	
25%ZIF-7-8-IL(1%)		35 °C, 4 bar, CO_2/CH_4 (50/50 vol%)	1166	24	
25%ZIF-7-8-IL(1%)		-45 °C, 4 bar, CO_2/CH_4 (50/50 vol%)	1060	66	
Enhancement(%)			**59~292**	**-12~164**	
0	Matrimid	35 °C, 3.5 bar	9	35	[19]
30%ZIF-8			38	21	
40%ZIF-8			100	12	
30%ZIF-8-DA			19	36	

40%ZIF-8-DA			22	20	
30%ZIF-8-DA		35 °C, 3.5 bar, 40:60 mol % CO_2/CH_4	16	40.6	
40%ZIF-8-DA			18	34.3	
Enhancement(%)			**77~1011**	**-67~16**	
0	PSF	30 °C， 6 bar	200	22	[24]
6%ZIF-8			427	19	
[BMIM][Tf2N]/ZIF-8(6%)			307	38.3	
Enhancement(%)			**54~114**	**-13.6~74.1**	
0	Pebax-1657	25 °C, 1 bar	71[a]	18[a]	[36]
15%ZIF-8			125[a]	19[a]	
[bmim][Tf2N]@ZIF-8-15%			100[a]	35[a]	
Enhancement(%)			**41~76-**	**6~94**	
0	TBDA2-6FDA-PI	1 bar, 35 °C	285	35	[50]
ZIF-8(7%)			560	27	
ZIF-8(20%)			896	21	
ZIF-8(30%)			1437	16	

ZIF-8@PD(7%)			380	25	
ZIF-8@PD(20%)			702	23	
ZIF-8@PD(30%)			1056	20	
ZIF-8@PD-PI (20%)		1 bar.35 °C, CO_2/CH_4 (50/50 vol%)	630	23	
Enhancement(%)			**270~402**	**-34~-54**	
0			88[a]	21[a]	
30%ZIF-8		35 °C and 4 bar	277[a]	3[a]	
30%ZIF-8@PDA			195[a]	18[a]	
50%ZIF-8@PDA	TB		260[a]	16[a]	[51]
30%ZIF-8@PDA		35 °C and 4 bar, 50:50 vol% CO_2:CH_4	180[a]	23[a]	
50%ZIF-8@PDA			262[a]	21[a]	
Enhancement(%)			**105~214**	**-86~8.7**	
0			826	17	
40%UiO-66-NH_2	6FDA-DAM-PI	35 °C, 3 bar	2474	13	[52]
Enhancement(%)			**199**	**-23**	
0	PIM-1	35 °C, 3.5 bar	3874	17.6	[54]

0.1-ZIF-8			6338	18.8	
0.1-ZIF-8		35 °C, 3.5 atm，40:60 mol% CO_2/CH_4	6186	16.5	
Enhancement(%)			**0.60~0.64**	**-6.25~6.8**	
0			390	24	
15%ZIF-90	6FDA-DAM	25 °C, 2 bar, 1:1 CO_2/CH_4 mixture	720	37	[53]
Enhancement(%)			**85**	**54**	
0			7062	6.3	
10%UiO-66-NH2@IL	PIM-1	20 °C, 1 bar	8283	12.3	[55]
Enhancement(%)			**17**	**95**	
0			21	4.6	
10-N-HKUST-1			11	4.1	
30-N-HKUST-1			9	4.9	
50-N-HKUST-1	PEI	25 °C and 1.5 bar.	19	4.7	[56]
30-M-HKUST-1			46	2.7	
Enhancement(%)			**-57~119**	**-70~7**	
0	ODPA-TMPDA	25 °C and 1 bar.	112	36	[57]

30%ZIF-8	316	33	
2%ns-CuBDC	99	43	
20%ZIF-8+2%ns-CuBDC	177	42	
Enhancement(%)	**11.6~182**	**-8~19**	

Enhancement(%) refers to the percentage of improvement range of CO2 permeability and the CO2/CH4 selectivity compared to the pristine polymer. [a] Values are approximated from plots.