Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

Supporting Information

Polymer of Intrinsic Microporosity/Metal Organic Framework Hybrid Membrane with Improved Interfacial Interaction for High-performance CO₂ Separation

Zhenggong Wang,^{†a,b} Huiting Ren,^{†a,b} Shenxiang Zhang,^{a,c} Feng Zhang,^a and Jian Jin^{* a}

a. CAS Key Laboratory of Nano-Bio Interface, i-Lab, Suzhou Institute of Nano-Tech and

Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China.

- b. University of Chinese Academy of Sciences, Beijing 100049, China
- c. School of Nano-Tech and Nano-Bionics, University of Science and Technology of China,

Hefei 230026, China.

1. Supplementary Figures



Figure S1. SEM image of (a) NH₂-UiO-66 and (b) UiO-66 nanoparticles.



Figure S2. XRD patterns of UiO-66 and NH₂-UiO-66.



Figure S3. Nitrogen adsorption isotherms of NH₂-UiO-66 and UiO-66 measured at 77 K.



Figure S4. X-ray diffraction patterns of PAO-PIM-1/NH₂-UiO-66 hybrid membranes.



Figure S5. Cross-sectional SEM-EDX of PAO-PIM-1/NH₂-UiO-66 membrane. (a) SEM, (b) EDX spectra, and element mapping of (c) carbon, (d) zirconium, (e) oxygen, and (f) nitrogen.



Figure S6. Thermogravimetry (TG) analysis of PAO-PIM-1 and PAO-PIM-1/ NH_2 -UiO-66 with different NH_2 -UiO-66 loadings.



Figure S7. Cross-sectional SEM images with different magnifications of a-c) PAO-PIM-1, d-f) PAO-PIM-1/NH₂-UiO-66 (7%), g-i) PAO-PIM-1/NH₂-UiO-66 (15%), k-m) PAO-PIM-1/NH₂-UiO-66 (30%).

2. Supplementary Tables

Table S1. Diffusion coefficient (*D*), solubility coefficient (*S*), diffusion selectivity (α_D), and solubility selectivity (α_S) for different gases (N₂, CH₄, CO₂) of pure PAO-PIM-1 membrane, PAO-PIM-1-NH₂-UiO-66 (7%), PAO-PIM-1-NH₂-UiO-66 (15%), and PAO-PIM-1-NH₂-UiO-66 (30%) membranes.

Membranes	D (10 ⁻⁸ cm ² /g)		S (1	(10 ⁻² cm ³ /cm ³ cmHg ⁻¹)		CO_2/N_2		CO ₂ /CH ₄		
	N_2	CH ₄	CO ₂	N_2	CH ₄	CO ₂	α_D	α_S	α_D	α_S
PAO-PIM-1	59.7	11.3	54.4	1.72	10.7	53.3	0.91	31	4.81	4.98
PAO-PIM- 1/NH ₂ -UiO- 66 (7%)	57	22.3	136	2.32	7.08	28.1	2.38	12.1	6.1	3.97
PAO-PIM- 1/NH ₂ -UiO- 66 (15%)	106	36	224	1.52	5.93	21.6	2.11	14.2	6.22	3.64
PAO-PIM- 1/NH ₂ -UiO- 66 (30%)	-	67.7	650	-	5.58	13.0	-	-	9.6	2.33
PAO-PIM- 1/UiO-66 (30%)		74.9	1154		5.98	7.16			15.4	1.2

Table S2. Mixed gas performance of PAO-PIM- $1/NH_2$ -UiO-66 (30%) membrane for CO₂/N₂ gas pairs. The mixed gas permeation was tested at a pressure of 1 bar. The gas composition was determined via a calibrated gas chromatograph.

CO ₂ /CH ₄ gas ratio (Volume ratio)	P _{CO2} (barrer)	a (CO ₂ /CH ₄)		
Pure gas	8425	23		
3:7	8271	26.6		
1:1	8329	27.6		
7:3	8322	28.5		

CO ₂ /N ₂ gas ratio (Volume ratio)	P _{CO2} (barrer)	a (CO ₂ /N ₂)
Pure gas	8425	27.5
3:7	8351	31.5
1:1	8541	33.9
7:3	8446	34.9

Table S3. Mixed gas performance of PAO-PIM-1/NH₂-UiO-66 (30%) membrane for CO_2/N_2 gas pairs. The mixed gas permeation was tested at a pressure of 1 bar. The gas composition was determined via a calibrated gas chromatograph.

Table S4. Aging performance of PAO-PIM-1/NH₂-UiO-66 (30%) hybrid membrane.

PAO-PIM-1/NH ₂ - UiO-66 (30%)	Pe	rmeability	(barrer)	Ideal selectivity (α)		
Aging (days)	CO ₂	N_2	CH ₄	CO_2/N_2	CO ₂ /CH ₄	
1d	8425	306.1	377.6	27.5	23.0	
2d	7256	228.7	272.7	31.7	26.6	
3d	7125	189	233	37.7	30.6	
6d	7036	230	252	30.5	27.9	
11d	6518	184	212	35.4	30.7	
18d	6012	176	202	34.2	29.8	
21d	5805	177	188	33	30.9	
31d	5800	175	185	33	31.3	
80d	5630	175	-	32	-	

PAO-PIM-1/UiO66 (30%)	Perm	eability (l	oarrer)	Ideal selectivity (α)		
Aging (days)	CO ₂	N_2	CH ₄	CO_2/N_2	CO ₂ /CH ₄	
1d	8126	361	442	22.5	18.4	
7d	6300	252	289	25	21.8	
14d	4791	181	207	26.5	23.1	
21d	4230	156	174	27.2	24.3	
28d	3850	137	153	28.1	25.1	

 Table S5. Aging performance of PAO-PIM-1/UiO-66 (30%) hybrid membrane.

Table S6. Aging performance of PIM-1/NH₂-UiO-66 (30%) hybrid membrane.

PIM-1/NH ₂ -UiO66 (30%)	Perm	eability (l	barrer)	Ideal selectivity (a)		
Aging (days)	CO ₂	N_2	CH ₄	CO ₂ /N ₂	CO ₂ /CH ₄	
1	9420	603	768	15.6	12.3	
7d	6639	354	451	18.8	14.7	
14d	6010	286	369	20	16.3	
21d	5382	256	313	21.0	17.2	
28d	4782	210	256	22.7	18.7	