

Supporting Information

Interface Manipulation of CO₂-philic Composite Membranes Containing Designed UiO-66 Derivatives towards Highly-efficient CO₂ Capture

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Mixed gas tests

Mixed gas permeation properties of MPCM membrane were investigated based on a binary 50% CO₂ and 50% N₂ mixture under 35 °C. To ensure constant gas molarity in the retentate, small amounts of retentate are slowly discharged into water or the atmosphere via a silicon piping. The sampling process was initiated by evacuating the line from the receiving volume (the lower chamber: downstream) to GC by vacuum pump. The compositions of the feed and permeate were analyzed by GC. The choice of carrier gas in the GC setup is nitrogen.

Detailed experimental and set-up descriptions can also be found elsewhere.^[1,2] Permeability of each gas can be determined using the following equations:

$$P_A = \frac{273 \times 10^{10}}{760} \frac{y_A \times V \times l}{AT(P_2 \times \phi_A \times (76/14.7) \times x_A) dt} \frac{dp}{dt} \quad (1)$$

$$P_B = \frac{273 \times 10^{10}}{760} \frac{y_B \times V \times l}{AT(P_2 \times \phi_B \times (76/14.7) \times x_B) dt} \frac{dp}{dt} \quad (2)$$

where P_A and P_B refer to the permeability of CO₂ and N₂ respectively. P_2 symbolizes the upstream feed gas pressure (psi). x and y represent molar fractions of the gas in feed and permeate sides, respectively. ϕ_A , ϕ_B indicate fugacity coefficients of respective gases in the upstream.

The mixed gas selectivity is expressed by the following equation:

$$\alpha_A = \frac{P_A}{P_B} \quad (3)$$

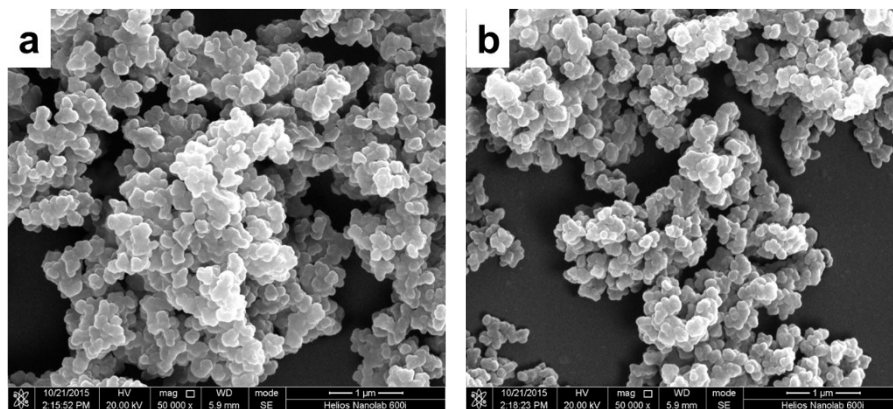


Fig. S1. SEM images of (a) UiO-66-NH₂ and (b) UiO-66-MA.

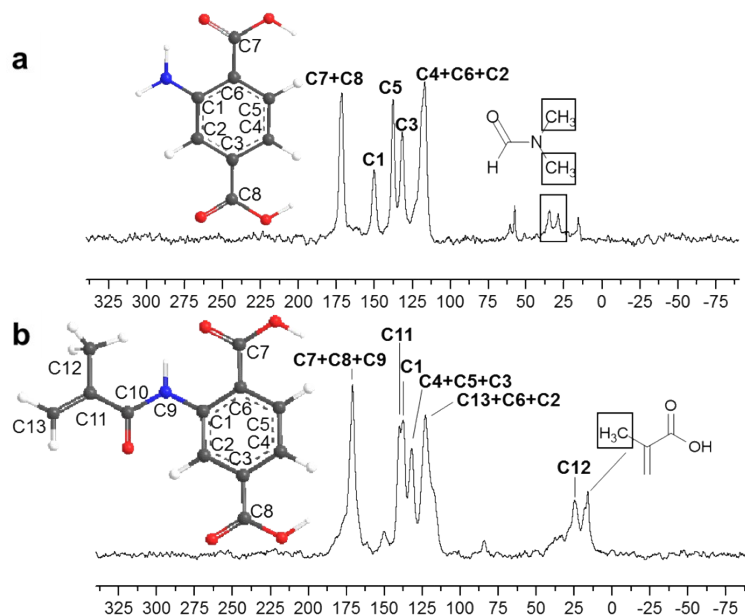


Fig. S2. ^{13}C MAS NMR spectra of a) UiO-66- NH_2 and b) UiO-66-MA.

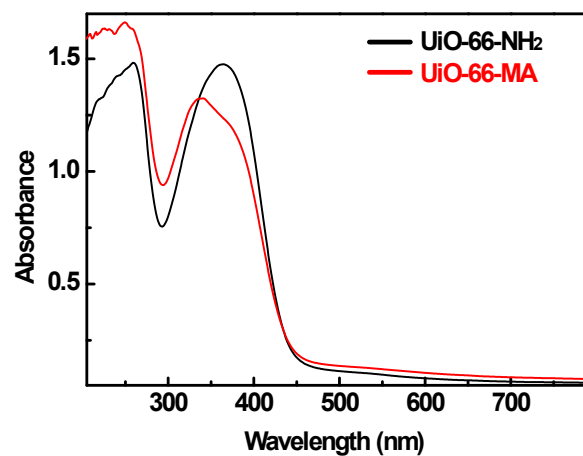


Fig. S3. UV-vis diffuse reflection spectra of UiO-66- NH_2 and UiO-66-MA.

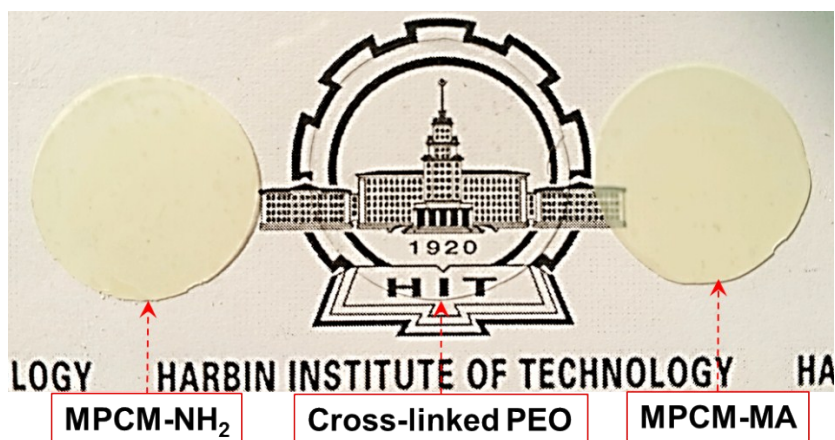


Fig. S4. Digital images of cross-linked PEO, MPCM7/3- NH_2 and MPCM7/3-MA.

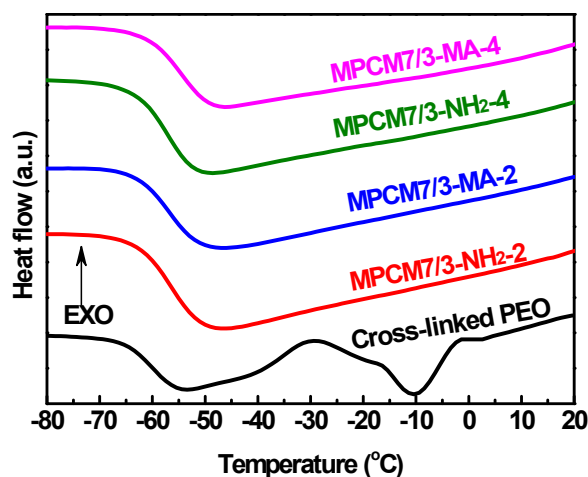


Fig. S5. DSC thermograms of cross-linked PEO and MPCMs.

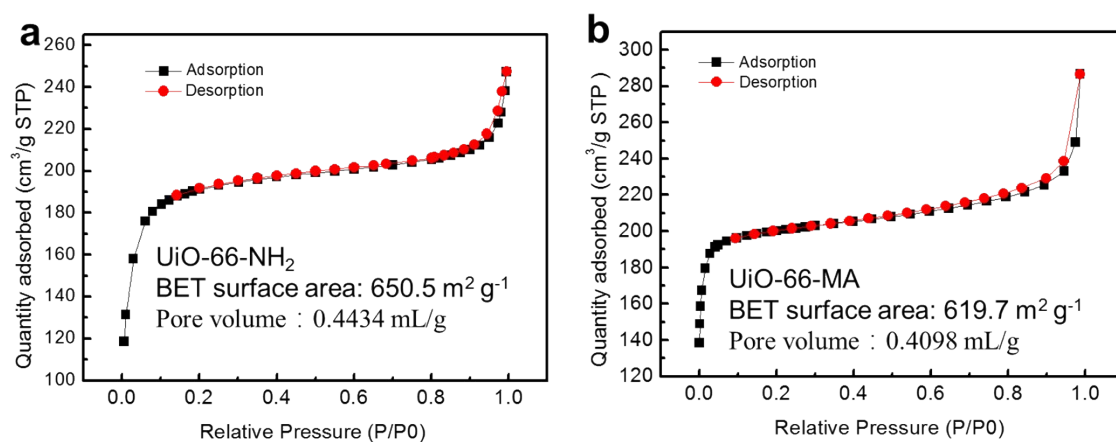


Fig S6. N₂ adsorption isotherms of (a) UiO-66-NH₂ and (b) UiO-66-MA

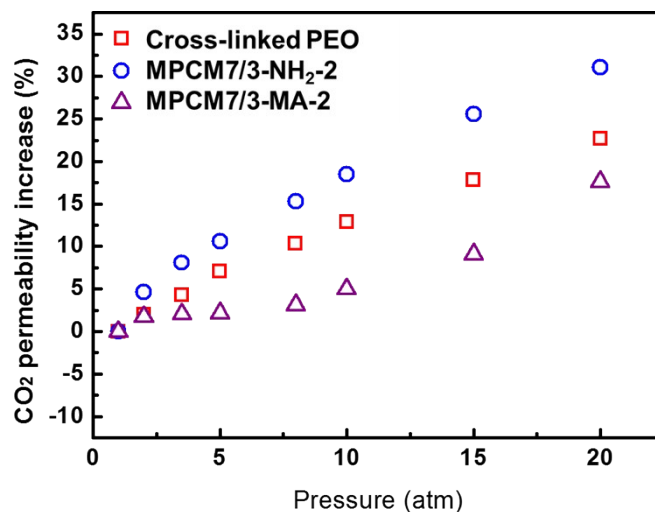


Fig S7. Plasticization behaviours of cross-linked PEO, MPCM7/3-NH₂-2 and MPCM7/3-MA-2 reflected in CO₂ permeability

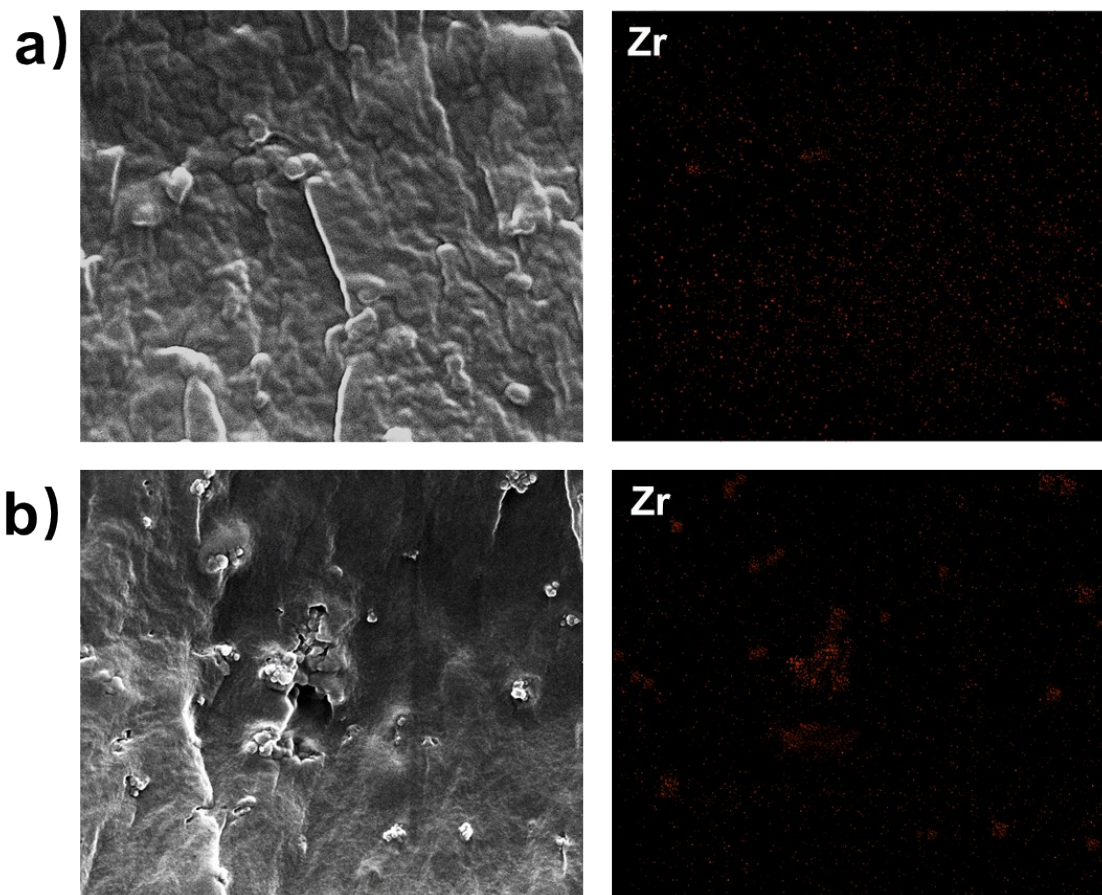


Fig S8. Cross-sectional view EDS mapping of Zr in a) MPCM7/3-MA-4 and b) MPCM7/3-NH₂-4

Table. 1. Diffusivity and solubility of CO₂, N₂, and CH₄, and CO₂ diffusivity and selectivity selectivity over N₂ and CH₄ for MPCM7/3-NH₂.

Membrane	CO ₂		N ₂		CH ₄		CO ₂ /N ₂		CO ₂ /CH ₄	
	D ^{a)}	S ^{b)}	D	S	D	S	α_D	α_S	α_D	α_S
Cross-linked PEO	1.66	2.45	1.27	0.0640	1.38	0.186	1.31	38.3	1.20	13.2
MPCM7/3-NH ₂ -1	1.67	2.48	1.29	0.0660	1.35	0.187	1.30	37.5	1.23	13.2
MPCM7/3-NH ₂ -2	1.90	2.54	1.49	0.0677	1.51	0.209	1.28	37.6	1.26	12.1
MPCM7/3-NH ₂ -3	1.85	2.69	1.46	0.0673	1.52	0.205	1.27	39.9	1.22	13.1
MPCM7/3-NH ₂ -4	1.79	2.78	1.45	0.0694	1.54	0.216	1.24	40.1	1.16	12.8

^{a)}D×10⁶ cm²/s, ^{b)}S×10² cm³/cm³ cm Hg

Table. 2. Diffusivity and solubility of CO₂, N₂, and CH₄, and CO₂ diffusivity and selectivity selectivity over N₂ and CH₄ for MPCM7/3-MA.

Membrane	CO ₂		N ₂		CH ₄		CO ₂ /N ₂		CO ₂ /CH ₄	
	D ^{a)}	S ^{b)}	D	S	D	S	α_D	α_S	α_D	α_S
Cross-linked PEO	1.66	2.45	1.27	0.0640	1.38	0.186	1.31	38.3	1.20	13.2
MPCM7/3-MA-1	2.31	2.75	1.61	0.0794	2.12	0.189	1.43	34.6	1.09	14.6
MPCM7/3-MA-2	3.22	2.93	2.40	0.0845	3.07	0.204	1.34	34.6	1.05	14.3
MPCM7/3-MA-3	3.02	3.00	2.24	0.0946	2.74	0.219	1.35	31.7	1.10	13.7
MPCM7/3-MA-4	2.18	3.03	1.48	0.0984	2.05	0.211	1.47	30.7	1.06	14.3

^{a)}D×10⁶ cm²/s, ^{b)}S×10² cm³/cm³ cm Hg

Table. 3. Glass-transition temperatures of pristine XLPEO and MPCM7/3 membranes

Membrane	Glass-transition temperature (°C)
Cross-linked PEO	-65.5
MPCM7/3-NH ₂ -2	-63.7
MPCM7/3-MA-2	-62.5
MPCM7/3-NH ₂ -4	-61.5
MPCM7/3-MA-4	-60.6

Table. 4. Diffusivity and solubility of CO₂, N₂, and CH₄, and CO₂ diffusivity and selectivity selectivity over N₂ and CH₄ for MPCM-MA.

Membrane	CO ₂		N ₂		CH ₄		CO ₂ /N ₂		CO ₂ /CH ₄	
	D ^{a)}	S ^{b)}	D	S	D	S	α_D	α_S	α_D	α_S
MPCM0/10-MA-2	0.849	2.39	0.434	0.0802	0.590	0.173	1.96	29.8	1.44	13.8
MPCM3/7-MA-2	1.59	2.47	0.802	0.0805	1.06	0.185	1.98	30.6	1.50	13.4
MPCM5/5-MA-2	2.29	2.70	1.56	0.0830	2.08	0.187	1.47	32.5	1.10	14.4
MPCM7/3-MA-2	3.22	2.93	2.40	0.0845	3.07	0.204	1.34	34.6	1.05	14.3
MPCM9/1-MA-2	4.60	3.15	3.70	0.0855	4.59	0.221	1.24	36.9	1.00	14.2

^{a)}D×10⁶ cm²/s, ^{b)}S×10² cm³/cm³ cm Hg

Table. 5 Mixed gas tests results.

Membrane	Permeability (Barrer)		Selectivity
	CO ₂	N ₂	CO ₂ /N ₂
Cross-linked PEO	366	9.2	39.8
MPCM7/3-MA-2	974	26.3	37.1
MPCM9/1-MA-2	1439	38.3	37.6

Reference:

1 J. Xia, T.-S. Chung and D. R. Paul, *J. Membr. Sci.*, 2014, 450, 457-468

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- 2 P. S. Tin, T. S. Chung, Y. Liu, R. Wang, S. L. Liu and K. P. Pramoda, *J. Membr. Sci.*, 2003, 225, 77-90.