

Supporting Information for

Developing mixed matrix membranes with good CO₂ separation performance based on PEG-modified UiO-66 MOF and 6FDA-durene polyimide

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Experimentals

S1. Gas Permeation Measurement: Constant-Volume/Variable-Pressure Measurements

S 1.1. Single gas separation analysis

Gas permeability measurements of pure gases were evaluated using a vacuum-applied time-lag instrument based on a constant-volume/variable-pressure method. All of the experiments were carried out at a feed pressure of 1 bar and a temperature of 30 °C. To remove all residual gases, before the measurement, both upstream and downstream were evacuated thoroughly to below 10^{-5} Torr (1.33×10^{-8} bar) until the readout appeared to be zero. The downstream volume was found to be 57 cm³ by calibration using a Kapton membrane. A Baraton transducer (MKS; Model No. 626B02TBE) with full scales of 10,000 and 2 Torr was used to measure the upstream and downstream pressures respectively. The permeate side pressure was recorded as a function of time using a transducer. The permeability coefficient was obtained from the linear slope of the downstream pressure versus a time plot (dp/dt) according to the following equation:

$$P = \frac{273 \text{ K}}{76 \text{ cmHg}} \times \frac{Vl}{ATp_0} \times \frac{dp}{dt} \quad (1)$$

Where P is the permeability expressed in barrer (1 Barrer = 10^{-10} [cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹], V (cm³) is the downstream volume, l (cm) is the membrane thickness, A (cm²) is the effective area of the membrane, T (K) is

the measurement temperature, p_o (Torr) is the pressure of the feed gas in the upstream chamber, and dp/dt is the rate of the pressure change under a steady state. The permeation tests were repeated at least three times for each gas and the standard deviation from the mean values of the permeabilities was within ca. 3%. The sample-to-sample reproducibility was high and within 3%. The effective membrane areas were 1.13 cm². The ideal perm-selectivity, $\alpha_{A/B}$, of the membrane for a pair of gases (A and B) is defined as the ratio of the individual gas permeability coefficients:

$$\alpha_{\frac{A}{B}} = \frac{P_A}{P_B} \quad (2)$$

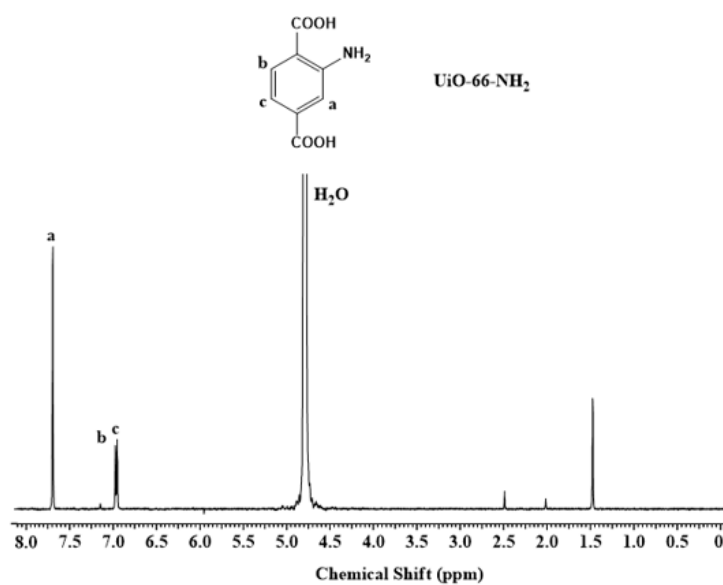
The diffusivity and solubility were obtained from the time-lag (θ) value according to the following equations:

$$D = \frac{l^2}{6\theta} \quad (3)$$

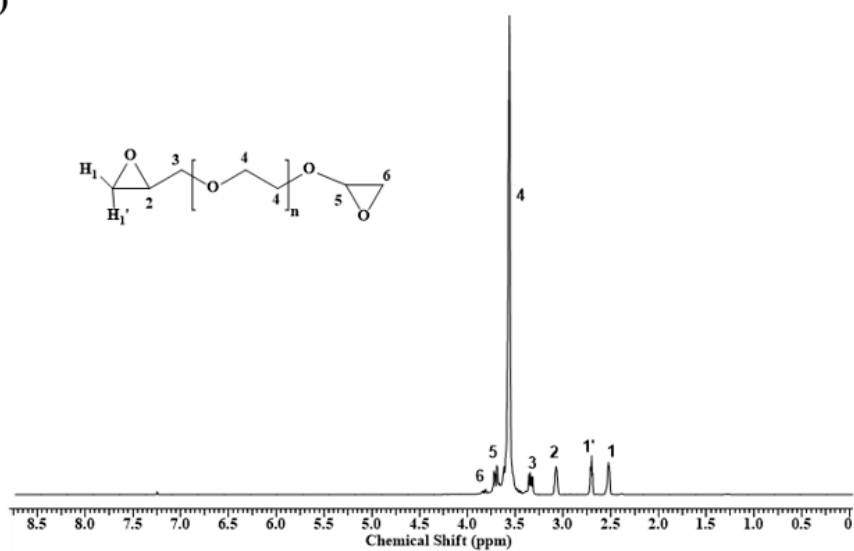
$$S = \frac{P}{D} \quad (4)$$

Where, D (cm² s⁻¹) is the diffusivity coefficient, l is the membrane thickness (cm), and θ is the time lag (s), as obtained from the intercept of the linear steady-state part of the downstream pressure versus a time plot. The solubility, S , was calculated from Equation (4) with the permeability and diffusivity obtained from Equation (3) and (4).

(a)



(b)



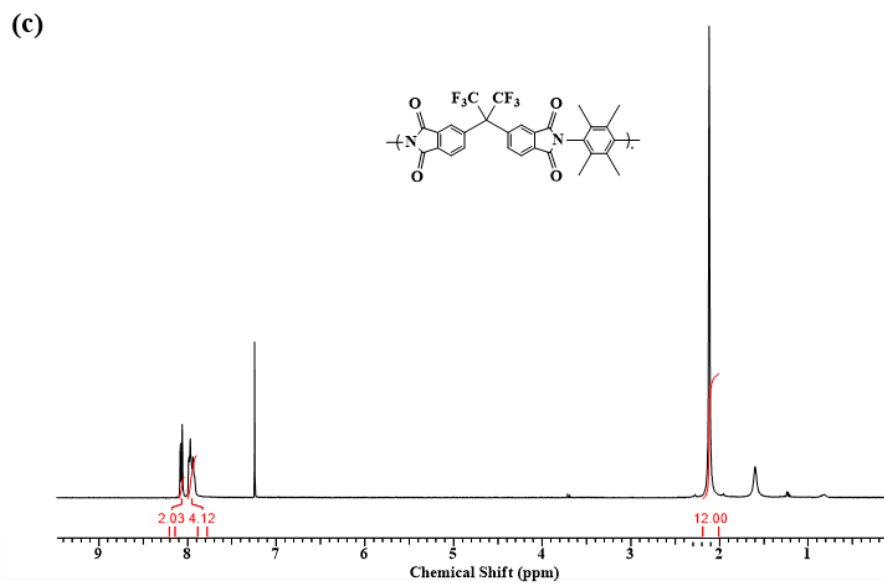


Figure S1. ¹H NMR spectra of (a) UiO-66-NH₂, (b) PEGDE and (c) 6FDA-durene

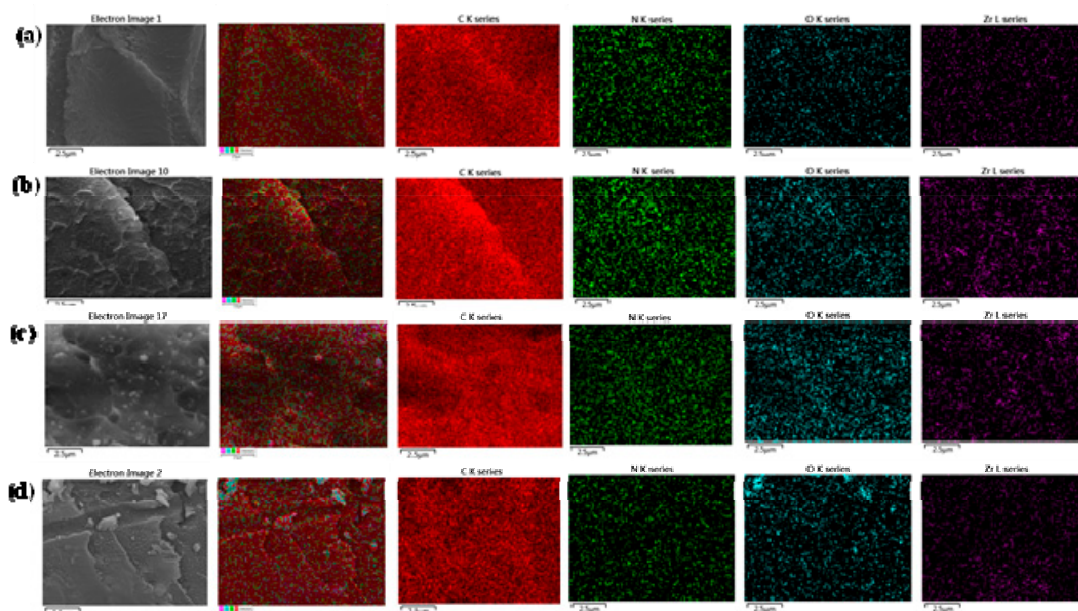


Figure S2. EDX elemental mapping images of (a) MMM-3, (b) MMM-5, (c) MMM-10, and (d) MMM-15

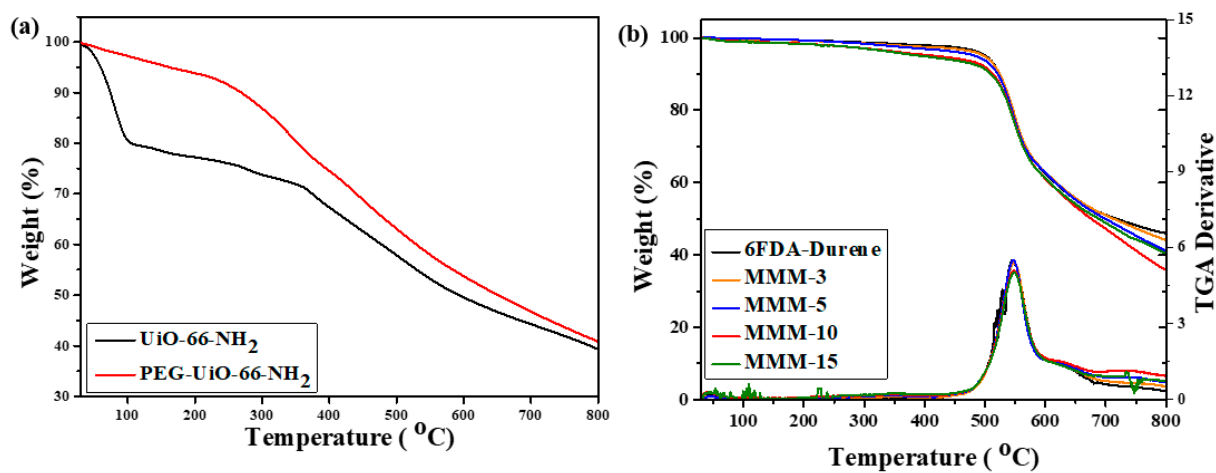


Figure S3. Thermal characteristics with respect to the PEG-MOF content (a) UiO-66-NH₂ and PEG-MOF and (b) MMMs

Table S1. BET surface area and pore volume of MOF and modified MOF

Name	Surface area m ² /g	Pore volume
UiO-66-NH ₂	1041.80	0.458
PEG-MOF	317.47	0.179

Table S2. Gas separation properties of various gas separation membranes

Filler	Polymer	Loading (wt %)	Measurement conditions	P _{CO2} (barrer)	CO ₂ /CH ₄ selectivity	CO ₂ /N ₂ selectivity	Ref.
PI membranes							
---	6FDA-MDA	---		15.8	44.9	24.7	[1]
---	PI-BAFL-6FDA	---	25 °C at 76 cmHg.	98	-----	29	[2]
---	6FDA-DAM-PI	---	15 psi and 35 °C	1100	20.9	19.1	[3]
Commercial Polymers							
---	polyurethane	---	4 bar	38.4	--	39.2	[4]
---	Pebax	---	6 bar; 298 K	299	8.8	27.2	[5]
---	Cellulose acetate	---		6.3	30	30	[6]
---	Polysulfone	---		5.6	22.4	22.4	
---	Polycarbonate	---		4.23	32.5	23.5	
MMMs							
ZIF-8	DMPBI-BuI	30	35 oC, 20 bar	53.9	15.7	11.3	[7]
UiO-66- NH2	6FDA-ODA	25	10 bar, 35 °C	13.7	44.7	---	[8]
UiO-66- NH2	6FDA-Durene	20	1 bar, 35 °C	1470	16.4	---	[8]
UiO 66- NH2	Matrimid 9725	30	9 bar; 308 K; equimolar CO2 and CH4	37.9	47.7	---	[5]
ZIF-8	PU	30	4 bar	14.2	13.7	---	[5]
ZIF-8	Polydopamine- polyimide	7	1 bar; 308 K	380	25	19	[5]
ZIF-8	Pebax	10	6 bar; 298 K	433	8.5	30.9	[5]
ZIF-8	6FDA-durene	33.3 wt %	35 °C and 3.5 atm	1552.9	11.07	11.3	[9]
UiO-66	Matrimid	10	4 bar, 37 °C	7.8	---	29.4	[10]
Azo-UiO- 66	Matrimid	10	4 bar, 37 °C	10	---	37	
PEG- UiO-66- NH ₂	6FDA-Durene	0	1 bar, 30 °C	973.9	14.7	12.7	
		3		1572.13	22.6	19.4	
		5		1600	22.2	19.1	
		10		1671	23.4	19.0	
		15		1789.5	18.1	14.0	

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