Electronic Supplementary Material

Asymmetric copolyimide membranes fabricated by nonsolvent-induced phase separation for He/CH_4 and He/N_2 separation

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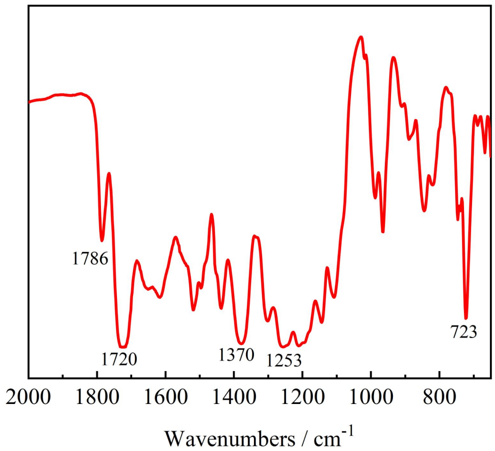

Fig. S1 ATR-FTIR spectra of 6FDA-APAF$_{0.5}$-BIA$_{0.5}$ copolyimide membrane.

The chemical structures of 6FDA-APAF$_{0.5}$-BIA$_{0.5}$ copolyimide were confirmed by ATR-FTIR (Fig. S1). Characteristic imide absorption bands were observed at around 1786 cm^{-1} (imide carbonyl asymmetric stretching), 1718 cm^{-1} (imide carbonyl symmetric stretching) [1] and 1253 cm^{-1} (CF_3 stretching) [2]. The bands at 1370 cm^{-1} and 723 cm^{-1} were transverse stretching and out-of-plane bending of C-N-C groups, respectively [3].

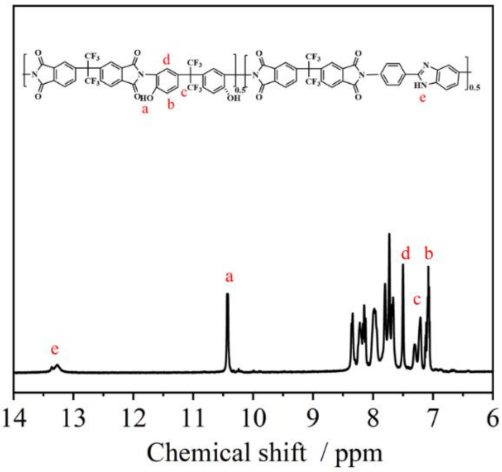

Fig. S2 ^{1}H NMR spectroscopy of 6FDA-APAF$_{0.5}$-BIA$_{0.5}$ copolyimide.

The presence of APAF was well demonstrated by the chemical shifts at 10.5 ppm, 7.1 ppm, 7.2 ppm, and 7.5 ppm (a, b, c, and d). The copolyimide exhibited an additional signal at 13.3 ppm (e) due to −N−H in the benzimidazole rings. The results were in accord with ^{1}H NMR spectra of 6FDA-APAF-BIA polymers [1].

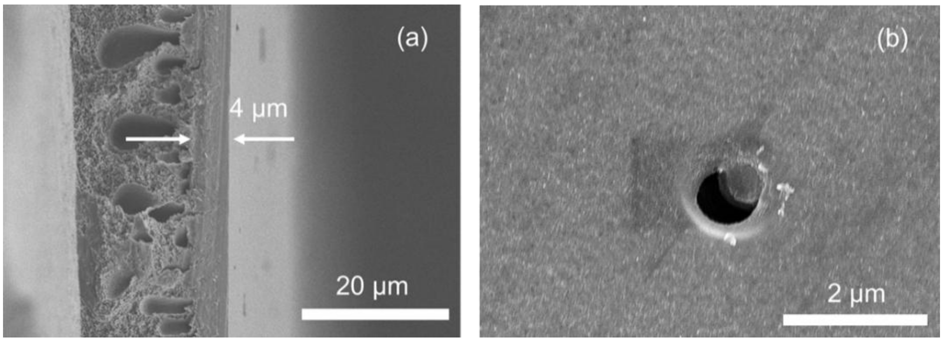

Fig. S3 Cross-sectional SEM images of (a) 30 wt.%. Top view of (b) 30 wt.%.

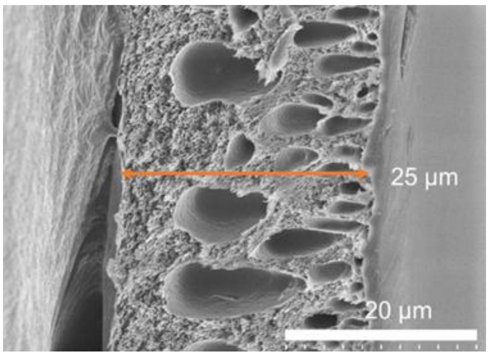

Fig. S4 Cross-sectional SEM image of the whole membrane.

Table S1 Molecular weight data.

No.	M_n / 10^4 g mol^{-1}	M_w / 10^4 g mol^{-1}	PDI / M_w/M_n
6FDA-APAF-BIA	1.38	2.95	2.14

Table S2 Dense membrane properties.

Density / $g \cdot cm^{-3}$	FFV / -	Thickness / μm	P_{He} / *Barrer*	α_{He/CH_4} / -	P_{He} / *Barrer*	$\alpha_{He/N2}$ /
1.584	0.149	60	72	101	74	72

Table S3 Physical properties of polymer, solvents and non-solvents.

	Molar volume mL/mol	ρ / g/mL	δ / $MPa^{1/2}$	χ parameter with polymer	Miscibility	χ parameter with water
Polymer	N.A.	1.290	21.3	N.A.	N.A.	5.10
NMP	96.60	1.032	22.7	0.08	Yes	0.51
THF	81.90	0.889	19.5	0.11	Yes	1.39
Ethanol	58.39	0.789	26.5	0.63	No	1.05
Water	18.01	1.000	47.8	5.10	No	N.A.

Table S4 Linear fitting parameters of and activation energy for He/N_2 and He/CH_4 mixture permeation and single gas permeation in M7 membrane at 0.1 MPa.

		Linear fitting parameters		E_{act} kJ mol^{-1}
		Intercept (a)	Slope ($-\frac{E_{act,i}}{R}$)	
He/N_2	He	-7.74	-1.00	8.3
	N_2	-6.15	-1.72	14.3
He/CH_4	He	-7.61	-0.97	8.1
	CH_4	-6.03	-1.83	15.2
Single gas	He	-7.91	-0.98	8.1
	N_2	-6.73	-1.84	15.3
	CH_4	-7.16	-2.10	17.5

Table S5 Comparison of the performance of the 6FDA-APAF$_{0.5}$-BIA$_{0.5}$ membranes with state-of-the-art membranes.

Membranes	He/CH_4 system			He/N_2 system			Ref
	P_{He} / GPU	$S_{He/CH4}$ / -	$\alpha_{He/CH4}$ / -	P_{He} / GPU	$S_{He/N2}$ / -	$\alpha_{He/N2}$ / -	
TR-6FDA-APAF	2.4	37.2	N.A.	2.4	26.4	N.A.	[4]
6FDA-APAF-BIA	1.8	317.4	N.A.	1.8	121.7	N.A.	[1]
Nafion-117	32.0	56.3	N.A.	32.0	94	N.A.	[5]
Poly(PFMD)	7.0	1650.0	N.A.	7.0	295.8	N.A.	[6]
Poly(PFMMD)	11.2	280.0	N.A.	11.2	72.7	N.A.	
PIM-EA-TB	14.2	3.7	N.A.	14.2	4.90	N.A.	[7]
PIM-SBI-TB	5.6	2.0	N.A.	5.6	3.8	N.A.	
Fluorinated PIM	202	61.2	N.A.	202	36.1	N.A.	[8]
FPIM-5	16.6	3770	N.A.	16.6	857	N.A.	[9]
Cellulose acetate	28.0	40.0	N.A.	28.0	46.7	N.A.	[10]
Polysulphone	0.52	49.0	N.A.	0.52	52.0	N.A.	[11]
PBDI	46	1000	N.A.	46	295	N.A.	[12]
STT	37.1	87.0	63.5	35.4	20.0	11.7	[13]
SAPO-34	554.1	N.A.	13.8	N.A.	N.A.	N.A.	[14]
DD3R	13.6	79.0	59.0	13.6	2.9	N.A.	[15]
TR-6FDA-APAF-Cardo	14.1	64	66.4	13.7	52	54.4	[16]
TR-6FDA-APAF$_{0.5}$-Cardo$_{0.5}$/Al_2O_3	40.0	71.2	74.3	40.0	60.0	50.0	
Membrane M7	85	124	80	86	74	60	This work
Membrane M11	88	N.A.	75	89	N.A.	54	
Membrane M12	80	N.A.	80	83	N.A.	59	
Membrane M13	91	N.A.	74	92	N.A.	52	
Membrane M14	76	N.A.	83	79	N.A.	61	

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