Supporting information for

High-Performance Polymer Molecular Sieve Membranes Prepared by Direct Fluorination for Efficient Helium Enrichment

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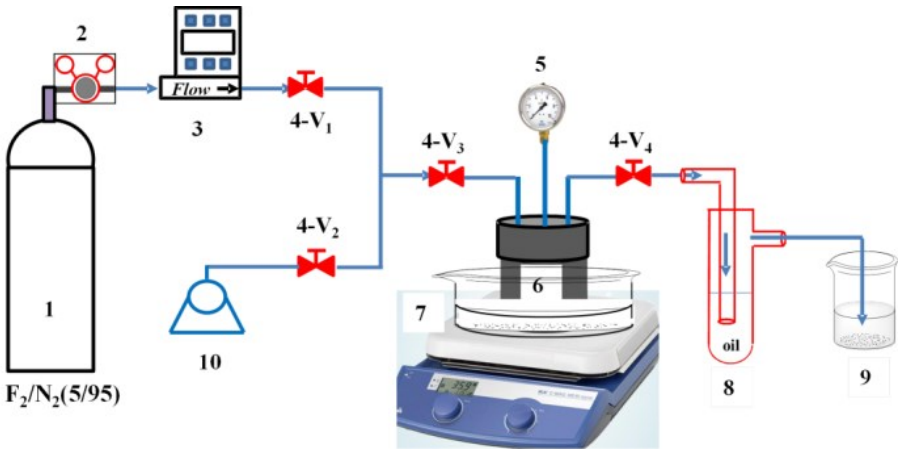

Fig. S1. Set-up for direct fluorination of PIM-1, 1: F_2/N_2 (5/95) mixed-gas cylinder, 2: Regulator, 3: Mass flow meter, 4: (4-V_1 to V_4), Ball valve, 5: Pressure gauge, 6: Autoclave for sample holder, 7: Water bath, 8: Vent gas with oil seal, 9: Sodium carbonate solution (aq), 10: Vacuum pump.

Fig. S2. Pictures of the directly fluorinated PIM-1 membranes.

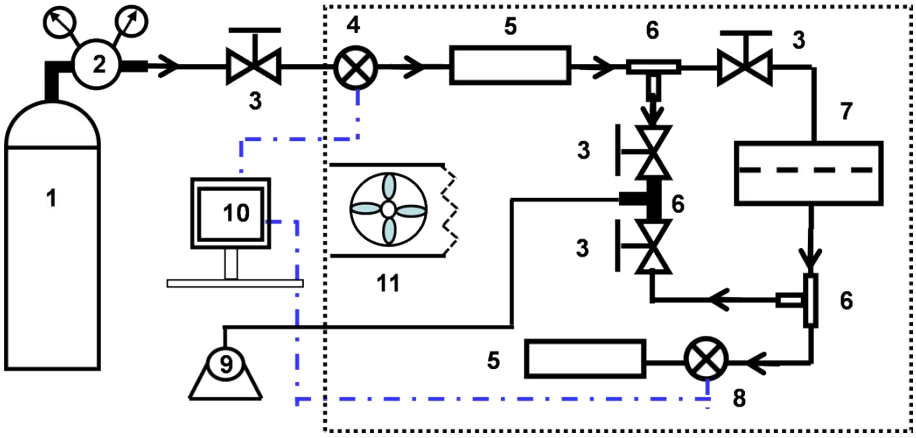

Fig. S3. Schematic set-up of pure-gas permeability measurement apparatus; 1: Cylinder, 2: Regulator, 3: Bellows sealed valve, 4: Upstream transducer, 5: Gas cylinder, 6: Welded T-pipe, 7: Membrane cell, 8: Downstream transducer, 9: Pump, 10: Computer, 11: Temperature control.

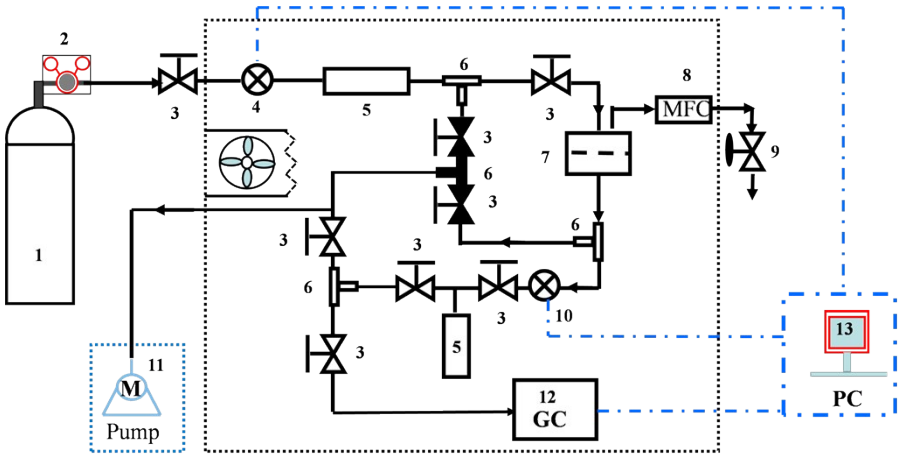

Fig. S4. Schematic set-up of mixed-gas properties testing system, 1: Mixed-gas cylinder, 2: Regulator, 3: Bellows sealed valve, 4: Upstream transducer, 5: Gas storage tank, 6: Tee pipeline with welding, 7: Membrane cell, 8: Mass flow meter, 9: Needle valve, 10: Downstream transducer, 11: Vacuum pump, 12: Gas chromatograph, 13: Computer.

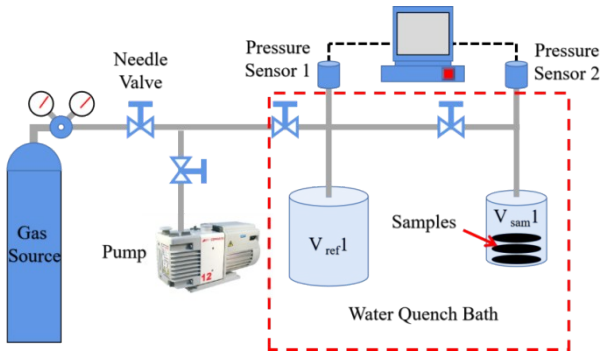

Fig. S5. Set up for barometric sorption testing instrument.

Table S1. Density of PIM-1 and the FPIM membranes.

Polymer	PIM-1	FPIM-1	FPIM-5	FPIM-10	FPIM-30
Density (g cm^{-3})	1.090	1.204	1.210	1.221	1.226

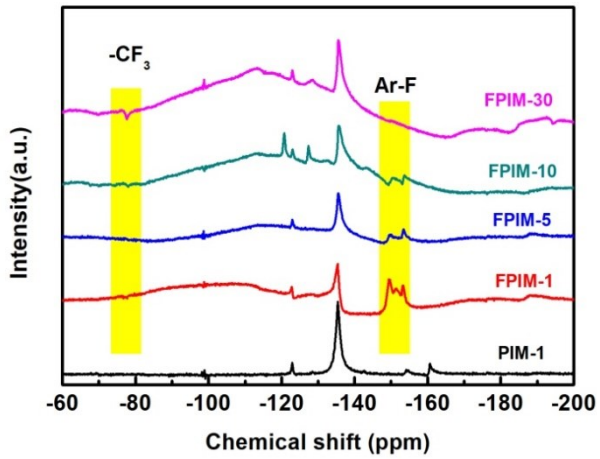

Fig. S6. Solid-state ^{19}F-NMR spectra of the polymer membranes.

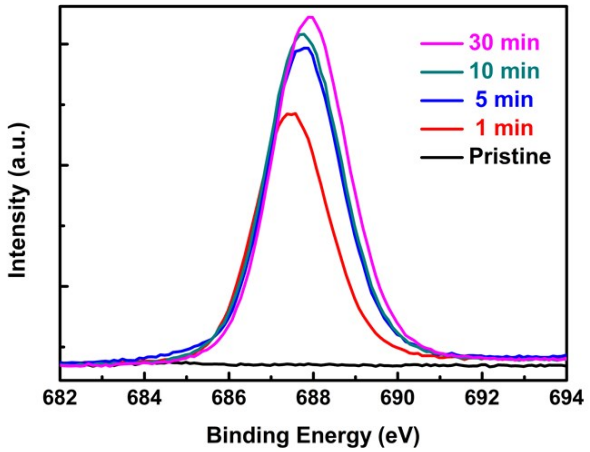

Fig. S7. F_{1s} XPS spectra of PIM-1 and FPIMs membranes at different fluorination times.

Table S2. F and C ratios from XPS results and the calculated repeat units.

	F	C	Repeat unit [a]
pristine	0.0	100	$C_{29}H_{20}N_2O_4$
FPIM-1	22.0	78.0	$C_{29}F_{8.2}H_{11.8}N_2O_4$
FPIM-5	27.6	72.4	$C_{29}F_{11}H_9N_2O_4$
FPIM-10	29.6	70.4	$C_{29}F_{12.2}H_{7.8}N_2O_4$
FPIM-30	30.7	69.3	$C_{29}F_{12.8}H_{7.2}N_2O_4$

[a] Calculated repeat unit based on the F/C ratio from the XPS result.

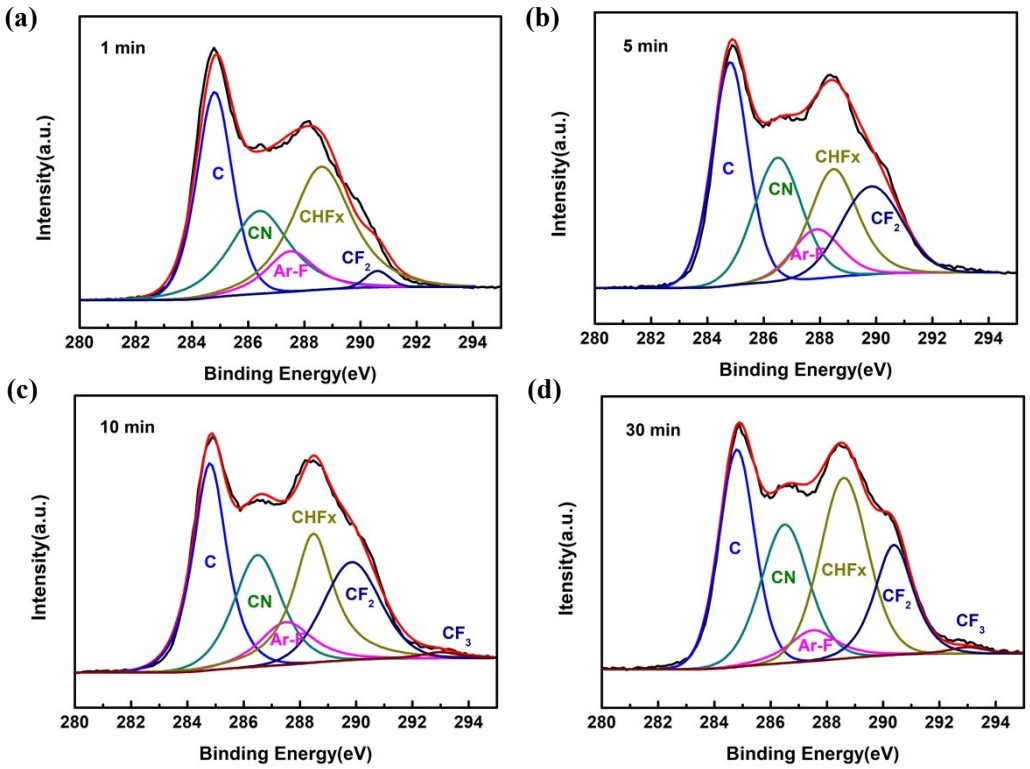

Fig. S8. XPS spectra of the C_{1s} for PIM-1 membrane at different fluorination times: (a) 1 min, (b) 5 min, (c) 10 min, (d) 30 min. The signals of 284.8 (C), 286.4 (CN), 287.5 (Ar-F), 288.6 (CHF_x), 290.6 (CF_2), and 293 (CF_3) eV were deconvoluted.

Table S3. Component ratio for different fluorinated carbons of PIM-1 with different fluorination times.

	C	-CN	Ar-F	CHF_x	CF_2	CF_3
PIM-1	0.68	0.32				
FPIM-1	0.32	0.23	0.09	0.34	0.02	0.00
FPIM-5	0.30	0.22	0.09	0.20	0.19	0.00
FPIM-10	0.30	0.22	0.10	0.25	0.22	0.01
FPIM-30	0.29	0.25	0.06	0.32	0.17	0.01

The ratio was calculated from the deconvolution results of C_{1s} XPS.

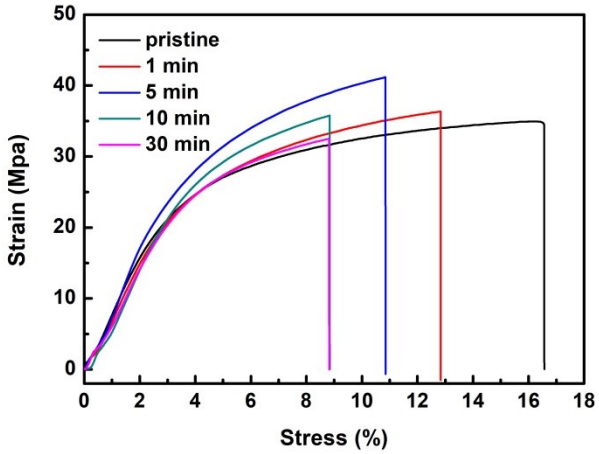

Fig. S9. Stress-strain curves of PIM-1 and FPIM membranes at different fluorination times.

Table S4. Mechanical properties of the PIM-1, FPIMs and other membranes.

Polymer	Young's modulus (GPa)	Elongation at break (%)	Strain (MPa)
Pristine PIM-1	0.80	17.0	34.1
FPIM-1	0.82	12.8	36.3
FPIM-5	1.0	10.8	41
FPIM-10	0.91	8.8	35
FPIM-30	0.84	8.8	32
PIM-1/ZIF-67(10)[a]	0.98	3.7	29.4
1%-MWCNT/PIM-1[b]	0.67	8.9	47
UIO-66-CN/PIM-1[c]	1.26	4.3	34.3

[a] Data from reference 1. [b] Data from reference 2. [c] Data from reference 3.

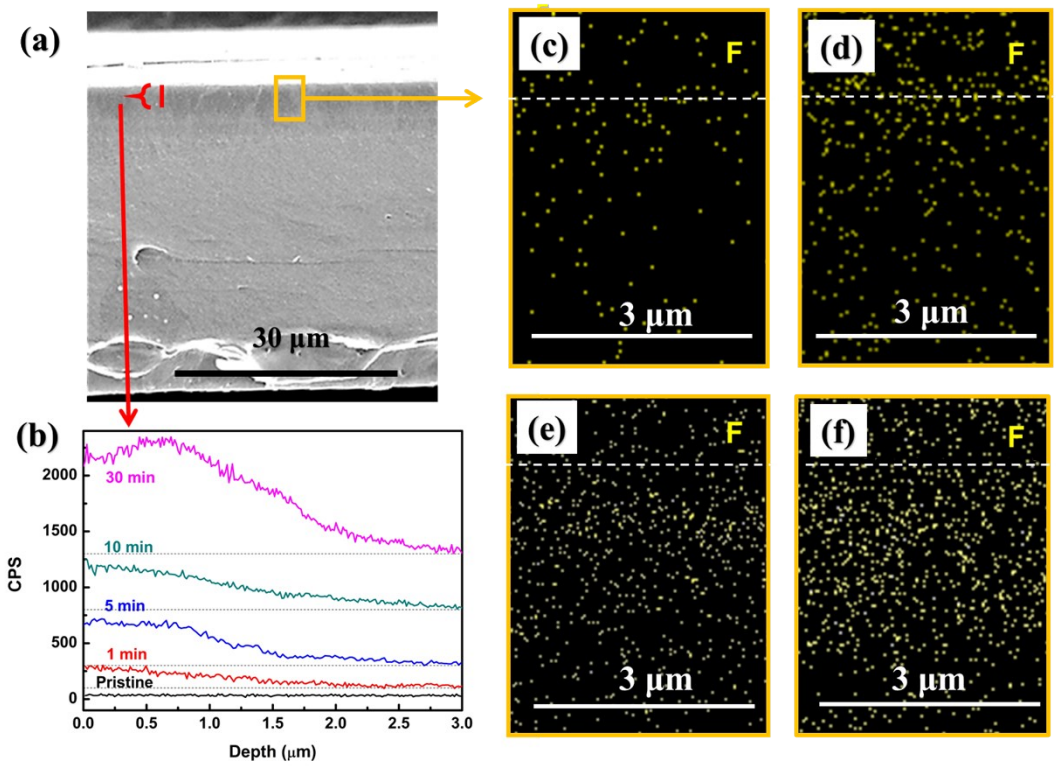

Fig. S10. (a) Cross-sectional image of PIM-1. (b) The depth of fluorine signals in cross-sectional EDS mapping of the FPIMs. (c), (d), (e), (f) EDS mapping of the fluorine signals during different fluorination time, (c) 1 min, (d) 5 min, (e) 10 min, (f) 30 min.

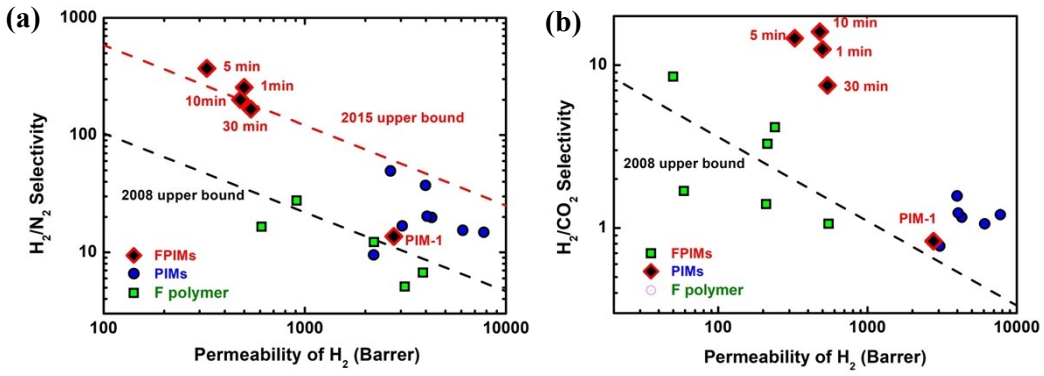

Fig. S11. Performance plot of (a) H_2/N_2 and (b) H_2/CO_2 for FPIMs (red), PIMs (blue) and fluorinated polymers (F polymers, green). The 2008 upper bounds for H_2/N_2 and H_2/CO_2 were from reference 4; the 2015 H_2/N_2 upper bound was from reference 5.

Table S5. Gas permeability and ideal gas pair selectivity of some representative polymers.

Polymers	Permeability (Barrer)			Selectivity ($a_{X/Y}$)			
	He	H_2	N_2	P_{He}/P_{CH4}	P_{He}/P_{N2}	P_{H2}/P_{CH4}	P_{He}/P_{CO2}
PIM-1	1336	2772	203	4	7	9	0.4
FPIM-1	824	500	1.96	1005	420	610	20.6
FPIM-5	754	326	0.88	3770	857	1630	33.8
FPIM-10	826	479	2.39	1271	346	737	27.6
FPIM-30	885	540	3.24	686	273	419	12.3
PIM-EA-TB [a]	2570	7760	525	3.7	4.9	11.1	0.4
KAUST-PI-1 [b]	1771	3983	107	16.9	16.6	37.9	0.7
TDA1-DMN [c]	1182	3050	182	5.5	6.5	14.1	0.3
PIM-TMN-Trip [d]	2300	6100	396	3.2	5.8	8.6	0.4
AO-PIM-1 [e]	412	912	33	27.6	26.8	4.5	0.36
PIM-Btrip-TB [f]	1470	4280	216	5.2	6.8	15.1	0.4
PIM-MP-TB [g]	1310	4050	200	5.0	6.6	15.3	0.4
Cytop [h]	170	59	5	85.0	34	30	4.85
PHFP [i]	597	312	48	25	12.4	13	1.6
Poly(PFMMD) [j]	560	240	7.7	280	73	120	9.7
Nafion [k]	37	7	0.24	446	154	84	16.1
HyflonAD80 [h]	430	210	24	28	18	14	2.87
Poly(PFMD) [h]	210	50	0.71	1650	296	394	35.6
Trithene B [l]	34	-	0.121	400	281	-	-
PPY-1(50/50) [m]	65.3	-	0.70	240	93	-	4.13
PPY-2(25/75) [m]	35.7	-	0.1	1600	360	-	11.4
PPY-3(10/90) [m]	22.5	-	0.036	3000	625	-	20.3
CA [n]	19.6	15.5	0.23	280	73	120	2.97
TBPC [o]	17.6	-	0.182	135	96.7	-	4.2

[a] Data from reference 6. [b] Data from reference 7. [c] Data from reference 8. [d] Data from reference 9. [e] Data from reference 10. [f] Data from reference 11. [g] Data from reference 12. [h] Data from reference 13. [i] Data from reference 14. [j] Data from reference 15. [k] Data from reference 16. [l] Data from reference 17. [m] Data from reference 18. [n] Data from reference 19. [o] Data from reference 20.

Table S6. Physical aging properties of FPIM-5 membrane.

Polymer	Permeability (Barrer) [a]				Ideal Selectivity ($\alpha_{x/y}$) [b]			
	He	H_2	N_2	CH_4	P_{He}/P_{CH4}	P_{H2}/P_{CH4}	P_{He}/P_{N2}	P_{He}/P_{CO2}
FPIM-5	754	326	0.88	0.20	3770	1630	854	33.8
Aged 7 days	754	332	0.94	0.20	3750	1660	802	33.1
Aged 30 days	779	367	0.96	0.18	4328	1913	811	33.0
Aged 60 days	708	312	0.72	0.15	4720	2080	983	32.1

[a] Permeability of the fluorinated FPIM-5, unit: 10^{-10} cm^3 cm cm^{-2} s^{-1} $cmHg^{-1}$.The aging properties of the FPIM-5 membrane were evaluated by putting the membrane in the permeation system and tested for 1, 7, 30 and 60 days, respectively. [b] Ideal gas selectivity of the FPIM-5.

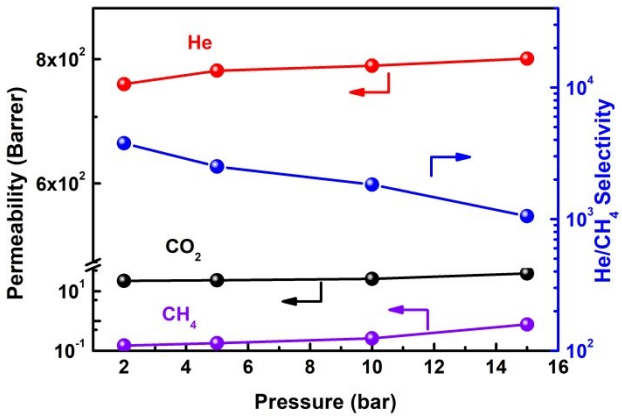

Fig. S12. Pressure dependent pure-gas permeability of the He, CH_4 and CO_2, and the ideal He/CH_4 selectivity under different upstream pressures.

Table S7. Pressure dependent separation properties of FPIM-5.

Pressure (bar)	He [a]	CH_4	CO_2	$\alpha_{He/CH4}$ [b]
2	755	0.20	22.3	3770
5	779	0.31	23.3	2512
10	788	0.43	26	1832
15	801	0.76	39.6	1054

[a] Permeability of the fluorinated FPIM-5, unit: 10^{-10} cm^3 cm cm^{-2} s^{-1} $cmHg^{-1}$. [b] Ideal gas selectivity of the FPIM-5.

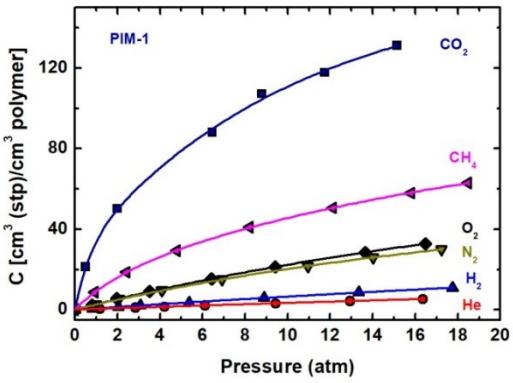

Fig. S13. Barometric gas sorption of PIM-1 at 35 °C from pressure ranging from 0 to ~ 18 bar.

Table S8. He/CH_4 (0.6/99.4) binary mixed-gas separation properties of FPIM-5 at different upstream pressures.

Pressure (bar)	He [a]	CH_4	He/CH_4 selectivity [b]	%He in permeate
10	790	0.487	1623	91.2
15	805	0.828	973	86.5
20	876	1.014	869	84.9

[a] Permeability of the fluorinated FPIM-5, unit: 10^{-10} cm^3 cm cm^{-2} s^{-1} $cmHg^{-1}$. [b] Ideal gas selectivity of the FPIM-5.

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