Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information

Fine-tuning ultramicroporosity in PIM-1 membranes by aldehyde functionalization for efficient hydrogen separation

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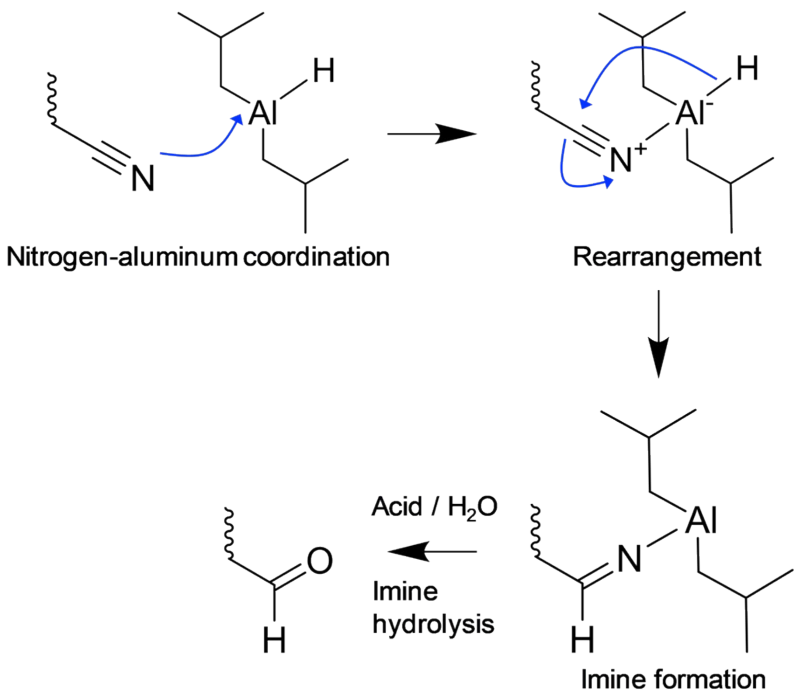

Fig. S1. Schematic illustration of reduction of nitrile with DIBAL and subsequent imine hydrolysis with acid.[1]

Table S1. Predicted and XPS-based elemental concentrations of PIM-1 and PIM-CHO.

Sample	Atomic ratio (at.%)		
	C	N	O
PIM-1 (Theory)	82.9	5.7	11.4
PIM-1 (XPS)	81.0	5.1	13.9
PIM-CHO (Theory)	82.9	-	17.1
PIM-CHO (XPS)	79.6	0.3	20.1

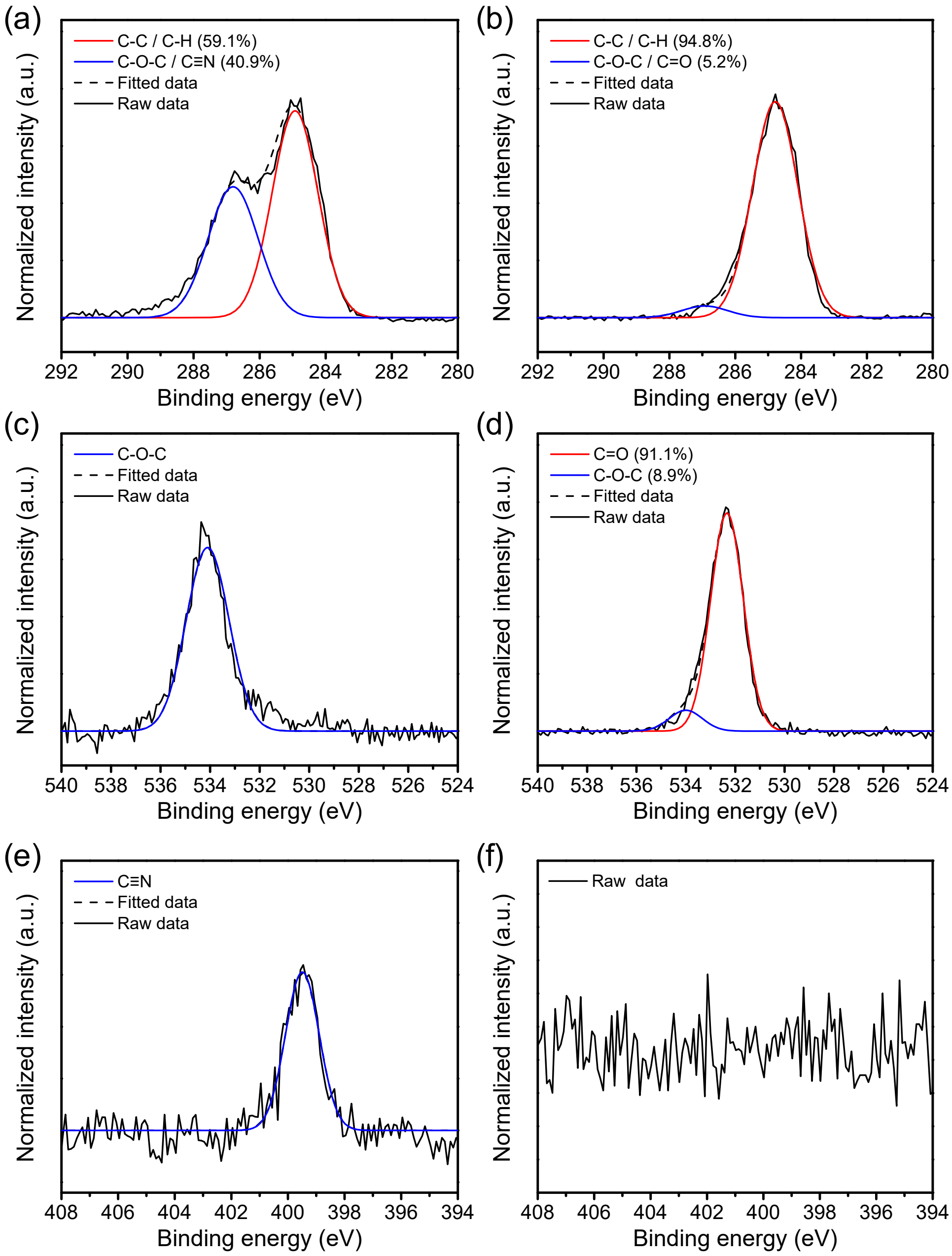

Fig. S2. High-resolution (a–b) C 1s, (c–d) O 1s, and (e–f) N 1s XPS spectra of (a,c,e) PIM-1 and (b,d,f) PIM-CHO.[2] Peak fitting for N 1s XPS spectrum of PIM-CHO was not performed due to the negligible presence of nitrogen.

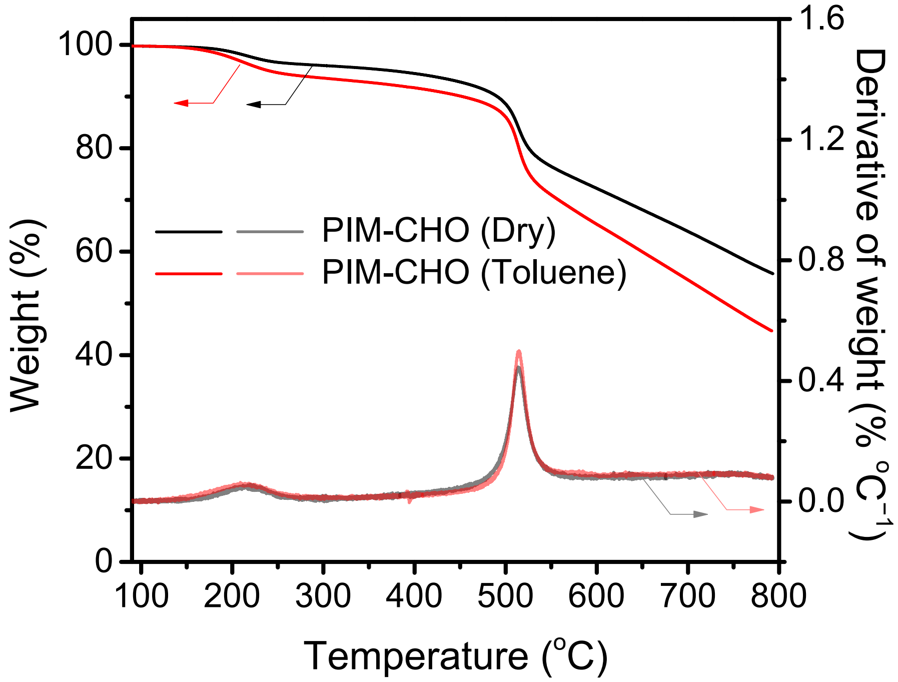

Fig. S3. TGA curves of PIM-CHO films prepared with (Dry) or without toluene pretreatment (Toluene).

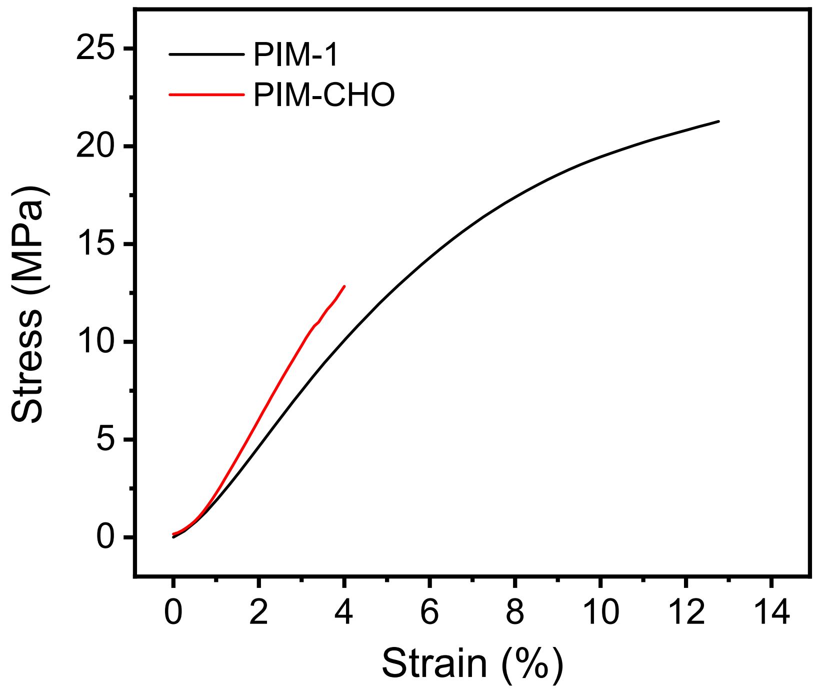

Fig. S4. Stress-strain curves of PIM-1 and PIM-CHO films.

Table S2. Mechanical properties of PIM-1 and PIM-CHO films calculated from the stress-strain curves in Fig. S4.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PIM-1	246	21.2	12.8
PIM-CHO	317	12.9	3.0

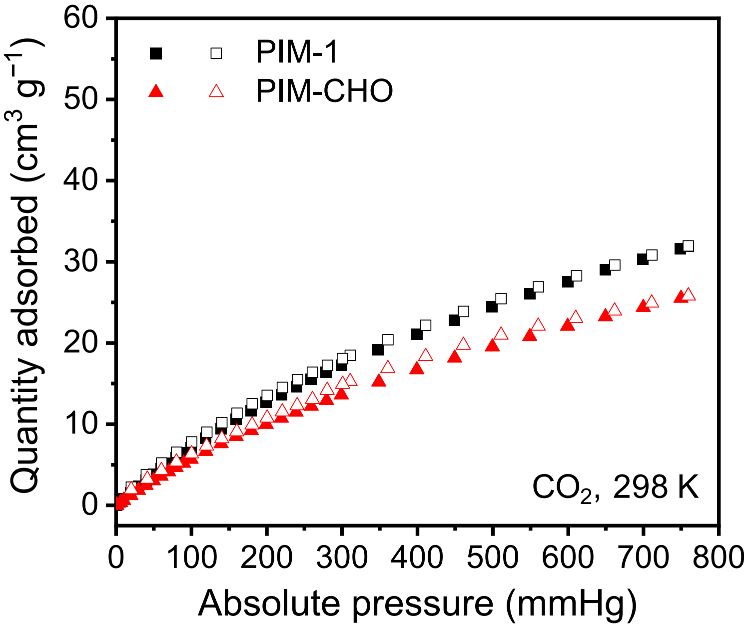

Fig. S5. CO_2 adsorption–desorption isotherms of PIM-1 and PIM-CHO up to 1 bar at 298 K.

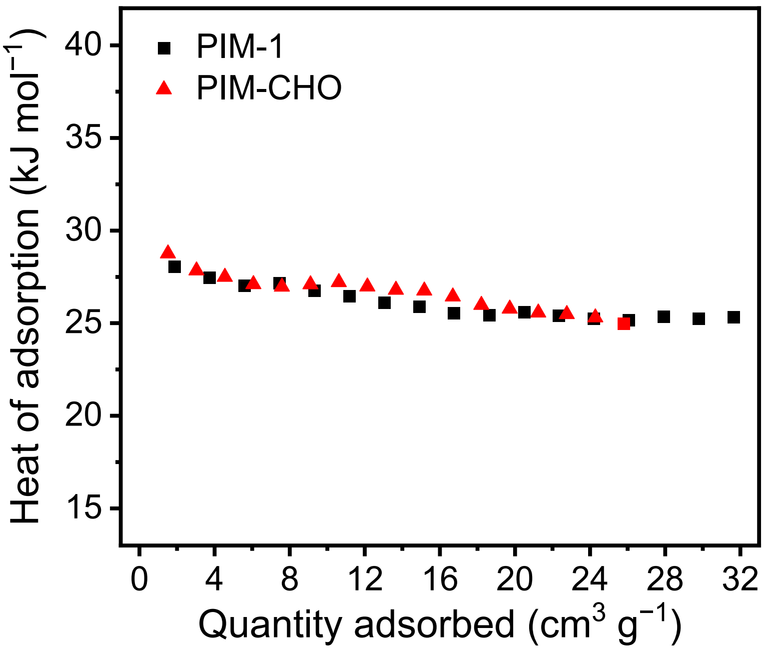

Fig. S6. Isosteric heat of adsorption for PIM-1 and PIM-CHO obtained from CO_2 sorption isotherms at 273 and 298 K (Fig. 2b and Fig. S5, respectively).

Table S3. Gas separation performance of functionalized PIM-1 membrane films reported in the literature and reported in this study. The corresponding chemical structures of membranes are shown in Fig. S5.

Polymer film	PIM-1[a]	PIM-Tol-HCl[a]	PIM-CHO[a]	PIM-COOH[3]	PIM-AO[5]	PIM-TZ[4]	PIM-NH_2[7]	PIM-deBOC (thermal)[6]	PIM-Thio[8]
Gas	Gas permeability (barrer)								
H_2	4190	4060	2550	270	910	-	1450	2000	610
O_2	1710	1680	300	44	150	-	430	500	140
CO_2	10300	10900	1510	290	1150	3000	-	2300	1120
N_2	590	560	55	9.0	33	100	134	120	37
CH_4	1020	960	49	9.0	34	136	210	170	56
Gas pair	Ideal selectivity (-)								
H_2/N_2	7.1	7.3	42.8	30.0	27.6	-	10.8	16.7	16.5
H_2/CH_4	4.1	4.2	52.4	30.0	26.8	-	6.9	11.8	10.9
O_2/N_2	2.9	3.0	5.5	4.9	4.5	-	3.2	4.2	3.8
CO_2/CH_4	10.1	11.4	31.0	32.2	33.9	22.1	-	13.5	20.0

[a] This study.

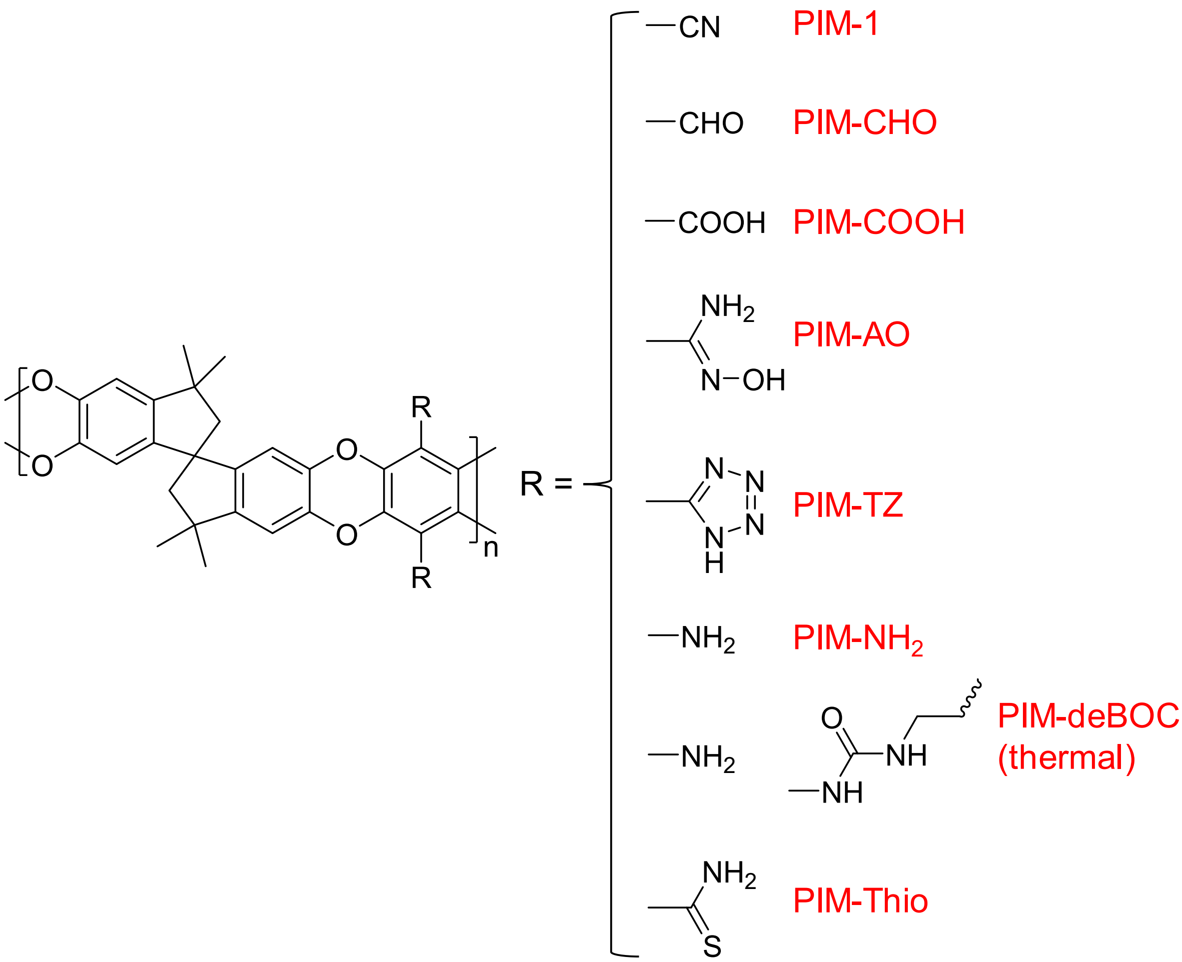

Fig. S7. Chemical structures of functionalized PIM-1 membranes reported in literature and reported in this study.[3–8]

Table S4. Dual-mode sorption model parameters calculated from CH_4 and CO_2 sorption isotherms at 35 °C (Fig. 4a).

Sample	Gas	k_D (cm^3_{STP} cm^{-3}_{pol} atm^{-1})	C'_H (cm^3_{STP} cm^{-3}_{pol})	b (atm^{-1})	S_{1atm} (cm^3_{STP} cm^{-3}_{pol} atm^{-1})
PIM-1	CH_4	1.43	42.5	0.16	7.3
	CO_2	4.05	65.8	0.59	28.5
PIM-CHO	CH_4	1.17	28.9	0.14	4.7
	CO_2	3.72	40.1	0.67	19.8

Table S5. Diffusion, sorption, and permeability coefficients and the corresponding selectivities of PIM-1 and PIM-CHO membrane films measured at 35 °C and 1 bar.

Sample	Gas	D ($10^{-7} \times cm^2\ s^{-1}$)	S_{1atm} ($cm^3_{STP}\ cm^{-3}_{pol}\ atm^{-1}$)	P (barrer)	D_{CO2} /D_{CH4}	S_{CO2} /S_{CH4}	P_{CO2} /P_{CH4}
PIM-1	CH_4	10.6	7.3	1020	2.6	3.9	10.1
	CO_2	27.4	28.5	10300			
PIM-CHO	CH_4	0.8	4.7	49	7.3	4.2	31.0
	CO_2	5.8	19.8	1510			

Table S6. Gas separation performance of PIM-1 and PIM-CHO membrane films before and after aging.

Polymer film	PIM-1 (0 day)	PIM-1 (53 days)	PIM-CHO (0 day)	PIM-CHO (56 days)
Gas	Gas permeability (barrer)			
H_2	4190	3860	2550	1980
CO_2	10300	7680	1510	960
O_2	1710	1390	300	210
N_2	590	400	55	39
CH_4	1020	580	49	34
Gas pair	Ideal selectivity (-)			
H_2/N_2	7.1	9.6	42.8	50.9
H_2/CH_4	4.1	6.7	52.4	58.2
O_2/N_2	2.9	3.5	5.5	5.5
CO_2/CH_4	10.1	13.3	31.0	28.1

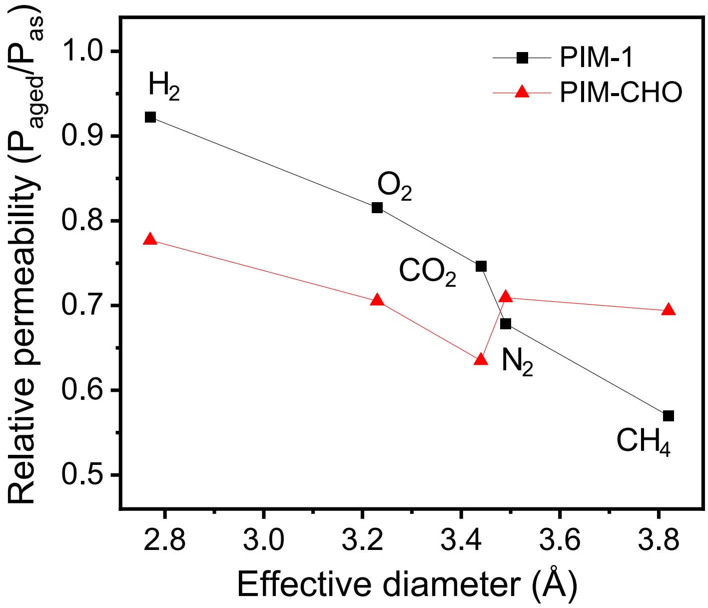

Fig. S8. Relative permeability (P_{aged}/P_{as}) as the ratio of the gas permeabilities of aged membrane films to those of as-prepared ones depending on effective gas diameters. PIM-1 and PIM-CHO membrane films were aged for 53 and 56 days, respectively. Effective diameters were used as reported by Robeson *et al.*.[9]

References

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