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Supporting Information

Supramolecular Assemblies of Polybenzimidazole and Aromatic Polycarboxylic Acids with Superior Mechanical and H_2/CO_2 Separation Properties

Leiqing Hu[a], Vinh T Bui[a], Shouhong Fan[b], Wenji Guo[a], Sankhajit Pal[a], Yifu Ding[b], and Haiqing Lin[a]

[a]Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA

[b]Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309, USA

* Corresponding author: Haiqing Lin, E-mail: haiqingl@buffalo.edu

Physical properties of pure acids and acid-doped PBIs

Table S1. Physical properties of PA, TMA, and PMA, including pKa, molar volume, $T_{d,10\%}$, and density in the pure form and supramolecular assemblies.

Samples	Acidity (pK_a)				Molar volume (cm^3/mol)	$T_{d,10\%}$ (°C)	Density (g/cm^3)	
	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}			Pure	Acid in PBI
PA	2.9	5.5	N/A[a]	N/A	104	209	1.59	1.73
TMA	3.1	3.9	4.7	N/A	146	342	1.44	2.02
PMA	1.9	2.9	4.5	5.6	160	234	1.59	1.99

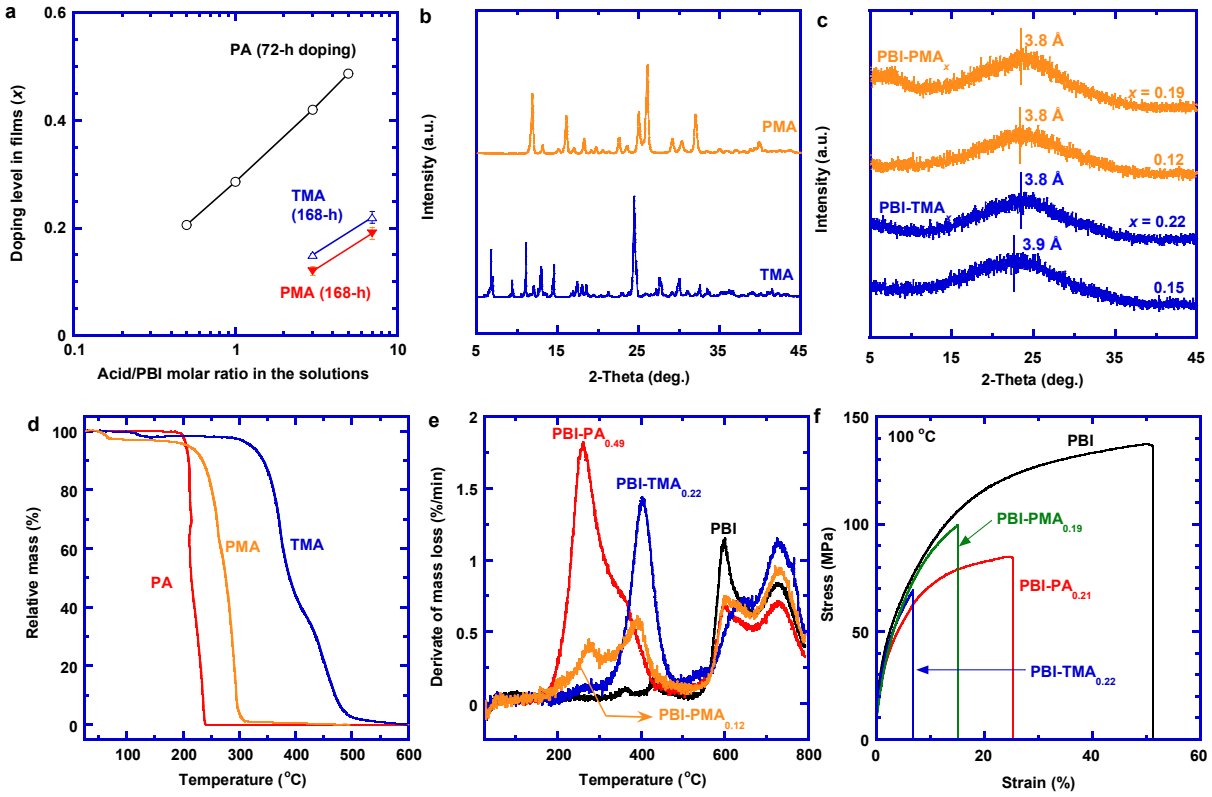

Fig. S1 (a) Effect of the acid content in the solutions on its doping level in the supramolecular assemblies. WAXD patterns of (b) the pure acids (PA, TMA, and PMA) and (c) PBI-acid samples. (d) TGA curves of pure acids. (e) Derivative thermogravimetric analysis (DTA) curves of PBI, PBI-$PA_{0.49}$, PBI-$TMA_{0.22}$, and PBI-$PMA_{0.19}$. (f) Stress−strain tensile plots at 100 °C.

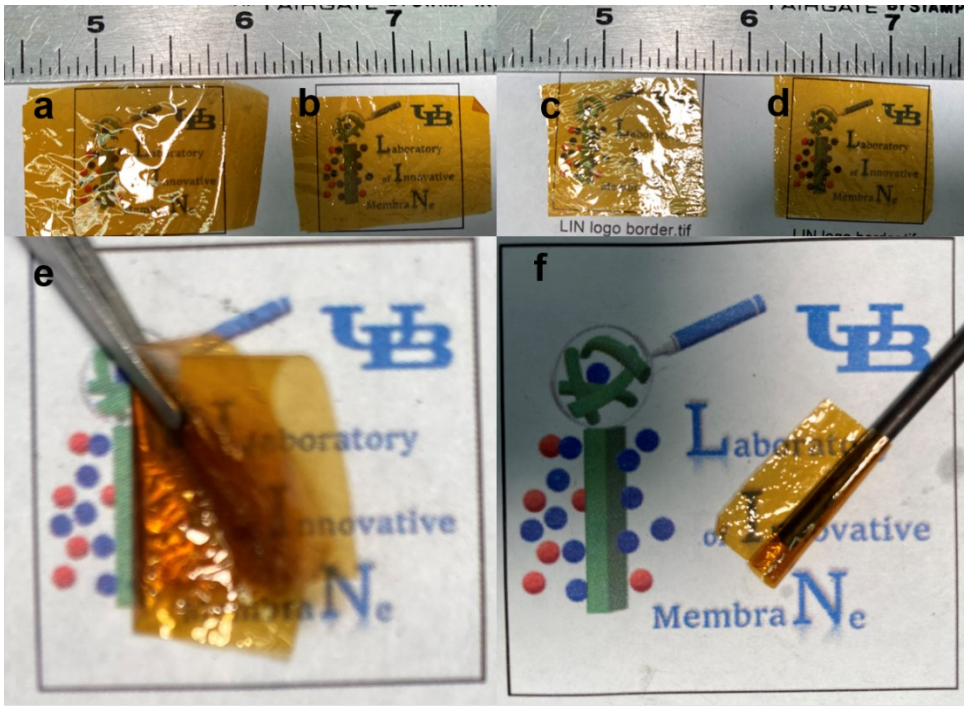

Fig. S2. Photos of (a) pure PBI, (b) PBI-$PA_{0.49}$, (c) PBI-$TrA_{0.22}$, and (d) PBI-$PyA_{0.19}$ films. Scale bar is 1 inch in the photos. Photos demonstrating high flexibility of PBI-$PyA_{0.19}$ films including (e) double-folded and (f) curled samples.

Table S2. Physical properties of the supramolecular assemblies, including acid content, density, FFV, *d*-spacing, and $T_{d,10\%}$.

Samples	Acid content (mass%)	Density (g/cm^3)	*FFV*	*d*-spacing (Å)	$T_{d,10\%}$ (°C)
PBI	0	1.286	0.161	4.0	652
PBI-$PA_{0.21}$	10.2	1.316	0.144	3.8	N/A
PBI-$PA_{0.29}$	13.5	1.331	0.135	3.8	N/A
PBI-$PA_{0.41}$	18.1	1.347	0.126	3.7	N/A
PBI-$PA_{0.49}$	20.9	1.361	0.118	3.6	253
PBI-$TMA_{0.15}$	9.28	1.330	0.139	3.9	N/A
PBI-$TMA_{0.22}$	13.0	1.350	0.129	3.8	429
PBI-$PMA_{0.12}$	9.00	1.331	0.140	3.8	548
PBI-$PMA_{0.19}$	13.6	1.35	0.133	3.8	N/A

N/A: Not available.

Table S3. Young's modulus, yield strength, and yield strain of PBI, PBI-$PA_{0.21}$ and PBI-$PA_{0.49}$, PBI-$TMA_{0.22}$, and PBI-$PMA_{0.19}$ at 35 and 100 ℃.

Samples	35 ℃			100 ℃		
	Young's modulus (MPa)	Yield strength (MPa)	Yield strain (%)	Young's modulus (MPa)	Yield strength (MPa)	Yield strain (%)
PBI	1600	46	2.6	1490	35	0.8
PBI-$PA_{0.21}$	1930	26	1.0	1890	21	0.5
PBI-$PA_{0.49}$	2450	54	4.3	1820	20	0.6
PBI-$TMA_{0.22}$	2880	47	1.8	2350	24	0.8
PBI-$PMA_{0.19}$	2730	44	1.6	1900	19	0.3

Effect of the acid doping level and temperature on gas transport properties

Table S4. Pure-gas transport properties of PBI and PBI-PA$_x$ samples at ≈ 8 atm and 35 ℃.

Samples	H_2 permeability (Barrer)		CO_2 permeability (Barrer)		H_2/CO_2 selectivity	
	S1†	S2†	S1	S2	S1	S2
PBI	2.2	2.2	0.16	0.15	14	15
PBI-PA$_{0.21}$	0.75	0.73	0.028	0.025	27	29
PBI-PA$_{0.29}$	0.61	0.65	0.018	0.018	34	36
PBI-PA$_{0.41}$	0.49	0.53	0.011	0.013	45	41
PBI-PA$_{0.49}$	0.42	0.44	0.0085	0.0088	49	50

Note: †S1 and S2 represents two testing samples for PBI or PBI-PA$_x$.

Table S5. Pure-gas transport properties of representative PBI and acid-doped PBI samples at ≈ 8 atm and varied temperatures.

Samples	H_2 permeability (Barrer)				CO_2 permeability (Barrer)				H_2/CO_2 selectivity			
	35 ℃	70 ℃	100 ℃	150 ℃	35 ℃	70 ℃	100 ℃	150 ℃	35 ℃	70 ℃	100 ℃	150 ℃
PBI	2.2	5.2	12	27	0.16	0.35	0.81	1.7	14	15	15	16
PBI-PA$_{0.21}$	0.75	3.9	7.6	12	0.028	0.16	0.33	0.52	27	25	23	23
PBI-PA$_{0.29}$	0.61	2.1	4.1	10	0.018	0.064	0.13	0.46	34	33	32	22
PBI-PA$_{0.41}$	0.49	2.8	5.6	15	0.011	0.077	0.18	0.64	45	37	31	23
PBI-PA$_{0.49}$	0.42	3.2	6.4	17	0.0085	0.077	0.21	0.80	49	42	31	22
PBI-TMA$_{0.15}$	1.0	4.4	8.8	20	0.033	0.15	0.30	0.84	30	29	29	24
PBI-TMA$_{0.22}$	0.8	3.7	6.8	16	0.019	0.11	0.22	0.58	42	33	31	28
PBI-PMA$_{0.12}$	1.2	5.6	8.0	18	0.029	0.15	0.26	0.67	40	37	31	27
PBI-PMA$_{0.19}$	0.89	5.4	10	19	0.017	0.12	0.27	0.72	52	44	37	26

Gas sorption (C_A) in the glassy polymers is often described using the dual-mode sorption model:[13]

$$C_A = k_D p_A + \frac{C_H' b p_A}{1 + b p_A} \quad \text{(S1)}$$

where k_D is Henry's constant, C_H' is Langmuir sorption capacity, and b is the affinity parameter. The fitting values of the parameters are listed in Table S6. The acid doping of PBI lowers C_H' values, consistent with the decreased free volume and then lower Langmuir sorption at 35 °C.

Table S6. Parameters of the dual-mode sorption model for CO_2 and C_2H_6 sorption in PBI, PBI-$PA_{0.21}$, PBI-$PA_{0.49}$, PBI-$TMA_{0.22}$, and PBI-$PMA_{0.19}$ at 35 and 150 °C. The units for k_D, b, and C_H' are $cm^3(STP)\ cm^{-3}\cdot atm^{-1}$, atm^{-1}, and $cm^3(STP)\ cm^{-3}$, respectively.

Samples	Temp. (°C)	CO_2			C_2H_6		
		k_D	b	C_H'	k_D	b	C_H'
PBI	35	0.53	0.52	16	--	--	--
	150	0.23	0.12	6.7	0.37	0.25	5.8
PBI-$PA_{0.21}$	35	0.81	0.47	13	--	--	--
	150	0.21	0.10	3.9	0.27	0.24	3.4
PBI-$PA_{0.49}$	35	0.71	0.47	10	--	--	--
	150	0.04	0.14	5.4	0.33	0.22	5.8
PBI-$TMA_{0.22}$	35	0.94	0.61	15	--	--	--
	150	0.24	0.13	7.2	0.33	0.24	4.4
PBI-$PMA_{0.19}$	35	0.99	0.62	16	--	--	--
	150	0.30	0.14	8.0	0.33	0.25	7.1

Table S7. CO_2 diffusivity and solubility, C_2H_6 solubility, and CO_2/C_2H_6 solubility selectivity of PBI, PBI-$PA_{0.21}$, PBI-$PA_{0.49}$, PBI-$TMA_{0.22}$, and PBI-$PMA_{0.19}$ at ≈ 8 atm and 35 and 150 °C.

Samples	CO_2 diffusivity ($\times 10^{-8}$ cm^2/s)		CO_2 solubility ($cm^3(STP)/(cm^3$ atm))		C_2H_6 solubility ($cm^3(STP)/(cm^3$ atm))	CO_2/C_2H_6 solubility selectivity
	35 °C	150 °C	35 °C	150 °C	150 °C	150 °C
PBI	0.051	2.0	2.4	0.65	0.87	0.75
PBI-$PA_{0.21}$	0.010	0.92	2.2	0.43	0.53	0.82
PBI-$PA_{0.49}$	0.0037	1.4	1.8	0.42	0.81	0.52
PBI-$TMA_{0.22}$	0.0056	0.60	2.6	0.73	0.75	0.98

TMA	N/A†	N/A	0.06	0‡	N/A	N/A
PBI-PMA$_{0.19}$	0.0047	0.64	2.8	0.86	0.96	0.89

Note: † Not available. ‡ The value is too low to be measured.

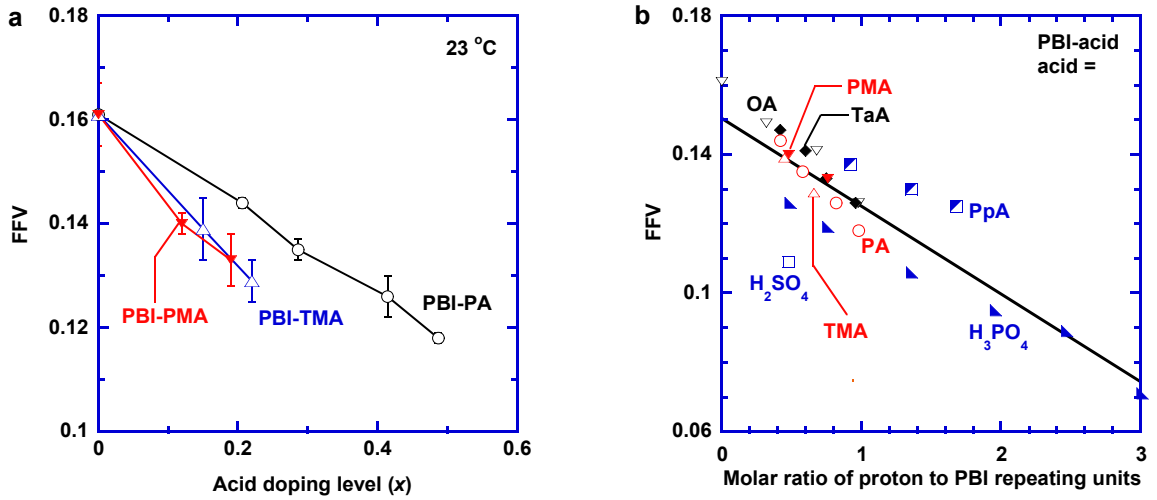

Fig. S3 (a) Effect of the acid doping level on the *FFV* of the PBI-PA, PBI-TMA, and PBI-PMA at 23 °C. (b) Correlation between the molar ratio of the proton to PBI repeating units and *FFV* for PBI doped with various acids, including OA, TaA, H_3PO_4, PpA, H_2SO_4, PA, TMA, and PMA.

Effect of temperature on gas transport properties

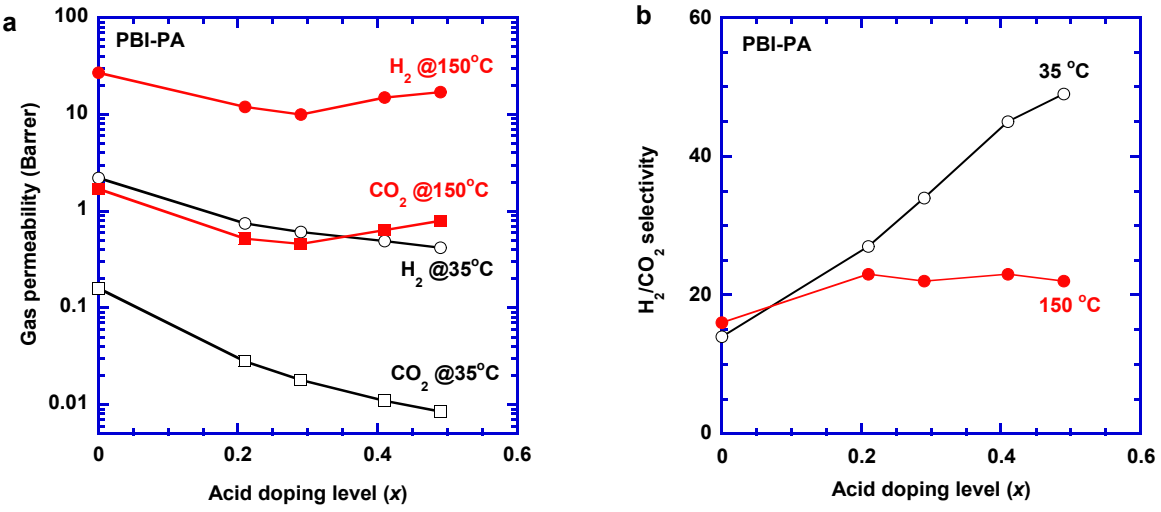

Fig. S4 (a) Pure-gas H_2 and CO_2 permeability and (b) H_2/CO_2 selectivity of PBI-PA as a function of the PA doping level at 35 and 150 °C.

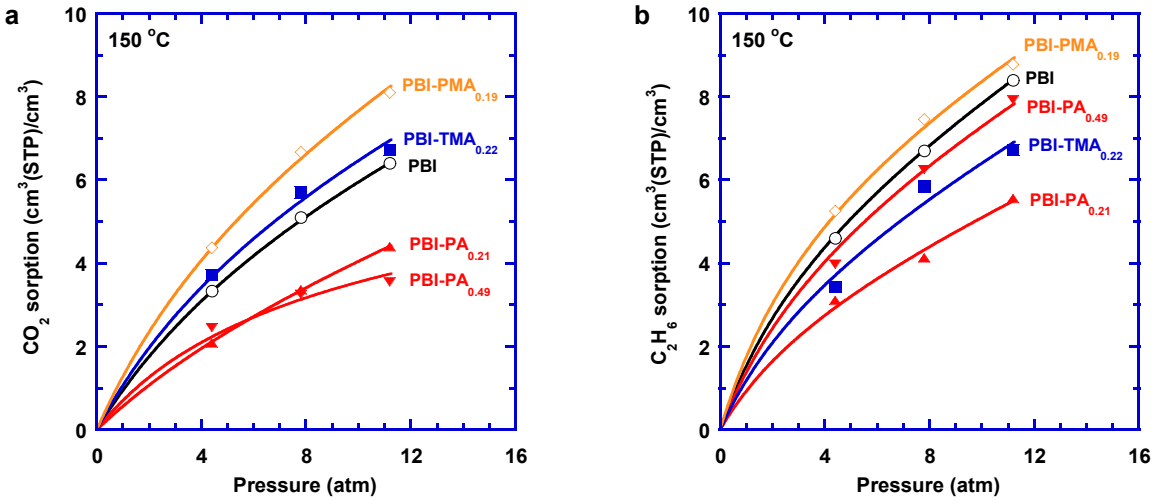

Fig. S5 Sorption isotherms of PBI, PBI-$PA_{0.21}$, PBI-$PA_{0.49}$, PBI-$TMA_{0.22}$, and PBI-$PMA_{0.19}$ for (a) CO_2 and (b) C_2H_6 at 150 °C.

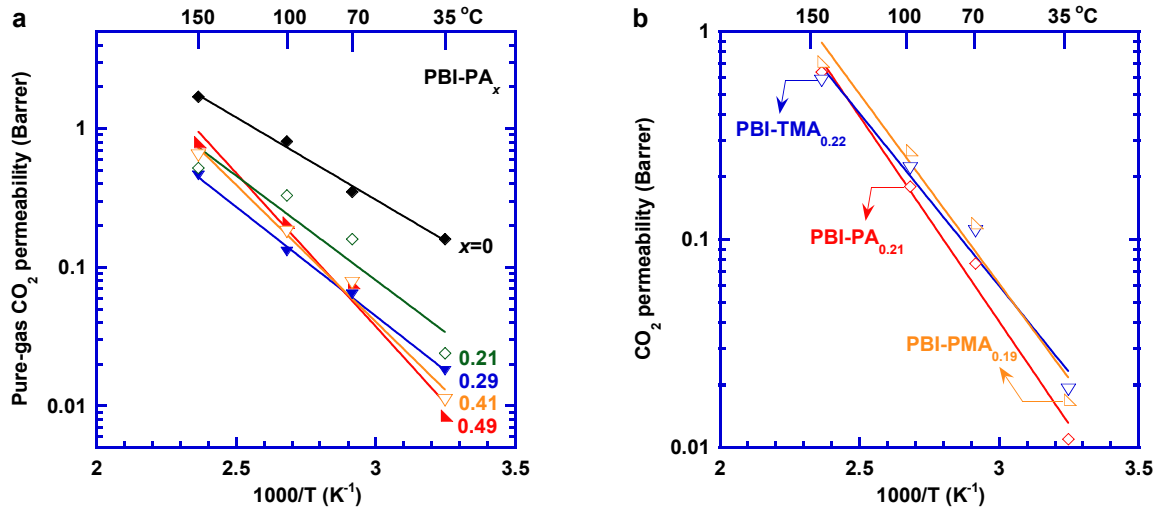

Fig. S6 Effect of temperature on pure-gas CO_2 permeability of (a) PBI-PA_x and (b) PBI-$PA_{0.21}$, PBI-$TMA_{0.22}$, and PBI-$PMA_{0.19}$ with similar molar ratio values of the proton to PBI repeating units. Lines in those figures are the best fits of the Arrhenius equation.

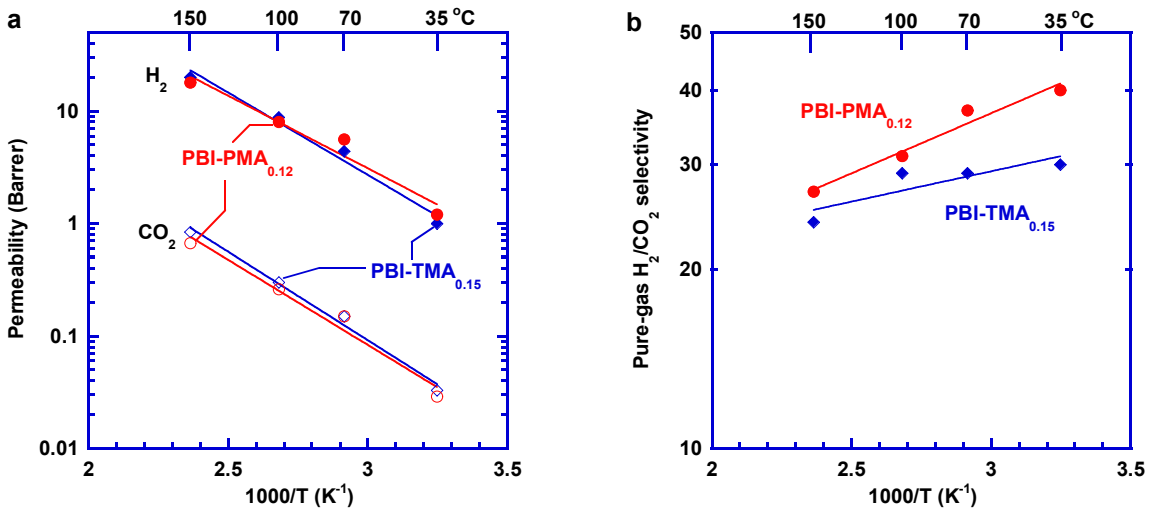

Fig. S7 Effect of temperature on (a) pure-gas H_2 and CO_2 permeability and (b) H_2/CO_2 selectivity of PBI-$TMA_{0.15}$ and PBI-$PMA_{0.12}$. The lines are the best fits of the Arrhenius equation.

Table S8. Values of $E_{P,A}$ and $P_{A,0}$ for H_2 and CO_2 permeation in the PBI-acid samples.

Samples	$E_{P,A}$ (kJ/mol)		$P_{A,0}$ ($\times 10^3$ Barrer)	
	H_2	CO_2	H_2	CO_2
PBI	24	23	25	1.1
PBI-$PA_{0.21}$	26	29	27	2.7
PBI-$PA_{0.29}$	26	30	18	2.3
PBI-$PA_{0.41}$	32	38	150	34
PBI-$PA_{0.49}$	34	42	360	160
PBI-$TMA_{0.15}$	28	30	66	4.8
PBI-$TMA_{0.22}$	28	32	50	5.7
PBI-$PMA_{0.12}$	25	29	23	2.9
PBI-$PMA_{0.19}$	28	35	80	18

Table S9. Comparison between the cross-linked PBIs in this study and leading polymeric membrane materials (cf. Figure 6).

MMMs		Thickness (μm)	Temp. (°C)	Pure- or mixed-gas	H_2 permeability (Barrer)	H_2/CO_2 selectivity	Ref. in the text
#	Materials						
1	PBI-TCL (6 h)	12	150	mixed	19	18	[13]
2	PBI-$TBB_{0.213}$	20	150	mixed	9.6	24	[12]
3	PBI-TaA_{032}	12	150	mixed	15	30	[25]
4	PBI-$OA_{0.49}$	12	150	pure	26	16	[25]
5	PBI/sPPSU-DBX	80	150	mixed	44	9.6	[38]
6	P84-BuDA (6 h)	15	100	pure	47	14	[14]
7	TX-AOPIM-1	60-70	25	pure	300	16	[20]
8	IP PBDI	0.30	150	mixed	72†	23	[40]
9	IP PA	0.02	140	pure	7.0†	50	[39]
10	IP BILPs	0.40	150	pure	9.6†	40	[41]
11	PBI-$PA_{0.49}$	12	100	pure	17	22	
12	PBI-$TMA_{0.22}$	12	100	mixed	16	28	This study
13	PBI-$PMA_{0.19}$	12	100	pure	19	26	

Note: †H_2 permeability was calculated using H_2 permeance and the thickness of the selective layer.