Supplemental Information for

Tightening Polybenzimidazole (PBI) Nanostructures via Chemical Cross-linking for Membrane H_2/CO_2 Separation

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Cross-linking of PBI Using TCL

The cross-linking agent, terephthaloyl chloride (TCL), can rapidly react with the secondary amine groups in polybenzimidazole (PBI). As shown in **Fig. S1**, the reaction was monitored when dilute TCL solution that contains 0.01 mol L^{-1}TCL in dimethylacetamide (DMAc) was gradually added into 0.5 wt.% PBI/DMAc solutions. Insoluble gel was observed at 66 millisecond (ms) after TCL were added.

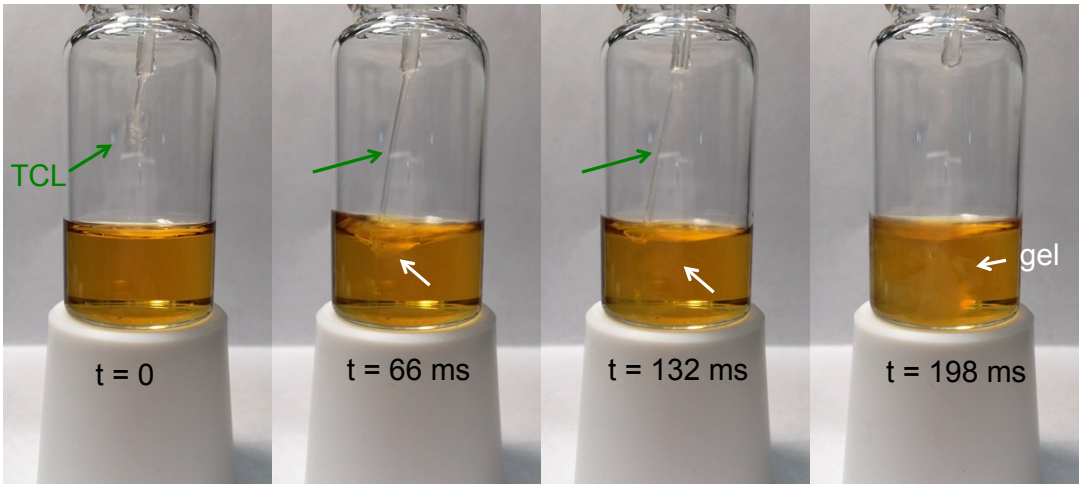

Fig. S1 Photographs of the reaction between TCL and PBI by adding 0.01 mol L^{-1} TCL solution into 0.5 wt.% PBI solution at room temperature. Gels are formed after 66 ms.

Kinetic of THF Sorption in PBI

The sorption of a solvent in glassy polymeric films typically follows two steps: (1) Fickian sorption, which is typically characterized by an approximately linear section at the initial stage of sorption; (2) non-Fickian sorption that is further contributed by the relaxation of the polymeric matrix.[1, 2] In this study, the sorption of THF in PBI was measured by immersing 12-μm-thick PBI films in THF and monitoring the mass change of the PBI films at varying immersion times. The mass uptake of THF by the PBI at an emersion time of t is defined as M_t, and the equilibrium mass update is denoted as M_∞. **Fig. S2** plots the values of M_t/M_∞ as a function of the

square root of immersion time ($t^{1/2}$), showing that M_t/M_∞ and $t^{1/2}$ has a linear relationship until $t^{1/2}$ equals to around 11 $min^{1/2}$ (*i.e.* t = 121 min). This indicates the PBI films began to relax after the immersion of 2 hrs, and then the sorption follows non-Fickian behavior.

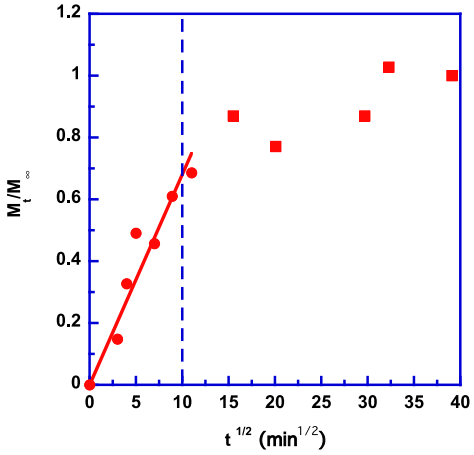

Fig. S2 Swelling test of 12-μm-thick PBI films in THF. M_t is the mass of THF sorbed by the PBI at an immersion time of t, and M_∞ is the equilibrium mass uptake in the sorption experiment.

Cross-linking of PBI Using Malonyl Chloride

The 12-μm-thick PBI films were also cross-linked using malonyl chloride (MCL). All the cross-linking procedures are the same as those used for TCL. **Fig. S3** shows pure-gas H_2 and CO_2 permeability and H_2/CO_2 selectivity at 35 °C as a function of the cross-linking time. Both H_2 and CO_2 permeability decreases with increasing the cross-linking time, while the H_2/CO_2 selectivity increases initially from 12 to 21 as the cross-linking time increases to 6 hrs, and then decreases to 16 after 24-hr cross-linking. These behaviors are similar to PBI cross-linked with TCL. Additionally, these PBI cross-linked by MCL shows the highest H_2/CO_2 selectivity (21) at 6-hr cross-linking, which is the same as those cross-linked with TCL.

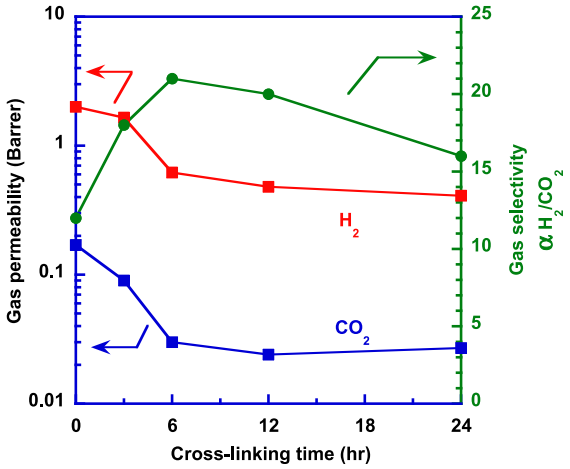

Fig. S3. Effect of the cross-linking time on H_2/CO_2 separation properties at 35 °C in the PBI films cross-linked using MCL.

Effect of Temperature on Gas Permeability

The effect of temperature on pure-gas permeation in PBI and XLPBI-6H (cross-linked with TCL) is modeled using Arrhenius equation (cf. eqn (11) in manuscript), and **Table S1** summarizes the fitting parameters of pre-exponential factor ($P_{A,0}$) and activation energy (E_p).

Table S1 Pre-exponential factor and activation energy for pure-gas permeability in PBI and XLPBI-6H.

	H_2		CO_2	
	$P_{A,0}$ (Barrer)	E_p (kJ mol^{-1})	$P_{A,0}$ (Barrer)	E_p (kJ mol^{-1})
PBI	18,000	23.1	770	21.4
XLPBI-6H	54,000	27.8	2,240	27.6

References:

1. C. C. McDowell, B. D. Freeman and G. W. McNeely, *Polymer*, 1999, **40**, 3487-3499.
2. G. M. Shi, H. Chen, Y. C. Jean and T. S. Chung, *Polymer*, 2013, **54**, 774-783.