Supporting Information

Engineering Hyperbranched Polyimide Membrane for Shape Memory and CO_2 Capture

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1. Calculation of the degree of branching (DB) for hyperbranched polyimides

For hyperbranched polymer, its structural perfection has generally been assessed by degree of branching (*DB*), which is often determined by Frechet's equation (S1):

$$DB = \frac{D+T}{D+T+L} \qquad \text{(S1)}$$

where *D*, *T* and *L* represent the amounts of dendritic, terminal and linear units, respectively. In this study, *DB* of the resulting HBPIs is calculated from the 1HNMR spectra based on Eq.(S2). $I_L$is related to the sum of the peak integrals ascribed to linear units. I_D is associated with the sum of the peak integrals assigning to dendritic

units, and I_T represents the sum of the peak integrals assigning to terminal units.

$$DB = \frac{I_D + I_T}{I_D + I_T + I_L} \qquad \text{(S2)}$$

Figure 2 gives the ^{1}HNMR spectra of select formulations of hyperbranched polyimides. As indicated, the peaks in the range of 8.21-7.51 ppm are assigned to the hydrogens of 6FDA, and the peaks at around 7.68-6.51 ppm are ascribed to the aromatic hydrogens of ODA and BOA, while the peaks in the range of 7.99-5.49 ppm are corresponding with the hydrogens in the pyrimidine ring and the free amines in TAP units, which contain the information on degree of branching. The 1H shift of TAP units in this range was shown in **Table S1**. H5 is the hydrogen in the pyrimidine ring of TAP units. In this research work, there were two kinds of linear units, which were TAP linear units and ODA+BOA linear units. So I_L is the sum of $I_{L\text{-}ODA}$, $I_{L\text{-}BOA}$ and $I_{L\text{-}TAP}$. I_T is the sum of the peak intensities at 5.49 and 5.87 ppm, while $I_{L\text{-}TAP}$ is the sum of the peak intensities at 6.74 and 6.93 ppm, and I_D is the peak intensities at 7.99 ppm. The hydrogens of ODA/BOA at around 7.26 ppm and 7.79 ppm were overlapped with those of 6FDA and NH_2 of 4,6-diimide, so $I_{L\text{-}ODA+BOA}$ can be obtained by Eq. (S3) using the molar ratio of TAP:(ODA+BOA).

$$\frac{Mol_{(ODA+BOA)}}{Mol_{(TAP)}} = \frac{I_{L-(ODA+BOA)} / 2}{I_D / 3 + T_{L-TAP} / 2 + I_T} \qquad \text{(S3)}$$

Finally, DB can be calculated according to Eq. (S2) and its values are summarized in **Table 1**.

Table S1. ^{1}H shift of TAP units

	Structure unit	Chemical shift (ppm)	
		H_5	$-NH_2$
T	2-monoimide	5.49	6.49
	4-, 6-monoimide	5.87	6.38
L	2,4-, 2,6-diimide	6.74	7.79
	4,6-diimide	6.93	7.51
D	triimide	7.99	no

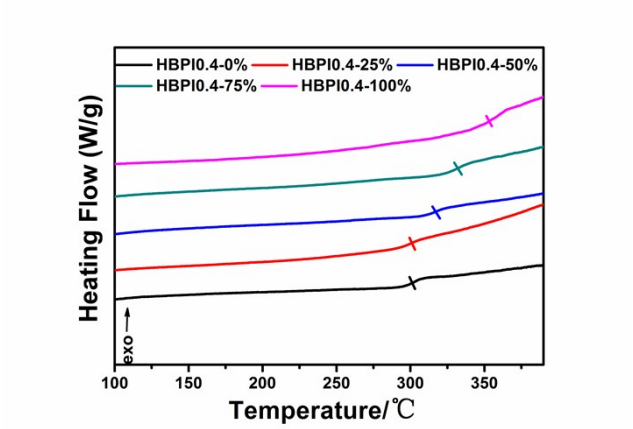

Figure S1. DSC curves for HBPI0.4-*x*% with different BOA content.

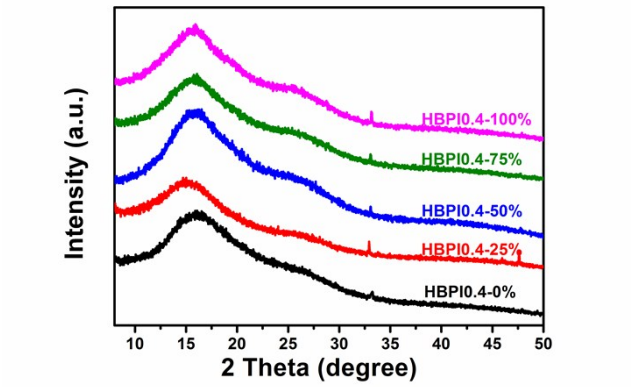

Figure S2. WAXD curves for HBPI0.4-*x*% with different BOA content.

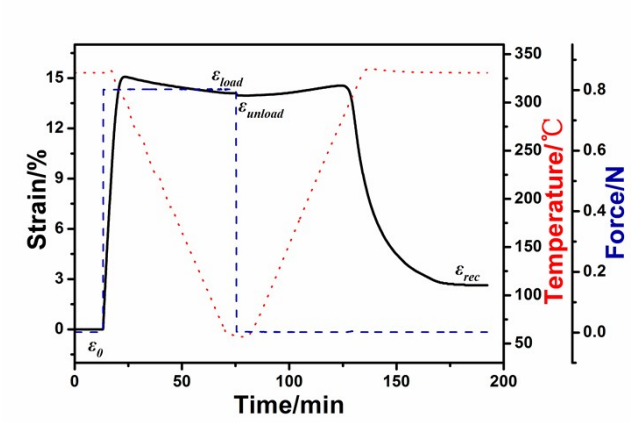

Figure S3. Once Shape memory cycle.

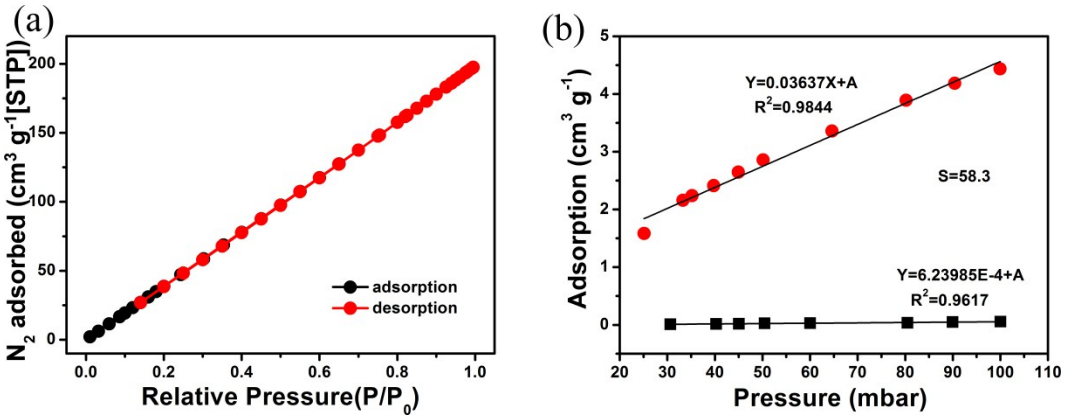

Figure S4. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.4-0%.

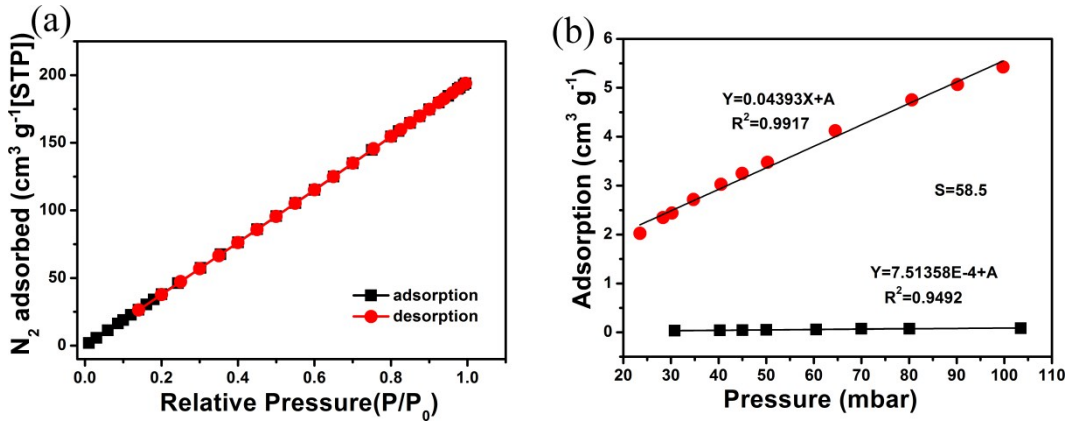

Figure S5. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.4-25%.

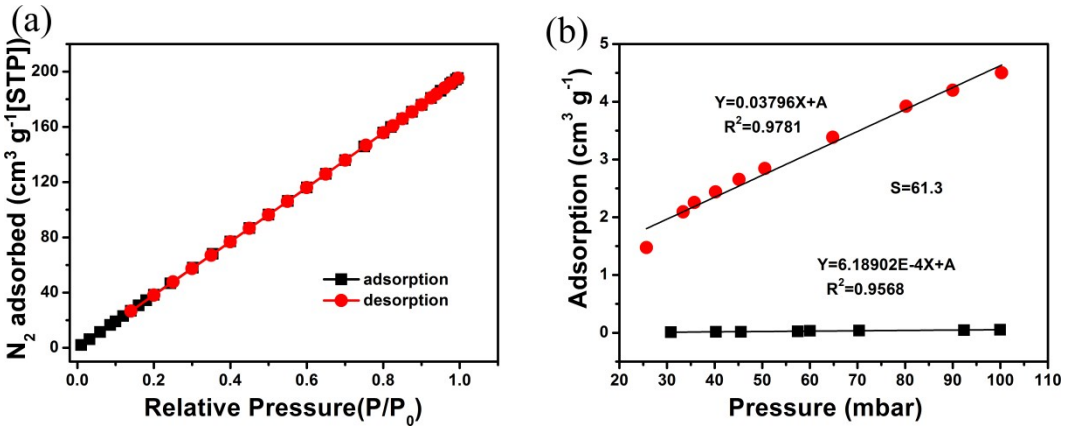

Figure S6. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.4-50%.

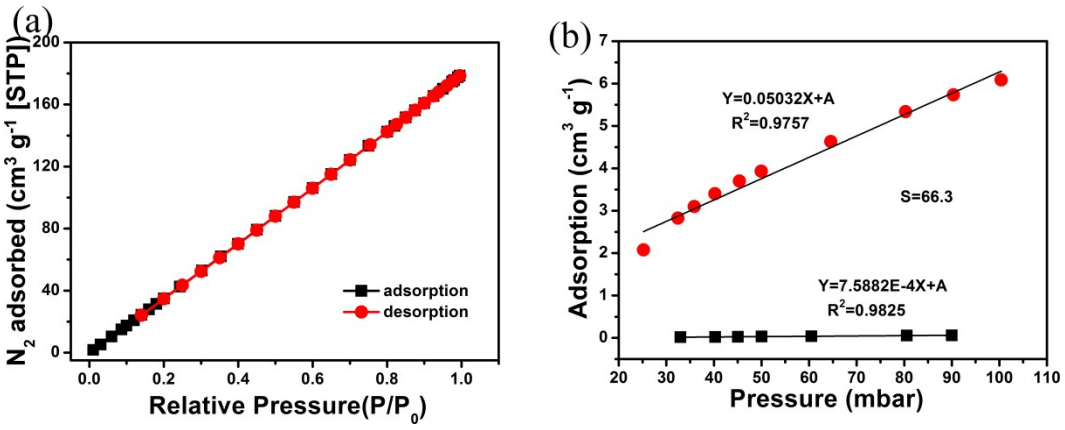

Figure S7. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.4-75%.

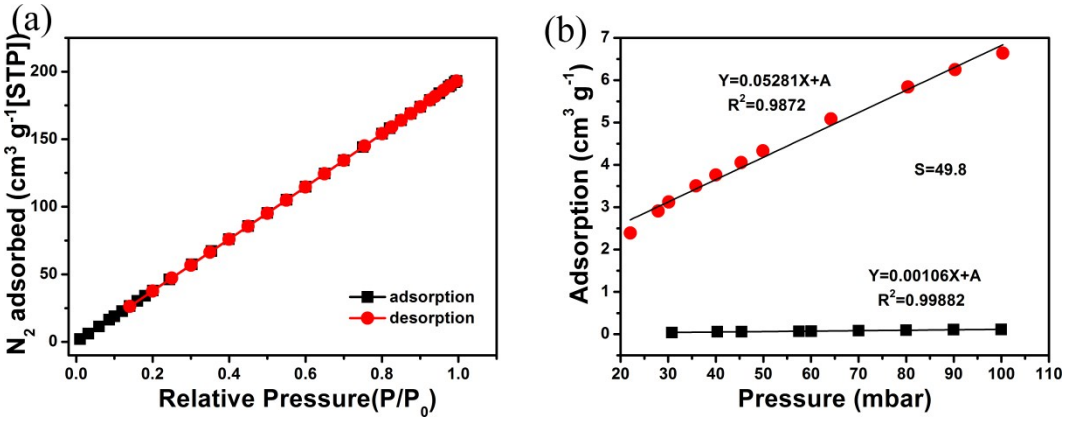

Figure S8. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.4-100%.

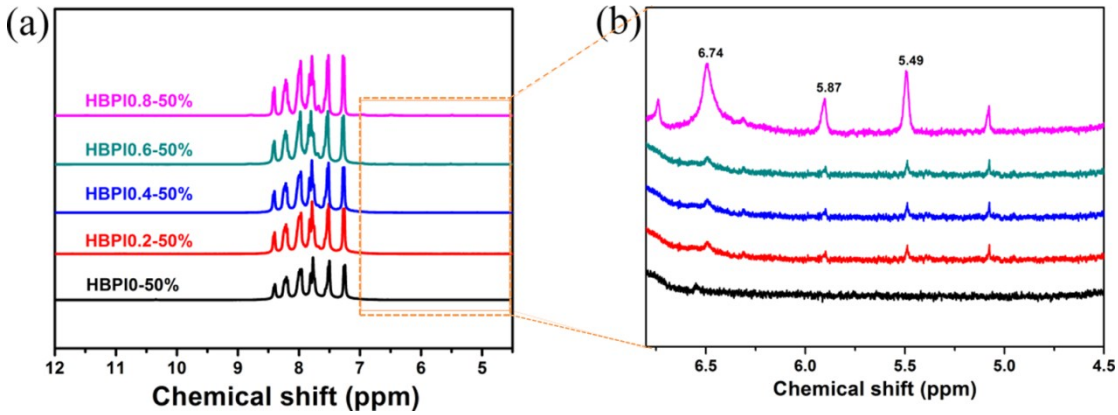

Figure S9. [1]HNMR spectra of (a) HBPI*y*-50%, (b) amplification of (a).

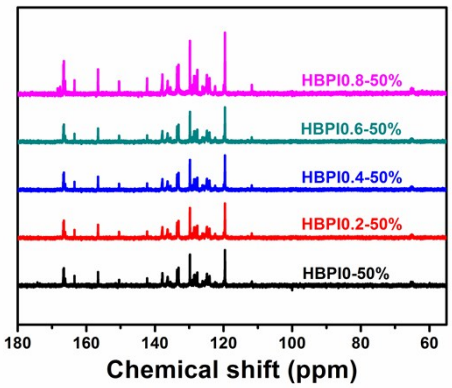

Figure S10. ^{13}CNMR spectra of HBPI*y*-50%.

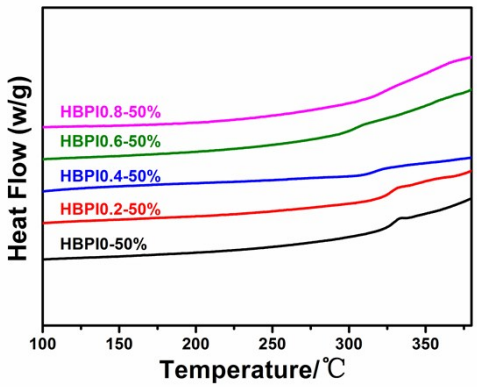

Figure S11. DSC curves for HBPI*y*-*50*% with different DB.

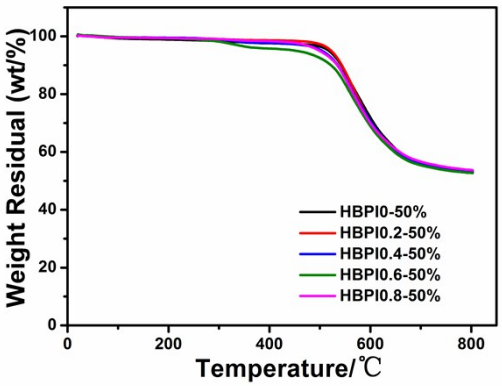

Figure S12. TGA curves for HBPI*y*-*50*% with different DB.

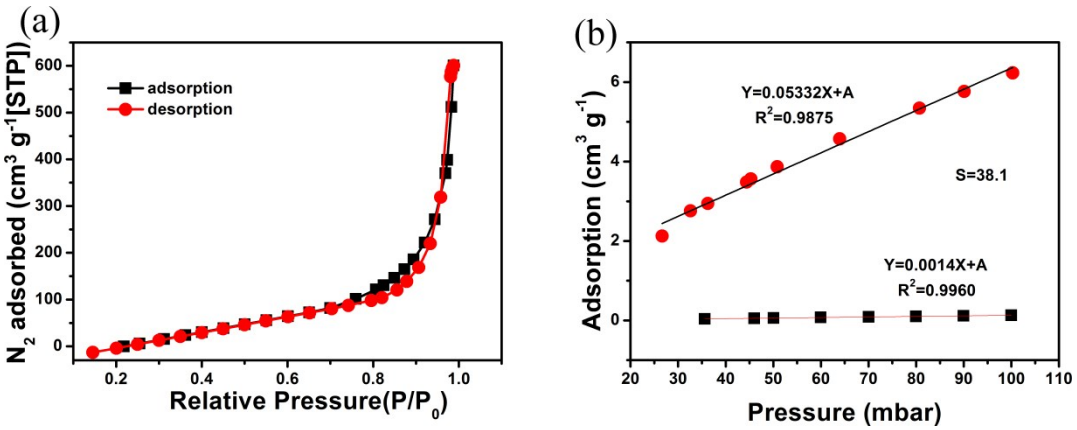

Figure S13. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.2-50%.

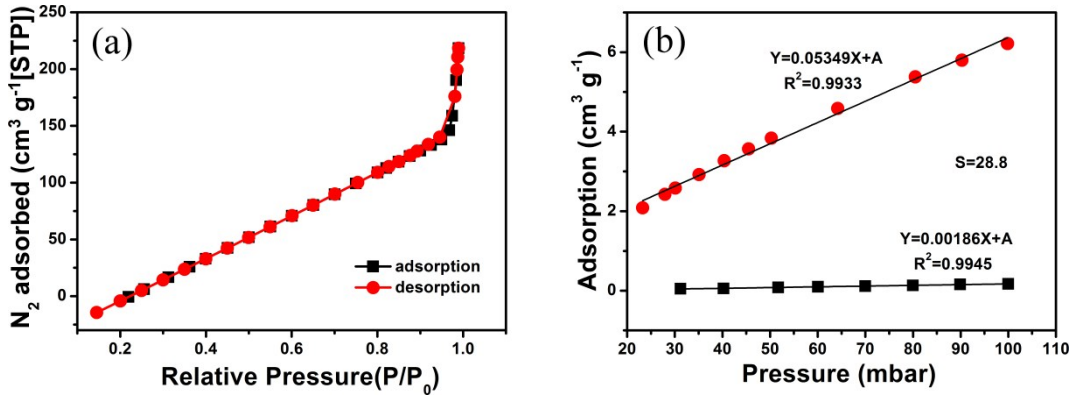

Figure S14. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.6-50%.

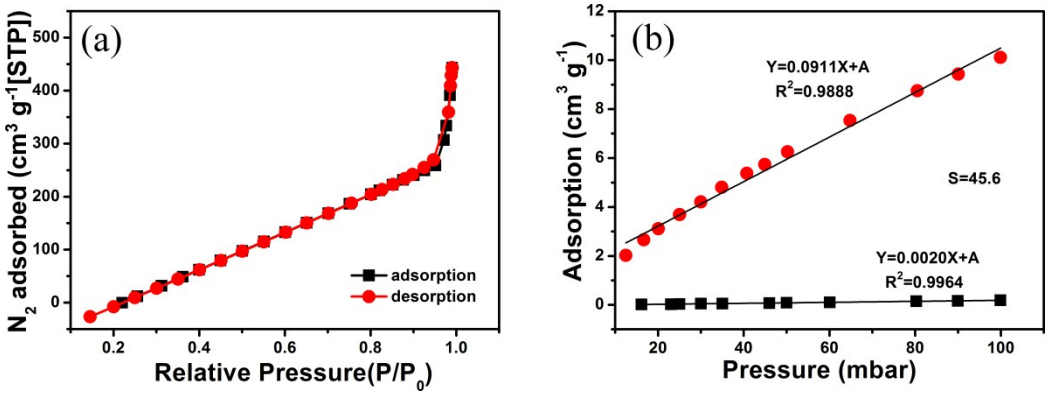

Figure S15. Nitrogen adsorption and desorption isotherms at 77 K (a) and CO_2/N_2 selectivity at 273 K (b) for HBPI0.8-50%.