

*Supporting Information*

# **Tetramine-based Hyperbranched Polyimide Membranes with Rigid Crosslinker for Improved Gas Permeability and Stability**

**Xiangyun Liu <sup>1,2</sup>, Honglei Ling <sup>2,\*</sup>, Jiangzhou Luo <sup>2</sup>, Xueping Zong <sup>2</sup> and Song Xue <sup>2,\*</sup>**

<sup>1</sup> School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

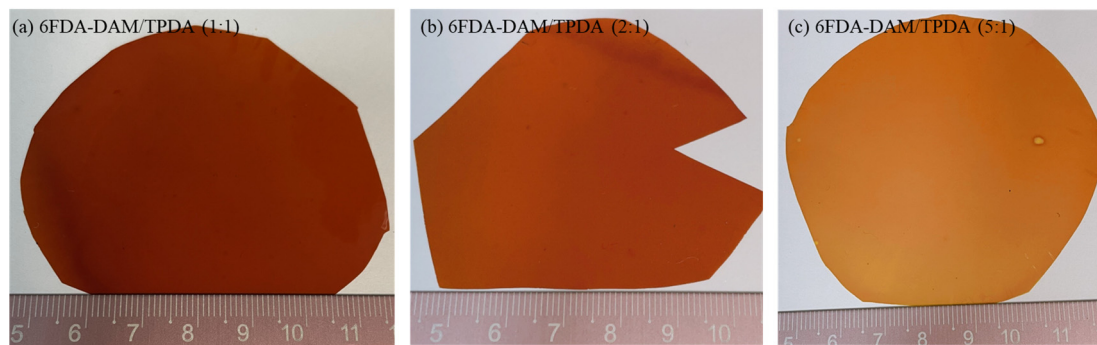
<sup>2</sup> Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China

\* Correspondence: linghl@email.tjut.edu.cn (H.L.); xuesong@ustc.edu.cn (S.X.)

**Table S1.** Gel content of 6FDA-DAM/TPDA membranes in different solvents.

Sample	Gel content (%)		
	THF	DCM	DMF
6FDA-DAM/TPDA(1:1)	99.92	99.89	99.90
6FDA-DAM/TPDA(2:1)	99.97	99.96	99.93
6FDA-DAM/TPDA(5:1)	99.98	99.96	99.93

Note: The acronyms for THF, DCM and DMF represent tetrahydrofuran, dichloromethane, and N,N-dimethylformamide, respectively.



**Figure S1.** Physical appearances of 6FDA-DAM/TPDA membranes with varied DAM contents.

**Table S2.** Gas permeabilities and selectivities of the 6FDA-DAM/TPDA(5:1) membrane after aging for different days.

Time (days)	P (Barrer)			Ideal selectivity ( $\alpha$ )	
	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
0	9.75	40.78	190.2	4.18	19.51
50	8.76	36.7	172.3	4.19	19.67
80	7.46	31.63	147.8	4.24	19.82
120	7.33	31.22	142.2	4.26	19.71
360	6.43	29.77	131.2	4.63	20.41

**Table S3.** Pressure-dependent gas permeabilities and selectivities for the 6FDA-DAM/TPDA(5:1) membrane.

Pressure (MPa)	P (Barrer)			Ideal selectivity ( $\alpha$ )	
	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
0.2	9.75	40.78	190.2	4.18	19.51
0.4	10.48	38.15	174.3	3.64	16.63
0.6	10.12	34.35	163.8	3.39	16.19
0.8	9.63	33.68	161.2	3.49	16.74
1.0	9.11	33.66	162.7	3.69	17.86
1.2	9.01	33.19	161.9	3.68	17.97

**The gas diffusion and solubility coefficients calculation:**

The pure gas diffusion coefficient ( $10^{-8}\text{cm}^2/\text{s}$ ) was calculated by the equation of  $D = l^2/6\theta$ , where  $\theta$  is the time-lag of the permeability measurement. Ideal diffusion selectivity( $\alpha$ ) for a gas pair (A/B) is calculated as the ratio of their pure-gas diffusion coefficients:

$$\alpha_{A/B} = \frac{D_A}{D_B}$$

The solubility coefficient S ( $10^{-2}\text{cm}^3/(\text{cm}^3\text{cmHg})$ ) was obtained via the diffusion-solution model using the formula of  $S = P/D$ . Ideal solubility selectivity( $\alpha$ ) for a gas pair (A/B) is calculated as the ratio of their pure-gas solubility coefficients:

$$\alpha_{A/B} = \frac{S_A}{S_B}$$