

## Supporting Information

### Tröger's Base-Based Microporous Polyimide Membranes for High-Performance Gas Separation

Zhengong Wang, Dong Wang\*, Feng Zhang, and Jian Jin\*

Nano-Bionics Division and *i-LAB*, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China.

#### Experimental details

##### Materials and equipments

2-methyl-4-nitroaniline (99%), 2-methyl-3-nitroaniline (98%), trifluoroacetic acid, and Pd/C (Pd, 10%) were purchased from Aladdin Reagent and were used without further purification. Paraformaldehyde, sodium hydroxide, anhydrous ethanol, m-cresol, and anhydrous toluene were purchased from Sinopharm Chemical Reagent Co., Ltd.. Hydrazine monohydrate (98%) and quinoline (99%) were purchased from Alfa Aesar. 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA), 4,4'-oxydiphthalic anhydride (ODPA) were purchased from Alfa Aesar, which were dried at 120 °C under reduced pressure for 12 h before used.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of the precursor of monomers, monomers and the resulting polymers, which were dissolved in either  $\text{CDCl}_3$ -*d* or  $\text{DMSO-}d_6$ , were recorded on a Varian nuclear magnetic resonance (NMR) spectroscopy at a resonance frequency of 400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR. Molecular weights and polydispersity index (PDI) of the polymers were determined by Varian (PL-GPC 50) gel permeation chromatography (GPC) using Ultrastaygel columns and THF eluent for TBDA1-6FDA-PI and TBDA2-6FDA-PI and  $\text{CHCl}_3$  eluent for TBDA1-ODPA-PI and TBDA2-ODPA-PI at a flow rate of 1 ml/min at 40 °C. The values were determined by comparison with a series of polystyrene standards.

Temperatures of polymer thermal degradation were obtained from TG/DTA 6200. For TG measurement, samples were initially heated to 120 °C under nitrogen gas and maintained at that temperature for 1 h for removal of moisture and then heated to 800°C at 5°C/min for measurement of degradation temperature ( $T_d$ ). Wide-angle X-ray diffraction (WAXD) was conducted on a Bruker D8 instrument utilized with Cu K $\alpha$  radiation of wavelength ( $\lambda$ ) 1.54 Å. The value of d-spacing was calculated by means of Bragg's law ( $d = n\lambda/2\sin\theta$ ). Accelerated Surface Area and Porosimetry (ASAP) 2020 system (Micromeritics Instrument Corporation) was used to study N<sub>2</sub> adsorption/desorption of the samples. Apparent surface areas were calculated from N<sub>2</sub> adsorption data by multi-point Brunauer-Emmet-Teller (BET) method.

Dense membranes of TB-based polyimides were obtained by casting their 2-3 wt% chloroform solution which filtered by 0.45 µm PTFE filter into a 9 cm circular Teflon mould covered with a transparent glass plate. After 3 days, the films were formed and placed in high vacuum oven at 120 °C for 24 h to remove residual solvent. Then the films were immersed in methanol for 24 h, dried in air and placed in high vacuum oven at 120 °C for 24 h again. Gas permeation testing was measured at 35 °C and at a feed pressure of 1 bar with pure gas (99.999%) in the order of He (2.69Å), H<sub>2</sub> (2.8Å), O<sub>2</sub> (3.46Å), N<sub>2</sub> (3.64Å), CH<sub>4</sub> (3.87Å), CO<sub>2</sub> (3.3Å) using a fixed-volume pressure increase instrument time-lag apparatus, starting with an oil free vacuum. Permeability coefficient,  $P$ , was calculated from the slope in the steady state region by using the equation (1) and apparent diffusion coefficient  $D$ , from the time-lag  $\theta$ , using the equation (2):

$$P = \frac{273.15 \times 10^{10}}{760} \frac{Vl}{A\Delta p} \left( \frac{dp}{dt} \right) \quad (1)$$

$$D = \frac{l^2}{6\theta} \quad (2)$$

Where  $P$  is the permeability represented in barrer (1 barrer =  $10^{-10}$  [cm<sup>3</sup>(STP) cm]/(cm<sup>2</sup>s cmHg));  $dp/dt$  the rate of pressure rise under the steady state;  $V$  (cm<sup>3</sup>) the downstream volume;  $l$  (cm) the membrane thickness;  $\Delta p$  (cmHg) the pressure difference between the two

sides;  $T$  (K) the measurement temperature;  $A$  (cm<sup>2</sup>) the effective area of the membrane. The solubility of the gas in the polymer matrix is determined indirectly, via the equation (3):

$$S = \frac{P}{D} \quad (3)$$

All gas permeation tests were performed more than three times. The ideal selectivity for pure gas A and B is defined as the equation (4):

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (4)$$

## Monomer synthesis

### 2,8-Dinitro-4,10-dimethyl-6H,12H -5,11-methanodibenzo[1,5]-diazocine

12 g (78.86 mmol) 2-methyl-4-nitroaniline and 4.98 g (165.62 mmol, 2.1 equiv) paraformaldehyde were dissolved in 150 mL (2.02 mol, 25.5 equiv) trifluoroacetic acid (TFA) in ice-bath giving a dark-brown colored reaction mixture, which was stirred for two days at nitrogen atmosphere under room temperature and then poured into 200 mL pure water under continuously stirring giving a yellow precipitate. About 340 mL Aq NaOH (6 mol/L) was gradually added to this suspension adjusting pH to 8.5-9, the precipitate was filtered off and refluxed in 300 mL acetone for 1 h. The mixture was cooled down and stored at -20 °C overnight and the yellow product was filtered off giving a yield of 10.8 g (31.73 mmol, 81 %), mp >300 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.97 (s, 2H), 7.81 (s, 2H), 4.68 (d,  $J$  = 16.0 Hz, 2H), 4.36 (s, 2H), 4.31 (d,  $J$  = 16.0 Hz, 2H), 2.47 (s, 6H).

### 2,8-Diamino-4,10-dimethyl-6H, 12H-5,11-methanodibenzo[1,5]-diazocine (TBDA1)

Under a nitrogen atmosphere, the yellow solid 2,8-Dinitro-4,10-dimethyl-6H,12H-5,11-methanodibenzo[1,5]-diazocine (5 g, 14.7 mmol) was dispersed in ethanol (100 mL) followed by mixing with Pd/C (0.5 g, Pd 10 wt%), which was heated to reflux. Then, N<sub>2</sub>H<sub>4</sub>H<sub>2</sub>O (98%, 10 mL) was added dropwise to the hot solution. After refluxing for 8 h, the precipitate was taken off by filtration and the resulting solution was concentrated to half under reduced pressure at 40

°C. The product was obtained by adding 100ml water and recovered by filtration. It was dried under reduced pressure at 50°C to give a white powder (3.7 g, 90.2%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 6.26 (d, *J* = 4.0 Hz, 2H), 5.94 (d, *J* = 3.9 Hz, 2H), 4.55 (s, 4H), 4.26 (d, *J* = 16.1 Hz, 2H), 4.06 (s, 2H), 3.62 (d, *J* = 16.2 Hz, 2H), 2.18 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 149.31, 140.64, 137.45, 133.71, 120.16, 114.11, 73.12, 60.16, 22.01.

### **3,9-Dinitro-4,10-dimethyl-6H,12H-5,11-methanodibenzo[1,5]-diazocine**

3,9-Dinitro-4,10-dimethyl-6H,12H-5,11-methanodibenzo[1,5]-diazocine was obtained dimerization of 2-methyl-3-nitroaniline as the same of that of 2,8-Dinitro-4,10-dimethyl-6H, 12H-5,11-methanodibenzo[1,5]-diazocine. Yield: 83%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.58 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.66 (d, *J* = 16.2 Hz, 2H), 4.34 (s, 2H), 4.15 (d, *J* = 15.9 Hz, 2H), 2.50 (s, 6H).

### **3,9-Diamino-4,10-dimethyl-6H,12H-5,11-methanodibenzo[1,5]-diazocine (TBDA2)**

The synthesis of 2,8-Diamino-4,10-dimethyl-6H,12H-5,11-methanodibenzo[1,5]-diazocine (TBDA2) was the same as TBDA2. Yield: 92%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 6.45 (d, *J* = 8.1 Hz, 2H), 6.31 (d, *J* = 8.1 Hz, 2H), 4.59 (s, 4H), 4.36 (d, *J* = 16.2 Hz, 2H), 4.12 (s, 2H), 3.66 (d, *J* = 16.3 Hz, 2H), 2.04 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 151.25, 150.67, 129.06, 120.98, 119.98, 115.73, 72.48, 60.07, 16.05.

## **Polymer synthesis**

### **Synthesis of TBDA1-6FDA-PI**

To a solution of TBDA1(0.51 g, 1.83 mmol) dissolved in m-cresol (10 ml), 4, 4'-(hexafluoro isopropylidene)-diphthalic anhydride (6FDA) (0.81 g, 1.83 mmol) were added in portions, occurring in a dried 25 ml three-neck flask equipped with a Dean-Stark trap and reflux condenser under a nitrogen atmosphere. After the reaction mixture stirred for 1 h, quinoline (0.1 ml), and anhydrous toluene(2 ml) were added to the mixture. Then the temperature was raised gradually to 200 °C and held for 6 h. During this time water was removed from the reaction mixture by azeotropic distillation. 30 ml Chloroform was added to

the resulting viscous solution on cooling, afterwards the solution was poured slowly to 500 ml methanol. The resulting thread-like solid precipitate was collected by filtration. Purification was achieved by reprecipitation from chloroform (20 ml) into methanol (500 ml) twice and drying in a vacuum oven at 120 °C for 12 h, giving TBDA1-6FDA-PI as a light-yellow powder (1.15g, 92% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.00 (d,  $J$  = 8.0 Hz, 2H), 7.90 (s, 2H), 7.84 (d,  $J$  = 8.4 Hz, 2H), 7.09 (s, 2H), 6.84 (s, 2H), 4.67 (d,  $J$  = 16.7 Hz, 2H), 4.33 (s, 2H), 4.08 (d,  $J$  = 16.2 Hz, 2H), 2.45 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz)  $\delta$ : 166.20, 146.36, 139.05, 135.83, 134.65, 132.64, 132.35, 128.97, 127.14, 126.60, 125.04, 124.07, 122.59, 121.93, 67.09, 65.18, 54.64, 17.26. ATR-FTIR (film,  $\nu$ ,  $\text{cm}^{-1}$ ): 2960 (str, aromatic C-H), 2920, 2850 (str, aliphatic C-H), 1781 (asym str of imide C=O), 1720 (sym str of imide C=O), 1376 (str of imide C-N), 750 (str, imide ring C-N-C). Molecular mass: (GPC, eluent-THF, against polystyrene standards)  $M_n$ = 3 0000,  $M_w$ = 78 000  $\text{g mol}^{-1}$ , PDI= 2.6. BET surface area =80  $\text{m}^2/\text{g}$ .

#### Synthesis of TBDA1-ODPA-PI

The synthesis procedure of TBDA1-ODPA-PI was same as that of TBDA1-6FDA-PI. Yield: 93%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.95 (d,  $J$  = 8.1 Hz, 2H), 7.51 (s, 2H), 7.42 (d,  $J$  = 8.2 Hz, 2H), 7.09 (s, 2H), 6.85 (s, 2H), 4.66 (d,  $J$  = 16.2 Hz, 2H), 4.33 (s, 2H), 4.08 (d,  $J$  = 19.8 Hz, 2H), 2.45 (s, 6H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.38, 161.09, 146.11, 134.59, 134.48, 128.87, 127.26, 127.12, 126.86, 126.14, 124.67, 122.55, 113.97, 67.14, 54.68, 17.25. ATR-FTIR (film,  $\nu$ ,  $\text{cm}^{-1}$ ): 2960 (str, aromatic C-H), 2920, 2850 (str, aliphatic C-H), 1778 (asym str of imide C=O), 1712 (sym str of imide C=O), 1373 (str of imide C-N), 742 (str, imide ring C-N-C). Molecular mass: (GPC, eluent- $\text{CHCl}_3$ , against polystyrene standards)  $M_n$ =26000,  $M_w$ =71 000  $\text{g mol}^{-1}$ , PDI=2.7. BET surface area = 24  $\text{m}^2/\text{g}$ .

#### Synthesis of TBDA2-6FDA-PI

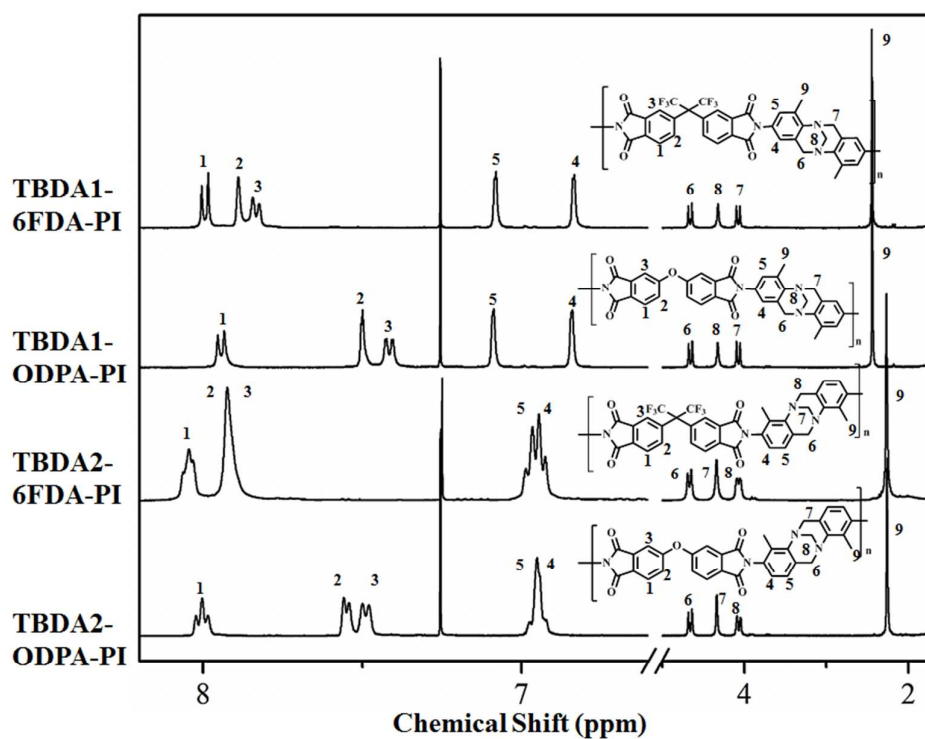
The synthesis procedure of TBDA2-6FDA-PI was same as that of TBDA1-6FDA-PI. Yield: 91%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.05 (dd, 2H), 7.93 (s, 4H), 6.96 (dd,  $J$  = 8.1 Hz,

4H), 4.68 (d,  $J = 16.1$  Hz, 2H), 4.35 (s, 2H), 4.08 (d,  $J = 12.1$  Hz, 2H), 2.28 (s, 6H).  $^{13}\text{C}$  NMR (100MHz  $\text{CDCl}_3$ )  $\delta$ : 166.08, 147.30, 139.08, 135.82, 132.80, 132.57, 132.20, 129.71, 129.42, 125.46, 125.08, 124.18, 123.95, 121.92, 66.88, 65.22, 55.20, 12.44. ATR-FTIR (film,  $\nu$ ,  $\text{cm}^{-1}$ ): 2960 (str, aromatic C-H), 2920, 2850 (str, aliphatic C-H), 1785 (asym str of imide C=O), 1722 (sym str of imide C=O), 1370 (str of imide C-N), 746 (str, imide ring C-N-C). (GPC, eluent-THF, against polystyrene standards)  $M_n=23\ 000$ ,  $M_w=52\ 000\ \text{g mol}^{-1}$ , PDI= 2.3. BET surface area =  $325\ \text{m}^2/\text{g}$ .

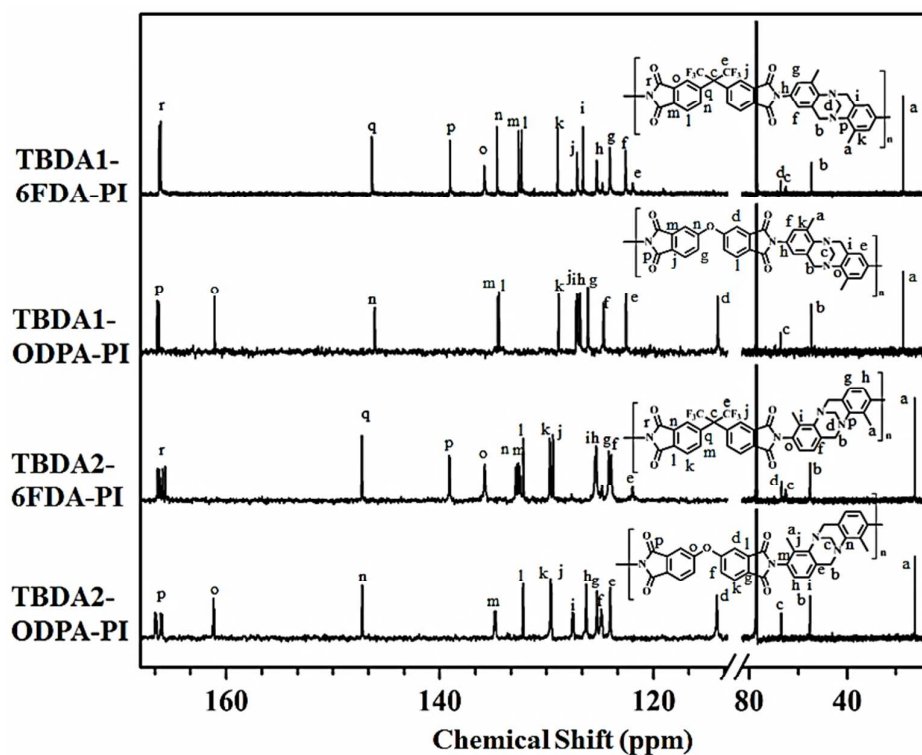
### Synthesis of TBDA2-ODPA-PI

The synthesis procedure of TBDA2-ODPA-PI was same as that of TBDA1-6FDA-PI. Yield: 92%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.01 (t,  $J = 7.6$  Hz, 2H), 7.56 (d,  $J = 8.0$  Hz, 2H), 7.50 (d,  $J = 7.8$  Hz, 2H), 7.00–6.87 (m, 4H), 4.67 (d,  $J = 15.8$  Hz, 2H), 4.34 (s, 2H), 4.07 (d,  $J = 16.1$  Hz, 2H), 2.27 (s, 6H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.40, 161.20, 147.27, 134.79, 132.20, 129.65, 127.54, 126.30, 125.29, 124.86, 124.04, 114.08, 66.93, 55.21, 12.41. ATR-FTIR (film,  $\nu$ ,  $\text{cm}^{-1}$ ): 2960 (str, aromatic C-H), 2920, 2850 (str, aliphatic C-H), 1778 (asym str of imide C=O), 1712 (sym str of imide C=O), 1369 (str of imide C-N), 744 (str, imide ring C-N-C). (GPC, eluent- $\text{CHCl}_3$ , against polystyrene standards)  $M_n=27\ 000$ ,  $M_w=73\ 000\ \text{g mol}^{-1}$ , PDI=2.7. BET surface area =  $38\ \text{m}^2/\text{g}$ .

## Supplemental Figures and Tables

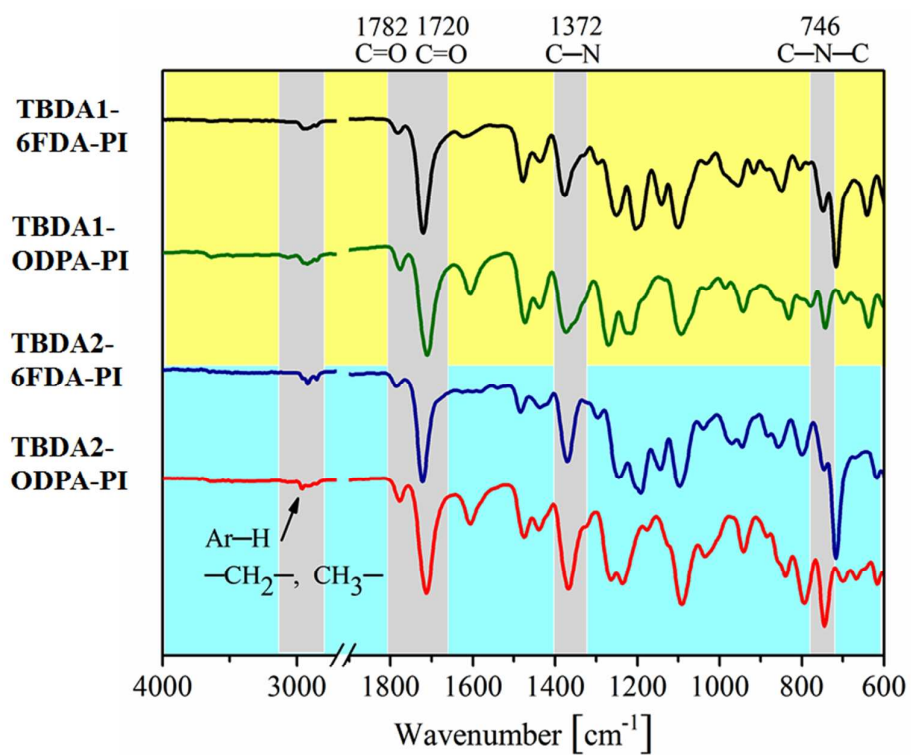


**Figure S1.**  $^1\text{H}$  NMR spectra of TBDA1-6FDA-PI, TBDA2-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI.

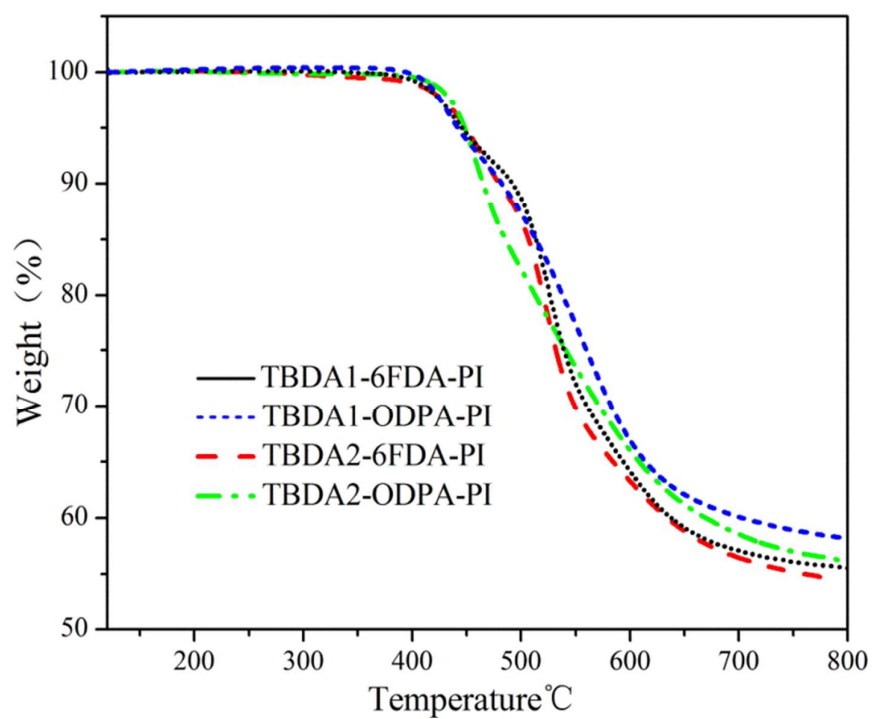


**Figure S2.**  $^{13}\text{C}$  NMR spectra of TBDA1-6FDA-PI, TBDA2-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI.

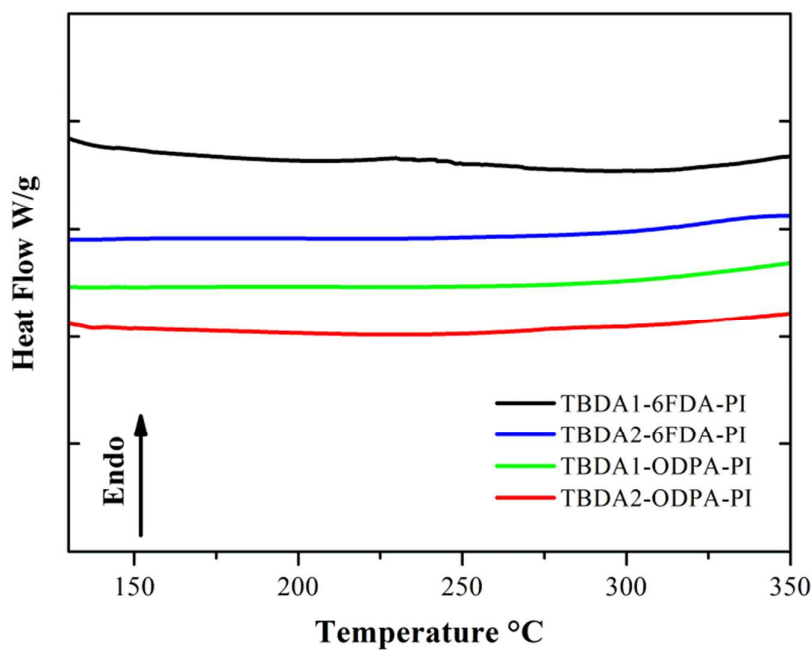




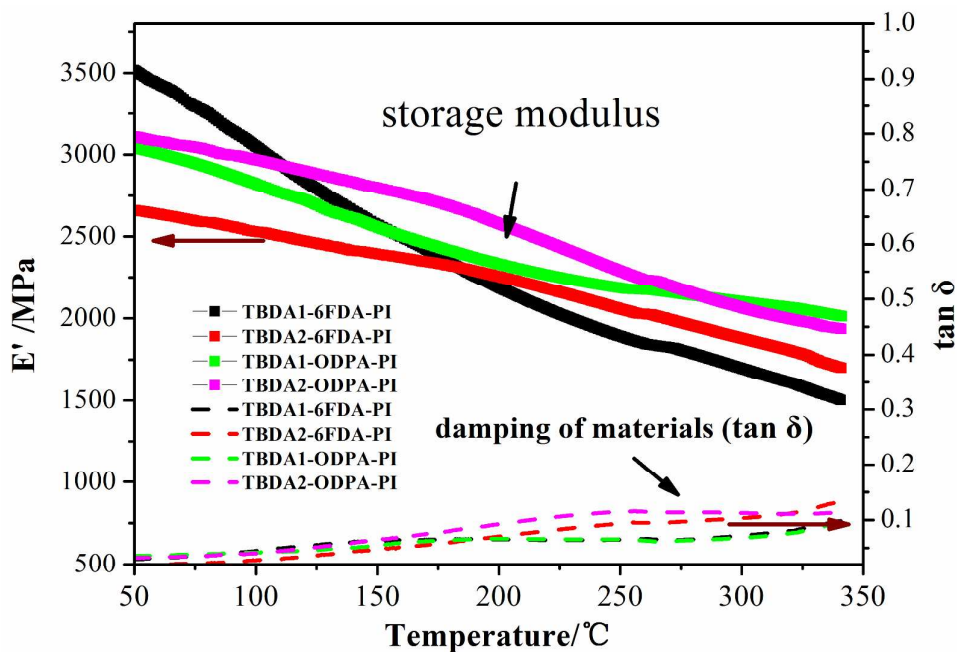
**Figure S3.** ATR-IR spectra of TBDA1-6FDA-PI, TBDA2-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI membranes



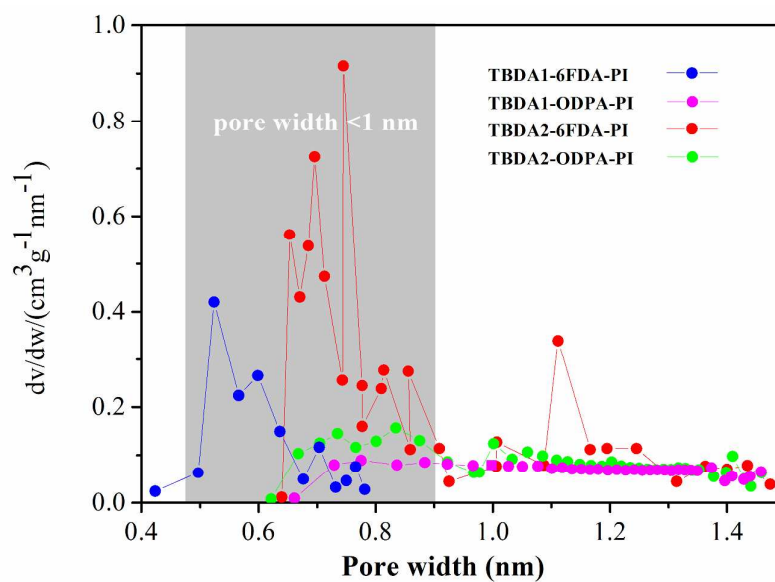
**Figure S4.** TG data of TBDA1-6FDA-PI, TBDA2-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI.



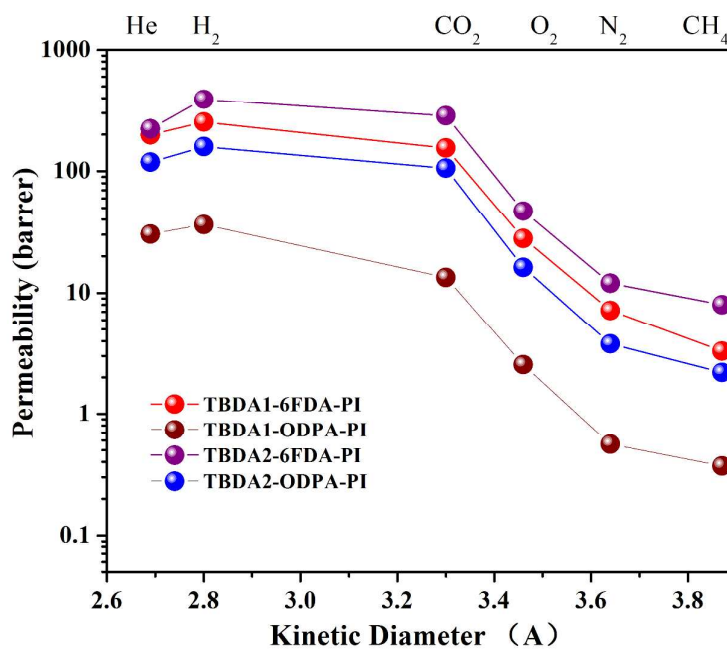
**Figure S5.** DSC curves of TBDA1-6FDA-PI, TBDA2-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI.



**Figure S6.** DMA (Dynamic Mechanical Thermal Analyses) curves of TBDA1-6FDA-PI, TBDA2-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI.



**Figure S7.** Pore width distributions obtained by analysis of N<sub>2</sub> adsorption at 77 K by the Horvath-Kawazoe method



**Figure S8.** Gas permeation properties for different TB-based polyimide membranes

**Table S1.** Physical properties of TB-based polyimides

TB-based-PI	Mn /10 <sup>4</sup>	M <sub>w</sub> / 10 <sup>4</sup>	PDI	$\rho$ (g/cm <sup>3</sup> )	FFV	BET (m <sup>2</sup> /g)	Td (5%)	Td (10%)	Tensile strength at break [MPa]	Elongation at break [%]
TBDA1-6FDA-PI	3.0	7.8	2.6	1.31	0.21	89	446	492	85.2 ± 1.2	8.9
TBDA1-ODPA-PI	2.6	7.1	2.7	1.27	0.18	24	441	481	90.5±2.2	11.2
TBDA2-6FDA-PI	2.3	5.2	2.3	1.28	0.23	349	449	479	80.5 ± 2.3	7.3
TBDA2-ODPA-PI	2.7	7.3	2.7	1.24	0.20	38	448	465	94.5 ± 3.1	13.2

**Table S2.** Solubility of TB-based polyimides in various solvents

polymers	Solvents						
	THF	CHCl <sub>3</sub>	CHCl <sub>2</sub>	NMP	DMF	DMSO	m-cresol
TBDA1-6FDA-PI	√	√	√	√	√	√	√
TBDA1-ODPA-PI	×	√	×	√	×	×	√
TBDA2-6FDA-PI	√	√	√	√	√	√	√
TBDA2-ODPA-PI	×	√	√	√	√	√	√