

Supplementary information

Synthesis and Effect of Physical Aging on Gas Transport Properties of a Microporous Polyimide Derived from a Novel Spirobifluorene-based Dianhydride

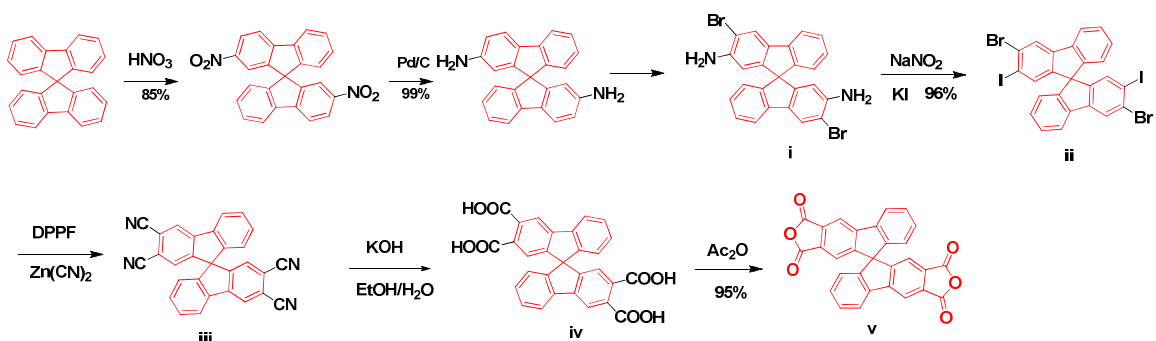
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Materials. 3,3'-dibromo-2,2'-diamino-9,9-spirobifluorene was synthesized from our previous report.¹ Sodium nitrite, Potassium iodide (KI), methanol, sulfonic acid, Tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$), 1,1'-Bis(diphenylphosphino)ferrocene (DPPF), Zinc cyanide ($\text{Zn}(\text{CN})_2$), potassium hydroxide, *m*-cresol, tetrahydrofuran, ethanol, hydrochloride acid, celite, *N*-bromosuccinimide (NBS), dichloromethane, petrol oil ether, dimethylacetamide and isoquinoline were obtained from Sigma-Aldrich and used as its. 3,3'-dimethylnaphthidine was obtained from TCI and used as received.

Characterization Methods. NMR spectra of the newly synthesized monomer and polymers were recorded using a Bruker AVANCE-III 400MHz or 500MHz spectrometer in deuterated chloroform with tetramethylsilane as an internal standard. Elemental analysis was carried out using a Perkin-Elmer 2400 CHN elemental analyzer. Fourier transform infrared spectra (FT-IR) of the polyimide was acquired using a Varian 670-IR FT-IR spectrometer. High-resolution mass spectroscopy (HRMS) was conducted on a Thermo LC/MS system with LTQ Orbitrap Velos detectors. Molecular weights and weight distribution of the polymers were obtained by gel permeation chromatography (Malvan HT-350) using chloroform was used as eluent and polystyrene as external standard. Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere using TGA Q5000 (TA Instruments), the heating is recorded from room temperature to 800 °C at a heating rate of 3 °C/min. DSC of the polyimide was done on DSC Q2000 (TA Instruments), at the heating rate of 5 °C/min from room temperature to 400 °C. The BET surface areas of the polymers were determined by N_2 sorption at 77 K (Micrometrics ASAP 2020). The polymer powder was degassed for 12 hours at 120 °C before testing.

Synthesis of the spirobifluorene-based non-extended dianhydride



Scheme S1. Synthetic route of the spirobifluorene-based dianhydride (SBFDA)

3,3'-dibromo-2,2'-diamino-9,9'-spirobifluorene was synthesized according to the previous procedure.¹

3,3'-dibromo-2,2'-diiodo-9,9'-spirobifluorene (ii). 3,3'-dibromo-2,2'-diamino-9,9'-spirobifluorene (i) (501 mg, 1.00 mmol) was dissolved in the mixed solvent of H_2SO_4 (80% percent, 10 mL) and water (10 mL), which was cooled to ice-bath for 15 min before NaNO_2 (207 mg dissolved in 3 mL water) solution was added in drops. The resulting yellow diazonium salt solution was further stirred for 30 min before KI (1.48 g, 10 mmol, in 10 mL water) solution was added in one portion. The system was stirred for half an hour at the cold-bath and thereafter 1 hour at room temperature before been filtrated and washed with water for 3 times. The solid was dried in oven and the pure product was obtained as a light yellow powder purified by flash column. (690 mg, 96% yield). TLC: dichloromethane/petrol oil ether = 1/2, R_f = 0.9; ^1H NMR (400MHz, CDCl_3): δ 8.09 (s, 2H), 7.80 (d, 2H, J = 7.68 Hz), 7.40 (t, 2H, J = 7.48 Hz, 7.56 Hz), 7.19 (t, 2H, J = 7.56 Hz, 7.48 Hz), 7.16 (s, 2H). ^{13}C NMR (125MHz, CDCl_3): δ 147.9, 147.4, 143.6, 139.5, 135.4, 129.4, 129.3, 128.5, 124.2, 120.6, 99.6, 64.4.

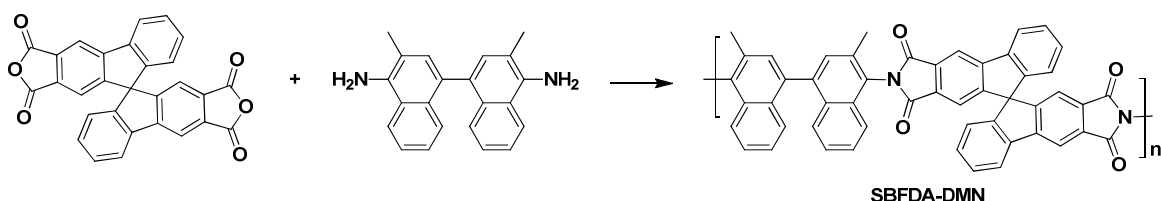
2,2',3,3'-tetracyano-9,9'-spirobifluorene (iii). 3,3'-dibromo-2,2'-diiodo-9,9'-spirobifluorene (**ii**) (702 mg, 1.00 mmol), Pd(DPPF)Cl₂ (60 mg) and Zn(CN)₂ (117 mg, 1.0 mmol) were added to anhydrous DMAc (5.6 mL) under Ar atmosphere. The system was heated to 100 °C and kept for half an hour, and thereafter, four portions of Zn(CN)₂ (117 mg, 117 mg, 117 mg and 117 mg) were added in 2 hours. The solution was kept at 100 °C for 2 hours before been cooled to room temperature. Finally, the solution was poured into methanol/water (50 mL / 50 mL) mixed solvent to form a large quantity of precipitate. The solid was collected by filtration, and the pure off-white crystal (375 mg, yield: 90%) can be obtained by column. TLC: Dichloromethane, R_f = 0.35. ¹H NMR (500MHz, CDCl₃): δ 8.27 (s, 2H), 7.99 (d, 2H, *J* = 7.75 Hz), 7.58 (t, 2H, *J* = 7.5 Hz, 7.5 Hz), 7.37 (t, 2H, *J* = 7.5 Hz, 7.5 Hz), 7.05 (s, 2H), 6.79 (d, 2H, *J* = 7.7 Hz).

9,9'-spirobifluorene-2,2',3,3'-tetracarboxylic acid (iv). 2,2',3,3'-tetracyano-9,9'-spirobifluorene (**v**) (624 mg, 1.50 mmol) was suspended in water/ethanol (10/10 mL) mixed solvent. To it, KOH (1.74 g, 30 mmol) was added in one portion and the system was thereafter refluxed overnight before been cooled to room temperature. The solution was filtrated to remove trace insoluble solid and then acidified with HCl (6M) to adjust the pH to 1~2. A large quantity of white precipitate was formed and collected by filtration and washed several times with water. The solid was dried in vacuum oven at 40 °C for two days and an off-white powder (664 mg, yield: 90%) was obtained. ¹H NMR (500MHz, DMSO-*d*₆): δ 8.33 (s, 2H), 8.22 (d, 2H, *J* = 7.65 Hz), 7.48 (t, 2H, *J* = 7.5 Hz, 7.5 Hz), 7.23 (t, 2H, *J* = 7.5 Hz, 7.5 Hz), 6.87 (s, 2H), 6.70 (d, 2H, *J* = 7.65 Hz).

9,9'-spirobifluorene-2,2',3,3'-dianhydride (v). The intermediate (**vi**) (1.06 g, 2.15 mmol) was added to 15 mL Ac₂O and refluxed for 6 hrs before cooling to room temperature. An off-white precipitation was formed, which was filtrated and washed several times with cold acetic

anhydride, a needle crystal 0.9 g (yield: 98%) can be obtained after drying under vacuum oven for 24 hrs at 120 °C. ^1H NMR (400MHz, CDCl_3): δ 8.45 (s, 2H), 8.07 (d, 2H, $J = 7.72$ Hz), 7.58 (t, 2H, $J = 7.48$ Hz, 7.50 Hz), 7.36 (t, 2H, $J = 7.48$ Hz, 7.50 Hz), 7.24 (s, 2H), 6.82 (d, 2H, $J = 7.68$ Hz). ^{13}C NMR (125MHz, CDCl_3): δ 162.4, 162.2, 155.3, 150.1, 146.9, 138.8, 132.5, 131.5, 130.4, 129.8, 124.5, 122.3, 121.2, 117.3, 65.7. HRMS (ESI): for $\text{C}_{29}\text{H}_{12}\text{O}_6$ $[\text{M}]^+$, 456.0634, found, 456.0628. Anal. Calcd. for $\text{C}_{29}\text{H}_{12}\text{O}_6$: C, 76.32; H, 2.65; Found: C, 74.62; H, 2.59.

Synthesis of the polymers



Scheme S2. Synthesis of the polymer

Synthesis of SBFDA-DMN

9,9'-spirobifluorene-2,2',3,3'-tetracarboxylic dianhydride (456 mg, 1.00 mmol) and 3,3'-dimethylnaphthidine (312 mg, 1.00 mmol) were added to *m*-cresol (3 mL). The solution was heated to 70 °C for 2 hr before isoquinoline (5 drops) was added. Thereafter, the system was heated up to 120 °C, 150 °C till 180 °C and kept for 1 hr at each temperature. Finally, the polymer was precipitated into methanol (100 mL), filtrated, dried and re-precipitated in methanol twice. After filtration, the polymer was further dried in a vacuum oven at 120 °C overnight and an off-white filament (730 mg, yield: 95%) was obtained. ^1H NMR (400MHz, CDCl_3): δ 8.56 (s, 2H), 8.09 (s, 2H), 7.42 - 7.62 (m, 16H), 6.97 (s, 2H), 2.42 (s, 6H); FT-IR (polymer film, ν , cm^{-1}): 3055 (m, str C-H), 1780 (s, str, imide), 1714 (s, str, imide), 1608 (m, str, Ph), 1389, 1373 (s, str,

C-N), 747 (s, astr, imide); Anal. Calcd. for: C, 83.36; H, 4.12; N, 3.81. Found: C, 81.27; H, 4.36; N, 3.46; Molecular weight (GPC in chloroform) $M_n = 6.5 \times 10^4$; $M_w = 12.5 \times 10^4$; PDI = 1.92. $T_d = 520$ °C; $S_{BET} = 686$ m²/g.

Membrane Fabrication. The polymer was dissolved in chloroform (2~3% wt/v) and then purified using small 1.0 µm PTFE filter cartridges. The solution was carefully transferred into a flat petri dish. The solvent was evaporated slowly over two days at ambient conditions. The isotropic polymer films (123 µm thick) were thereafter soaked in methanol for 24 h. The fresh made membrane was air-dried for 24 h before testing; the heat-treated membrane was thereafter heated at 120 °C and kept for 24 h under vacuum oven.

Gas Permeation Measurements. The gas permeability of the membranes was determined using the constant-volume/variable-pressure method. The membranes were degassed in the permeation system on both sides under high vacuum at 35 °C for at least 24 h. The increase in permeate pressure with time was measured by a MKS Baratron transducer. The permeability of all gases was measured at 2 bar at 35 °C and was calculated by:

$$P = D \times S = 10^{10} \times \frac{V_d \times l}{p_{up} \times T \times R \times A} \times \frac{dp}{dt}$$

where P is the gas permeability (Barrer) – 1 Barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg, p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg/s), V_d is the calibrated permeate volume (cm³), l is the membrane thickness (cm), A is the effective membrane area (cm²), T is the operating temperature (K), and R is the gas constant (0.278 cm³·cmHg/cm³(STP)·K). The apparent diffusion coefficient D (cm²/s) of the polymer membrane at 2 bar was calculated by $D = l^2/6\theta$, where l is the membrane thickness and θ is the time lag of

the permeability measurement. The solubility coefficient S ($\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{cmHg}$) was obtained from the relationship $S = P/D$. The pure-gas selectivity was calculated as: $\alpha_{A/B} = P_A/P_B$.

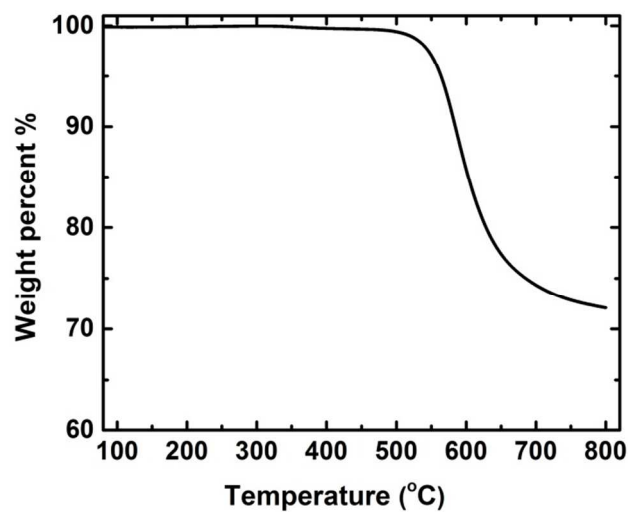


Figure S1. Thermal gravimetric analysis of SBFDA-DMN from room temperature to 800 °C under N_2 atmosphere at the heating rate of 3 °C/min.

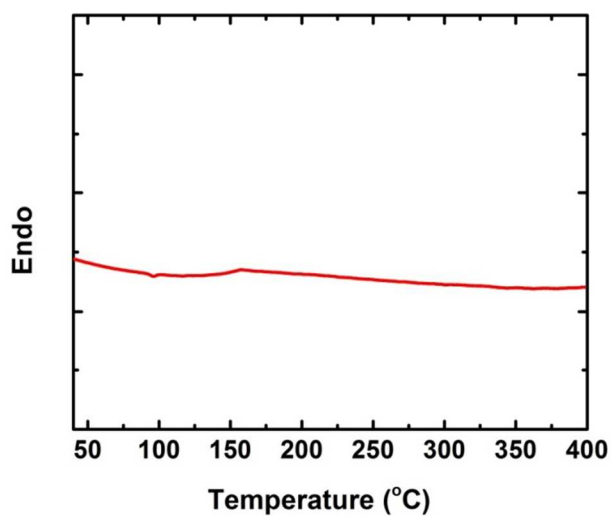


Figure S2. DSC of SBFDA-DMN, the temperature increment rate is 5 °C/min.

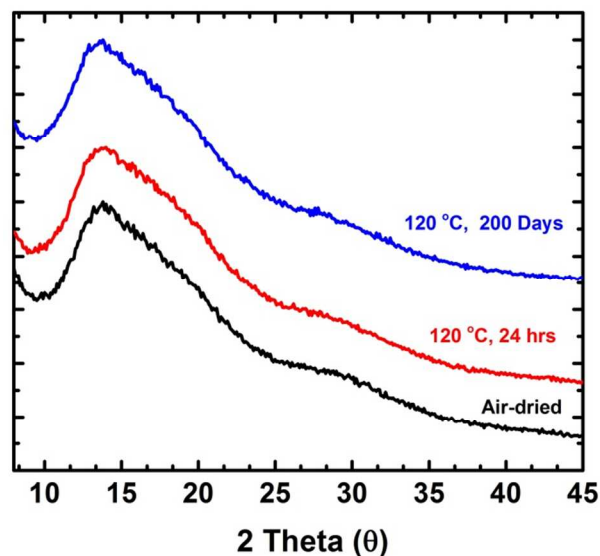


Figure S3. WAXD of the SBFDA-DMN membranes treated at different conditions.

Table S1. Diffusion Coefficient (D), Solubility Coefficient (S), Diffusion Selectivity (α_D) and Solubility Selectivity (α_S) for Different Gases of SBFDA-DMN

Polymers	D (10^{-8} cm ² /s)			S (10^{-2} cm ³ /cm ³ cmHg ⁻¹)			α_D	α_S
	N ₂	O ₂	CO ₂	N ₂	O ₂	CO ₂	O ₂ /N ₂	O ₂ /N ₂
SBFDA-DMN ^a	75.3	247	89.5	4.18	4.78	74.6	3.3	1.1
SBFDA-DMN ^b	11.4	49.6	19.6	2.89 ^c	3.24 ^c	36.0	4.3	1.1
PIM-PI-12 ^d	84	270	95	3.29	3.83	57.8	3.2	1.2
PIM-PI-12 ^e	32	144	48	3.3	3.4	50.1	4.8	1.1

^a Freshly made and air-dried SBFDA-DMN membrane; ^b SBFDA-DMN aged for 200 days; ^c Solubility coefficient obtained from barometric adsorption; ^d PIM-PI-12 soaked in methanol and air-dried; data from reference 32; ^e Air-dried PIM-PI-12 aged for 273 days; data from reference 32.

REFERENCES

1. Ma, X.; Salinas, O.; Litwiller, E.; Pinnau, I. *Macromolecules* **2013**, *46*, 9618.