Supporting Information:

The Spirobichroman-Based Polyimides with Different Side Group: From Structure-Property Relationships to Chain Packing and Gas Transport Performances

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1.1 Synthesis the 4,4,4',4'-tetramethyl-2,2'-spirobi[chromane]-7,7'-diol

Resorcinol (6.6066 g, 60 mmol), $FeCl_3$ (0.6488 g, 4 mmol) and toluene (24 mL) were added to three-necked flask, which equipped with mechanical agitation, reflux condenser and nitrogen guard. After the mixture was stirred 0.5 h at room temperature, the mesityl oxide (1.5702 g, 16 mmol) was added dropwise into the reaction mixture and heated to 85 °C for 12 h. The hot toluene phase was obtained by removing the black insoluble and concentrated by vacuum. The residue was purified by recrystallize with methanol/deionized water (Vmethanol:Vdeionized water=1:1). A yield of 15% (1.52 g). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.13 (d, J = 7.7 Hz, 1H), 7.15 (d, J = 8.5 Hz, 1H), 6.36 (dd, J = 8.4, 2.5 Hz, 1H), 5.95 (d, J = 2.5 Hz, 1H), 2.05 (d, J = 14.1 Hz, 1H), 1.91 (d, J = 14.1 Hz, 1H), 1.47 (s, 3H), 1.26 (s, 3H).

1.2 Synthesis the Spirobichroman-based dinitro monomers

The specific synthesis process of **4,4,4',4'-tetramethyl-7,7'-bis(4-nitrophenoxy)-2,2'-spirobi[chromane] (Spiro-FN)** was interpreted as an example. In a 100 mL three-necked flask equipped with nitrogen-protected and Dean−Stark trap, the Spiro-diol (3.4042 g, 10 mmol) was dissolved in DMF (30 mL), then K_2CO_3 (3.3170 g, 24 mmol), 4-Chloronitrobenzene (3.7812 g, 24 mmol) were added. After the mixture was stirred for 30 minutes at room temperature, 20 mL toluene was added as the azeotropic agent of reaction. The reaction mixture was heated to 150 °C at least 10 h, while the water was removed through toluene reflux. And the mixture solution was cooled to room temperature and poured into 200 mL deionized water. Then the crude product was purified by recrystallize from DMF/methanol (V_{DMF}:$V_{methanol}$=1:1) to afford a yellow powder for 5.36 g (92% of yield). Melting point: 230–231 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.26–8.15 (m, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.11–7.00 (m, 2H), 6.77 (dd, J = 8.5, 2.5 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H), 2.19 (d, J = 14.3 Hz, 1H), 2.07 (d, J = 14.4 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H). FTIR (powder, ν, cm^{-1}): 1523, 1342 (-NO_2 stretch).

6,6'-((4,4,4',4'-tetramethyl-2,2'-spirobi[chromane]-7,7'-diyl)bis(oxy))bis(3-nitropyridine) (Spiro-DN). Melting point: 192–194 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.02 (dd, J = 2.9, 0.6 Hz, 1H), 8.58 (dd, J = 9.0, 2.8 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.18 (dd, J = 9.1, 0.6 Hz, 1H), 6.81 (dd, J = 8.5, 2.5 Hz, 1H), 6.56 (d, J = 2.4 Hz, 1H), 2.19 (d, J = 14.4 Hz, 1H), 2.06 (d, J = 14.3 Hz, 1H), 1.55 (s, 3H), 1.35 (s, 3H). FTIR (powder, ν, cm^{-1}): 1509, 1350 (-NO_2 stretch).

2,2'-((4,4,4',4'-tetramethyl-2,2'-spirobi[chromane]-7,7'-diyl)bis(oxy))bis(3-methyl-5-nitropyridine) (Spiro-MN). Melting point: 249–250 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.82 (d, J = 2.8 Hz, 1H), 8.54–8.49 (m, 1H), 7.47 (d, J = 8.5 Hz, 1H), 6.82–6.78 (m, 1H), 6.53 (d, J = 2.4 Hz, 1H), 2.36 (s, 3H), 2.18 (d, J = 14.3 Hz, 1H), 2.06 (d, J = 14.3 Hz, 1H), 1.55 (s, 3H), 1.35 (s, 3H). FTIR (powder, ν, cm^{-1}): 1513, 1355 (-NO_2 stretch).

1.3 Synthesis the Spirobichroman-Based diamine monomers

The synthetic process was explained used **4,4'-((4,4,4',4'-tetramethyl-2,2'-spirobi[chromane]-7,7'-diyl)bis(oxy))dianiline (Spiro-FH)** as an example. In a 250 mL round-bottom flask, the Spiro-FN (2.9131 g, 5 mmol) was dissolved in 25 mL ethanol, and added Pd/C (1.0 g). The reaction system was heated to reflux, and the $N_2H_4 \cdot H_2O$ (5.0067 g, 100 mmol) was discreetly added to the mixture over 0.5 h. After maintained the reflux temperature about 10 h (monitored by TLC), Pd/C was removed through filtration. The filtrate was gathered and cooled to

room temperature. At last, the yellow powder was obtained by vacuum distillation. Melting point: 75–76 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.28 (d, J = 8.6 Hz, 1H), 6.76–6.68 (m, 2H), 6.59–6.52 (m, 2H), 6.47 (dd, J = 8.6, 2.6 Hz, 1H), 6.00 (d, J = 2.6 Hz, 1H), 4.97 (s, 2H), 2.06 (d, J = 14.2 Hz, 1H), 1.92 (d, J = 14.2 Hz, 1H), 1.44 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.91, 150.65, 145.41, 145.34, 127.49, 124.64, 120.96, 114.81, 110.17, 104.31, 98.18, 45.47, 32.05, 31.93, 29.85. FTIR (powder, ν, cm^{-1}): 3454, 3357 (N-H stretch).

6,6'-((4,4,4',4'-tetramethyl-2,2'-spirobi[chromane]-7,7'-diyl)bis(oxy))bis(pyridin-3-amine) (Spiro-DH). Melting point: 207–208 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.52 (dd, J = 2.9, 0.7 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 7.04 (dd, J = 8.6, 2.9 Hz, 1H), 6.71 (dd, J = 8.6, 0.6 Hz, 1H), 6.53 (dd, J = 8.5, 2.5 Hz, 1H), 6.15 (d, J = 2.5 Hz, 1H), 5.08 (s, 2H), 2.12 (d, J = 14.3 Hz, 1H), 1.98 (d, J = 14.3 Hz, 1H), 1.49 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.15, 153.28, 150.49, 141.92, 132.41, 127.30, 125.77, 125.22, 112.90, 112.39, 106.91, 98.17, 45.46, 32.06, 31.93, 29.96. FTIR (powder, ν, cm^{-1}): 3473, 3426 (N-H stretch).

6,6'-((4,4,4',4'-tetramethyl-2,2'-spirobi[chromane]-7,7'-diyl)bis(oxy))bis(5-methylpyridin-3-amine) (Spiro-MH). Melting point: 114–115 °C (DSC). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.35 (dd, J = 2.8, 0.7 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H), 6.91 (dd, J = 2.9, 0.8 Hz, 1H), 6.49 (dd, J = 8.5, 2.5 Hz, 1H), 6.10 (d, J = 2.5 Hz, 1H), 5.02 (s, 2H), 2.11 (d, J = 14.2 Hz, 1H), 2.06 (d, J = 0.9 Hz, 3H), 1.97 (d, J = 14.2 Hz, 1H), 1.49 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.31, 151.33, 150.42, 142.23, 129.89, 127.27, 125.72, 125.25, 122.44, 111.93, 106.35, 98.05, 45.37, 32.10, 31.96, 29.89, 15.53. FTIR (powder, ν, cm^{-1}): 3426, 3339 (N-H stretch).

1.4 Synthesis the Spirobichroman-based Polyimides

The 6FDA-FH was served as an example to illustrate the detailed synthesis process. The Spiro-FH (1.0453 g, 2 mmol) and 4.5 mL DMAc were added to 50 mL three-necked flask. The mixture was stirred until form a uniform solution, and added 6FDA (0.8885 g, 2 mmol) to the flask. Then the mixture was permitted to reaction about 12 h at room temperature to obtain a viscous polyamide acid solution. The acetic anhydride (4 mL) and pyridine (2mL) were added to the above mixture, and the reaction process was maintained for another 12 h at 100 °C. After cooling to room temperature, the polymer solution was poured into ionized water, and a fiber-like precipitate was produced. Finally, the product was collected by filtration and purified by Soxhlet extractor with methanol and water to give a pale fiber. The other two polymers, 6FDA-DH and 6FAD-MH were

synthesized using the similar process of 6FDA-FH.

6FDA-FH: ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.12 (d, J = 7.5 Hz, 1H), 7.92 (s, 1H), 7.71 (s, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.06 (s, 1H), 6.64 (s, 1H), 6.31 (s, 1H), 2.12 (s, 1H), 1.98 (d, J = 15.8 Hz, 1H), 1.49 (s, 3H), 1.29 (s, 3H). FTIR (membrane ν, cm^{-1}): 2966, 2873 (C-H stretching of aliphatic), 1783 (C=O symmetric stretching of imide), 1728 (C=O asymmetric stretching of imide), 1378 (N-H bending).

6FDA-DH: ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.22–8.10 (m, 2H), 8.00–7.84 (m, 2H), 7.71 (s, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 6.80–6.72 (m, 1H), 6.49 (d, J = 2.4 Hz, 1H), 2.17 (d, J = 14.2 Hz, 1H), 2.03 (d, J = 14.2 Hz, 1H), 1.54 (s, 3H), 1.33 (s, 3H). FTIR (membrane ν, cm^{-1}): 2961, 2868 (C-H stretching of aliphatic), 1780 (C=O symmetric stretching of imide), 1733 (C=O asymmetric stretching of imide), 1388 (N-H bending).

6FAD-MH: ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (d, J = 7.9 Hz, 1H), 7.95 (d, J = 11.5 Hz, 2H), 7.71 (s, 2H), 7.41 (d, J = 8.3 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 6.45 (s, 1H), 2.27 (s, 3H), 2.16 (d, J = 13.8 Hz, 1H), 2.02 (d, J = 15.0 Hz, 1H), 1.54 (s, 3H), 1.33 (s, 3H). FTIR (membrane ν, cm^{-1}): 2966, 2863 (C-H stretching of aliphatic), 1785 (C=O symmetric stretching of imide), 1738 (C=O asymmetric stretching of imide), 1375 (N-H bending).

2. FIGURE

Figure S1. FTIR spectroscopy of dinitro and diamine monomers.

Figure S2. ^{1}H NMR spectrum of diamine monomers Spiro-FH, Spiro-DH, and Spiro-MH.

Figure S3. ^{13}C NMR spectra of diamine monomers.

Figure S4. FTIR spectra of three polyimides.

Figure S5. ^{1}H NMR spectra of polyimide 6FDA-FH, 6FDA-DH, and 6FDA-MH.

Figure S6. TGA curves of three polyimides under air.

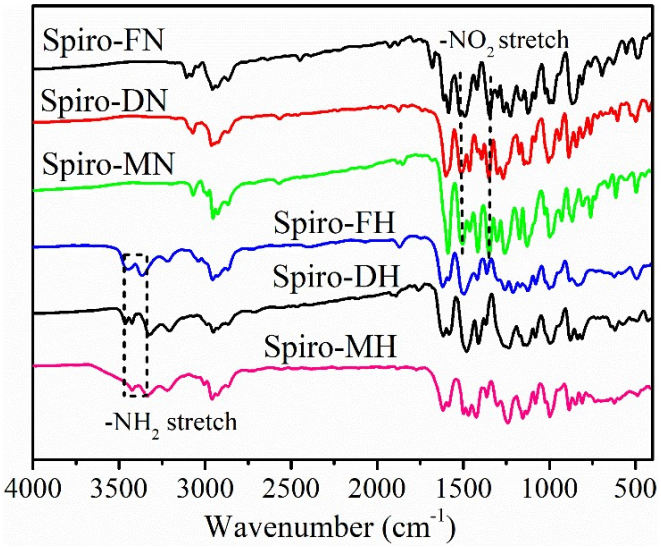

Figure S1. FTIR spectroscopy of dinitro and diamine monomers.

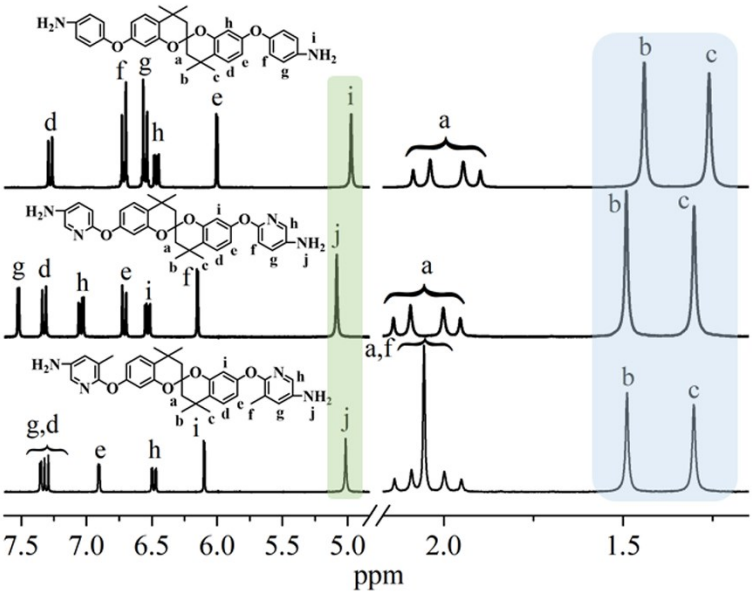

Figure S2. ^{1}H NMR spectrum of diamine monomers Spiro-FH, Spiro-DH, and Spiro-MH.

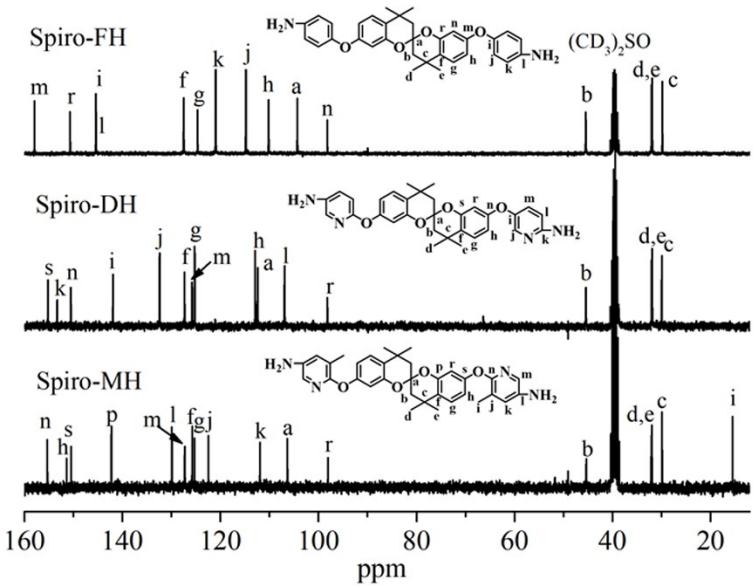

Figure S3. ^{13}C NMR spectra of diamine monomers.

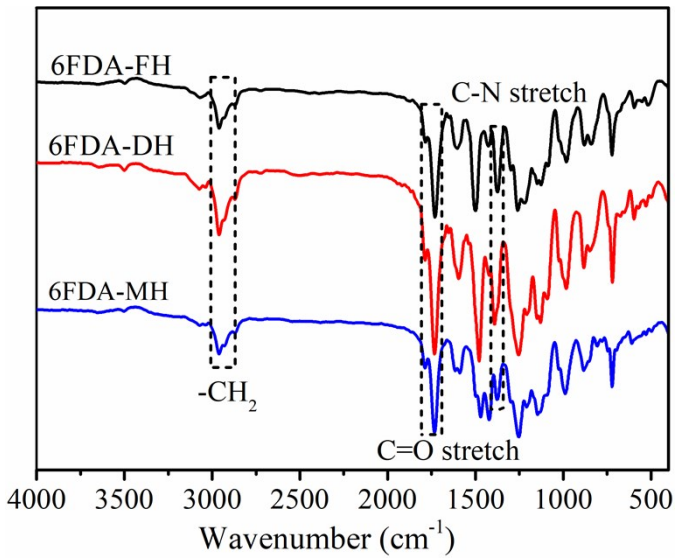

Figure S4. FTIR spectra of three polyimides.

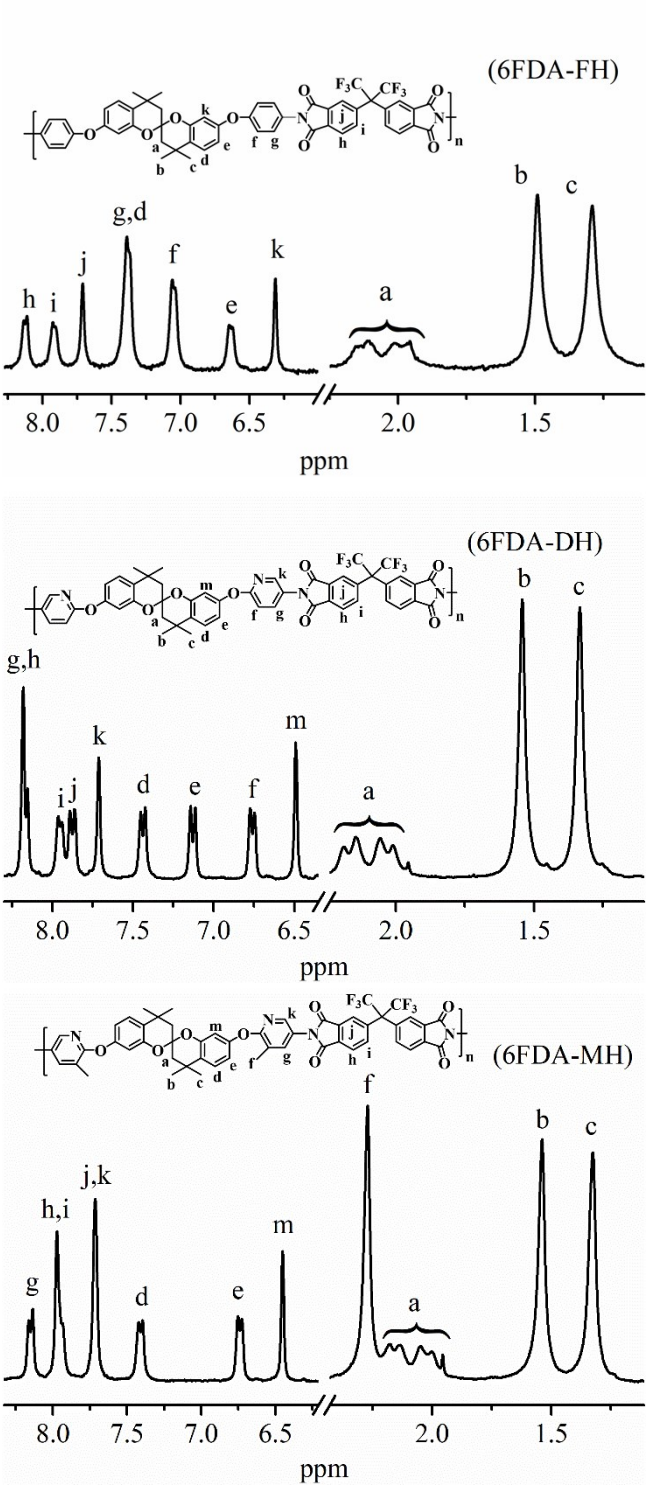

Figure S5. ^{1}H NMR spectra of polyimides 6FDA-FH, 6FDA-DH, and 6FDA-MH.

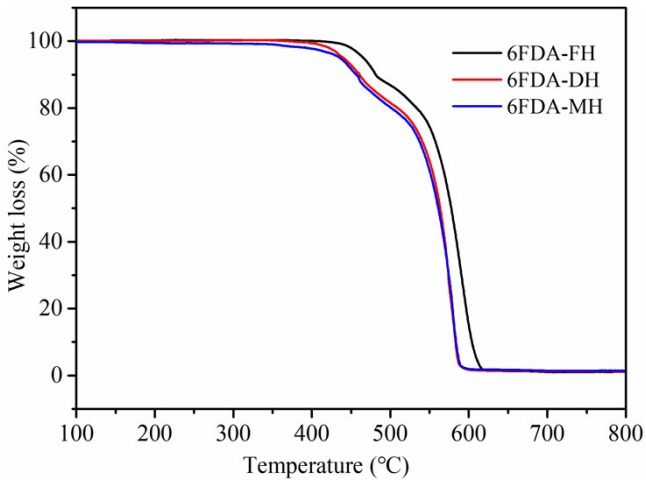

Figure S6. TGA curves of three polyimides under air.