

Perfluorocyclobutyl-containing transparent polyimides with low dielectric constant and low dielectric loss

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Experimental Materials

4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4-hydroxyphthalic acid, 1,2-dibromo-1,1,2,2-tetrafluoroethane and N-(4-hydroxyphenyl)acetamide were purchased from Bidepharm Co., Ltd. Bis(trifluoromethyl)-4,4'-Diaminobiphenyl (TFMB), m-cresol and other solvents were obtained from Energy Chemical Co., Ltd. M-cresol was treated by P₂O₅, followed by solvent distillation under reduced pressure. Zinc powder was obtained from Aladdin reagent Co., Ltd and activated by 1M hydrochloric acid. All other chemical solvents were used as received.

Synthesis of 5,5'-((perfluorocyclobutane-1,2-diyl)bis(oxy))bis(isobenzofuran-1,3-dione) (PFODPA)

Dimethyl 4-hydroxyphthalate

4-Hydroxyphthalic acid was (30 g of 0.16 mol) dissolved in 300 mL anhydrous methanol, then thionyl chloride (36 mL (0.247 mol)) was added dropwise at 0 °C under nitrogen atmosphere. The reaction mixture was warmed to room temperature and stirred for 20 hours. The solvent was removed under reduced pressure, the crude product was dissolved in ethyl acetate and washed with saturated NaHCO₃. The white solid (32g 93%) was obtained after removing the ethyl acetate using rotary evaporation. ¹HNMR (500 MHz, DMSO- *d*₆) δ 3.72 (s, 3H), 3.74 (s, 3H), 6.88 (dd, 2H), 7.64 (d, 1H), 10.58 (s, 1H). ¹³CNMR (500 MHz, *d*₆-DMSO) δ 166.44, 150.58, 134.72, 131.95, 130.44, 124.89, 122.11, 116.32, 113.31, 53.61.

Dimethyl 4-(2-bromo-1,1,2,2-tetrafluoroethoxy)phthalate

Dimethyl 4-(2-bromo-1,1,2,2-tetrafluoroethoxy)phthalate was prepared via fluoroalkylation reaction of dimethyl 4-hydroxyphthalate. Dimethyl 4-hydroxyphthalate (30 g, 0.143 mol) and cesium carbonate (50 g, 1.68 mol) were added to a 250 mL dried two-neck round-bottom flask fitted with a constant pressure dropping funnel under nitrogen atmosphere. Then 150 mL dried DMSO was added and stirred for 1h at room temperature. After that, 1,2-dibromotetrafluoroethane (73.2 g, 0.284 mol) was dropped slowly, keeping the temperature below 30 °C. The mixture was stirred for 24 h at 50 °C. The resulting mixture was poured into deionized water and extracted by ethyl acetate. The crude product was purified by silica column chromatography using petroleum as eluent. The

yield of dimethyl 4-(2-bromo-1,1,2,2-tetrafluoroethoxy) phthalate was 76% (42g). ¹HNMR (500 MHz, d₆-DMSO) δ 3.80 (s, 3H), 3.82 (s, 3H), 7.62 (m, 2H), 7.87 (m, 1H). ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -85.43, -70.34. ¹³CNMR (500 MHz, d₆-DMSO) δ 167.47, 165.96, 156.37, 149.55, 147.09, 144.79, 136.23, 135.76, 134.21, 132.74, 127.90, 118.62, 116.09, 53.44.

Dimethyl 4-((1,2,2-trifluorovinyl) oxy)phthalate

Newly activated zinc powder (5.05 g, 0.077mol) was added to a pre-dried two-neck round-bottom, dry acetonitrile (80 mL) was added and the mixture was heated to reflux. Then Dimethyl 4-(2-bromo-1,1,2,2-tetrafluoroethoxy) phthalate 3 (25 g, 0.064 mol) was dropped slowly into the mixture, keeping the mixture boiling slightly. The mixture keep reflux for 24 h. After the mixture cooled to room temperature, the mixture was filtered, and the solid salt was washed with ethyl acetate. The organic solution was evaporated and purified by silica column chromatography using petroleum as eluent. Colorless oil was obtained and yield 86% (16 g). ¹HNMR (500 MHz, d₆-DMSO) δ 3.79 (s, 3H), 3.81 (s, 3H), 7.54-7.59 (m, 2H), 7.87 (d, 1H), ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -135.55, -124.54, -116.73. ¹³CNMR (500 MHz, d₆-DMSO) δ 166.44, 153.83, 135.20, 132.42, 129.17, 120.84, 118.39, 115.06-105.78 (m), 53.44.

Tetramethyl 4,4'-((perfluorocyclobutane-1,2-diyl) bis(oxy))diphthalate

Dimethyl 4-((1,2,2-trifluorovinyl) oxy) phthalate (16 g, 0.055 mol) was placed in glass tube, distilled and degassed. The reaction was heated to 185 °C for 24 h. The tetramethyl 4,4'-((perfluorocyclobutane-1,2-diyl) bis(oxy))diphthalate was obtained and yield 96% (15.3 g). ¹HNMR (500 MHz, d₆-DMSO) δ 3.78 (d, 6H), 3.80 (d, 6H), 7.48-7.55 (m, 4H), 7.84-7.87 (dd, 2H). ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -131.20 – -127.02 (m).

4,4'-((perfluorocyclobutane-1,2-diyl) bis(oxy))diphthalic acid

Tetramethyl 4,4'-((perfluorocyclobutane-1,2-diyl) bis(oxy)) diphthalate (15 g) dissolved in DMSO (50 mL), sodium hydroxide aqueous solution (30 mL, 30wt%) were added into flask. The temperature was raised to 100 °C for 12 h. After the mixture cooled to room temperature, the mixture was poured into deionized water. The product was extracted from the water using ethyl acetate. The solution was evaporated, the white solid was obtained and yield 93% (13.4 g). ¹HNMR (500 MHz, d₆-DMSO) δ 7.39 (m, 4H), 7.80 (m, 4H), 13.29 (s, 4H), ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -131.41 – -126.72 (m). ¹³CNMR (500 MHz, d₆-DMSO) δ 167.95, 153.59, 136.47, 132.18, 130.44, 120.61, 118.39, 113.82-105.51 (m).

5,5'-((perfluorocyclobutane-1,2-diyl)bis(oxy))bis(isobenzofuran-1,3-dione) (PFODPA)

4,4'-((perfluorocyclobutane-1,2-diyl)bis(oxy))diphthalic acid (13 g) was added to a 100 mL two-necked flask. Acetic anhydride (30 mL) was added, keeping the mixture reflux for 5 h under nitrogen atmosphere. After that, acetic anhydride was removed via vacuum distillation. Then, 4,4'-((perfluorocyclobutane-1,2-diyl)bis(oxy))diphthalic acid was purified by sublimation in vacuum gives amorphous solid powder. The yield was 95% (12 g). ¹HNMR (500 MHz, d₆-DMSO) δ 7.78-7.84 (m, 2H), 7.86 (m, 2H), 8.14-8.19 (m, 2H). ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -131.51 – -126.94

(m). ¹³CNMR (500 MHz, d₆-DMSO) δ 162.56, 157.01, 134.96, 129.32, 128.71, 125.64, 114.74, 113.42-104.56 (m).

Synthesis of 4,4'-((perfluorocyclobutane-1,2-diyl)bis(oxy))dianiline (PFODA)

N-(2-bromo-1,1,2,2-tetrafluoroethoxy)phenyl)acetamide

N-(2-bromo-1,1,2,2-tetrafluoroethoxy)phenyl)acetamide was prepared via fluoroalkylation reaction of N-(4-hydroxyphenyl)acetamide. N-(4-hydroxyphenyl)acetamide (30 g, 0.2mol) and cesium carbonate (97.5 g, 0.3mol) were added to a 250 mL two-necked round-bottom flask fitted with a constant pressure dropping funnel flask. Then 150 mL dried DMSO was added and stirred for 1h at room temperature. After that, 1,2-dibromotetrafluoroethane (103.2 g, 0.4 mol) was dropped slowly, keeping the temperature below 30 °C. The mixture was stirred for 24 h at 50 °C. The resulting mixture was poured into deionized water and extracted by ethyl acetate. The crude product was purified by silica column chromatography using ethyl acetate/petroleum as eluent. The yield of N-(2-bromo-1,1,2,2-tetrafluoroethoxy)phenyl)acetamide was 61% (40 g). ¹HNMR (500 MHz, d₆-DMSO) δ 2.02 (s, 3H), 7.21 (d, 2H), 7.64 (m, 2H), 10.9 (s, 1H), ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -85.39, -70. ¹³CNMR (500 MHz, DMSO-*d*₆) δ 169.22, 143.52, 139.04, 122.43, 120.61, 116.32, 113.31, 24.73.

N-(4-((1,2,2-trifluorovinyl)oxy)phenyl)acetamide

Newly activated zinc powder (17.3 g, 0.264mol) was added to a pre-dried two-neck round-bottom, dry acetonitrile (150 mL) was added and the mixture was heated to reflux. Then N-(2-bromo-1,1,2,2-tetrafluoroethoxy)phenyl)acetamide (40 g, 0.12 mol) was dropped slowly into the mixture, keeping the mixture boiling slightly. The mixture keep reflux for 24 h. After the mixture cooled to room temperature, the mixture was filtered, and the solid salt was washed with ethyl acetate. The organic solution was evaporated and purified by silica column chromatography using ethyl acetate/petroleum as eluent. Colorless oil was obtained and yield 75% (20.8 g). ¹HNMR (500 MHz, d₆-DMSO) δ 1.94 (s, 3H), 7.17 (m, 2H), 7.61 (m, 2H), ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -133.7, -127.4, -119.51. ¹³CNMR (500 MHz, DMSO-*d*₆) δ 168.74, 149.87, 143.76, 138.53, 134.48, 120.61, 24.18.

N,N'-(((perfluorocyclobutane-1,2-diyl)bis(oxy))bis(4,1-phenylene))diacetamide

N-(4-((1,2,2-trifluorovinyl)oxy)phenyl)acetamide (20 g, 0.086 mol) was placed in glass tube, distilled and degassed. The reaction was heated to 185 °C for 24 h. The N, N'-(((perfluorocyclobutane-1,2-diyl)bis(oxy))bis(4,1-phenylene))diacetamide was obtained and yield 85% (16.8 g). ¹HNMR (500 MHz, d₆-DMSO) δ 1.98 (s, 6H), 3.80 (d, 6H), 7.13 (m, 4H), 7.58 (m, 4H), 10.2 (s,2H). ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -131.61 – -127.79 (m). ¹³CNMR (500 MHz, DMSO-*d*₆) δ 168.74, 147.57, 137.73, 121.16, 119.34, 114-106 (m), 24.97.

4,4'-((perfluorocyclobutane-1,2-diyl)bis(oxy))dianiline (PFODA)

N,N'-(((perfluorocyclobutane-1,2-diyl)bis(oxy))bis(4,1-phenylene))diacetamide (15 g) dissolved in DMSO (50 mL), sodium hydroxide aqueous solution (30 mL, 30wt%) were added into flask. The

temperature was raised to 100 °C for 12 h. After the mixture cooled to room temperature, the mixture was poured into deionized water. The product was extracted from the water using ethyl acetate. The solution was evaporated, the white solid was obtained and yield 91% (11.2 g). The isomers were separated by silica column chromatography using ethyl acetate/petroleum (1:3) as eluent. PFODA-*trans* ¹HNMR (500 MHz, d₆-DMSO) δ 5.09 (s, 4H), 6.51 (m, 4H), 6.85 (d, 4H), ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -130.35, -129.88, -128.64, -128.37, -128.16, ¹³CNMR (500 MHz, DMSO-*d*₆) δ 106-113 (m), 114.81, 120.23, 142.45, 147.33. PFODA-*cis* ¹HNMR (500 MHz, d₆-DMSO) δ 5.13 (s, 4H), 6.51 (m, 4H), 6.86 (d, 4H), ¹⁹FNMR (500 MHz, DMSO-*d*₆) δ -130.91, -130.43, -129.39, -129.10, -128.61, ¹³CNMR (500 MHz, DMSO-*d*₆) δ 147.50, 142.20, 120.36, 114.90, 106-113 (m).

Synthesis of polyimides

Perfluorocyclobutyl-containing polyimides were synthesized via traditional one-step polycondensation. 6FDA-PFODA was chosen as an example. PFODA (0.58 g, 1.67 mmol) was added into a 100 mL two-necked round bottom flask and dissolved in 5 mL *m*-cresol. After the diamine completely dissolved, PFODPA (0.6811 g, 1.67 mmol) was added to the bottle. The mixture was stirred for 1h at 80 °C, then 185 °C for 12 h. After the temperature drops to room temperature, the mixture was poured into 250 mL methanol to give fibrous precipitate and washed with methanol for three times. Then the polyimide was dried under vacuum at 150 °C for 12 h. The other polyimides were prepared by similar process as describe above.

Prepared of polyimide films

The polyimide powder was dissolved in anhydrous DMAc with a solid content of 15 wt%. Then the solution was casted on glass substrate, the solution was heating at 80 °C for 2 h, 150 °C for 2h, 200°C for 2h and 220 °C for 2h. After that, the films were immersed into deionized water to peeled from the substrates and dried at 100 °C for 12 h.

Characterization

¹H, ¹³C and ¹⁹F NMR spectra were carried on a Bruker 400 (400 MHz) instrument, deuterated dimethyl sulfoxide was chosen to dissolve samples using tetramethylsilane as internal reference. LC-MS was conducted on a Bruker Agilent 1100 using acetonitrile as the solvent. Gel permeation chromatography (GPC) analysis was performed on a WATERS 2695 at a flow rate of 1 mL min⁻¹ using polystyrenes as standard. DMF/LiBr solution (0.05 M of LiBr) was used as the eluent. Elemental analysis were determined by an elemental analyser (Vario EL cube). Intrinsic viscosities ([η]) of the PI were measured with an ubbelohde viscometer at 30 °C in DMAc at a concentration of 0.5 g/dL. Fourier-transform infrared spectroscopy spectra (32 accumulated scans at a resolution of 4 cm⁻¹ in the range of 4000-400 cm⁻¹ wavenumber range) were recorded on a Bruker Vector 33 FT-IR spectrometer by attenuated total reflection infrared (ATR-IR) mode. Wide-angle X-ray diffraction (WAXD) was carried out on a Homo Lab (Rigaku, Japan) X-ray diffractometer using Cu Kα radiation, 2θ ranging from 5° to 40°. Differential scanning calorimetry (DSC) were

performed on a TA instrument DSC 2500 under nitrogen atmosphere (50 mL min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was conducted on TA instrument Q800 under nitrogen atmosphere (50 mL min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from $30\text{-}800 \text{ }^\circ\text{C}$. Dynamic Thermomechanical Analyzer (DMA) was recorded on a TA instrument DMA Q800 at a heating rate of 5°C min^{-1} with a load frequency of 1 Hz in air atmosphere. Thermomechanical Analyzer (TMA) was carried out on a TA instruments Q 400 analyzer with a static load of 0.05N at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ from 50°C to 250°C . Mechanical properties were measured by a microcomputer controlled electronic universal testing machine (LD22.102, Shanghai) with a strain rate of 2 mm min^{-1} . The results were carried out with samples dimensions of $30 \text{ mm} \times 10 \text{ mm} \times 15 \text{ }\mu\text{m}$. The optical properties of the films were determined by SHIMADZU UV-3600 plus spectrophotometer (Japan) from 200 nm to 800 nm . Dielectric properties were recorded using Novocontrol Concept 40 Dielectric/Impedance Spectrometer with frequencies between 10MHz and 100 Hz , the films were sprayed with Au at both sides before the tests, the dielectric properties at 10 GHz was performed on a vector network analyzer (Japan). Water absorption was measured via the weight change of the films before and after immersed in deionized water for 72 h at room temperature. Water contact angles were recorded on a Contact Angle Meter (JC2000D1, Shanghai). The structural optimization of monomers and polymers was achieved by Density Functional Theory (DFT), B3LYP/6-31G (2d, p) with the Gaussian 09 program. Dipole moment (μ), polarizability (α), and volume were calculated by DFT (CAM-B3LYP/6-311++g(d,p)).

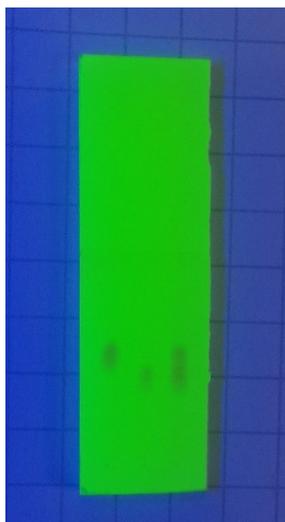


Figure S1 TLC (thin-layer chromatography) photograph of PFODA and its isomers;
PFODA-trans (left), PFODA-cis (middle), PFODA mixture (right).

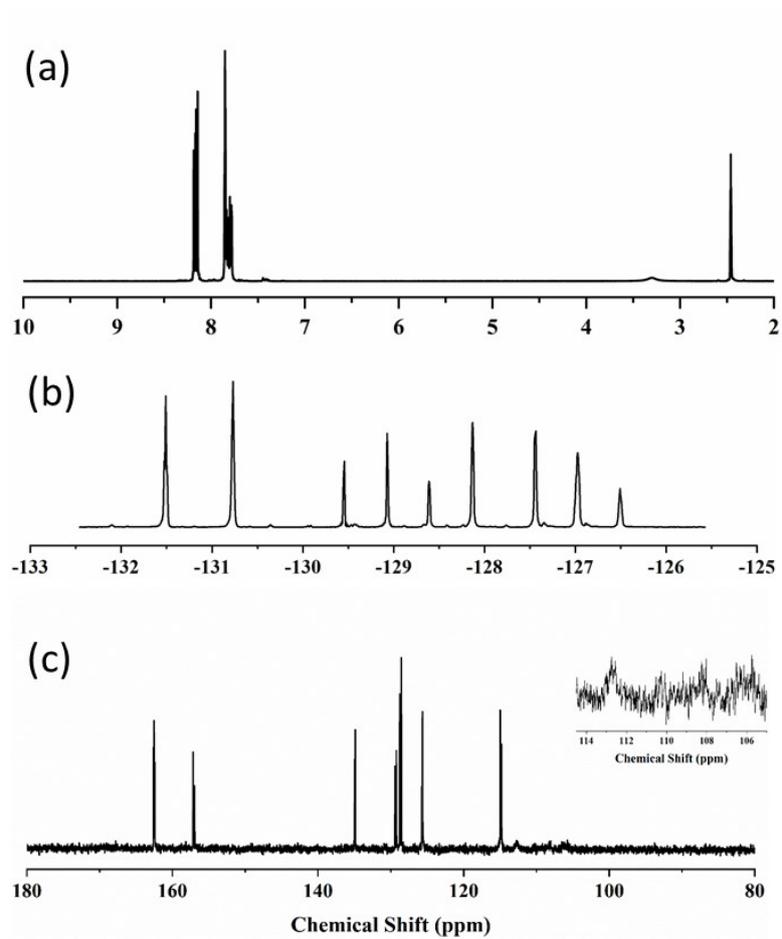


Figure S2 a) ^1H NMR spectra of PFODPA; b) ^{13}C NMR spectra of PFODPA; ^{19}F NMR spectra of PFODPA

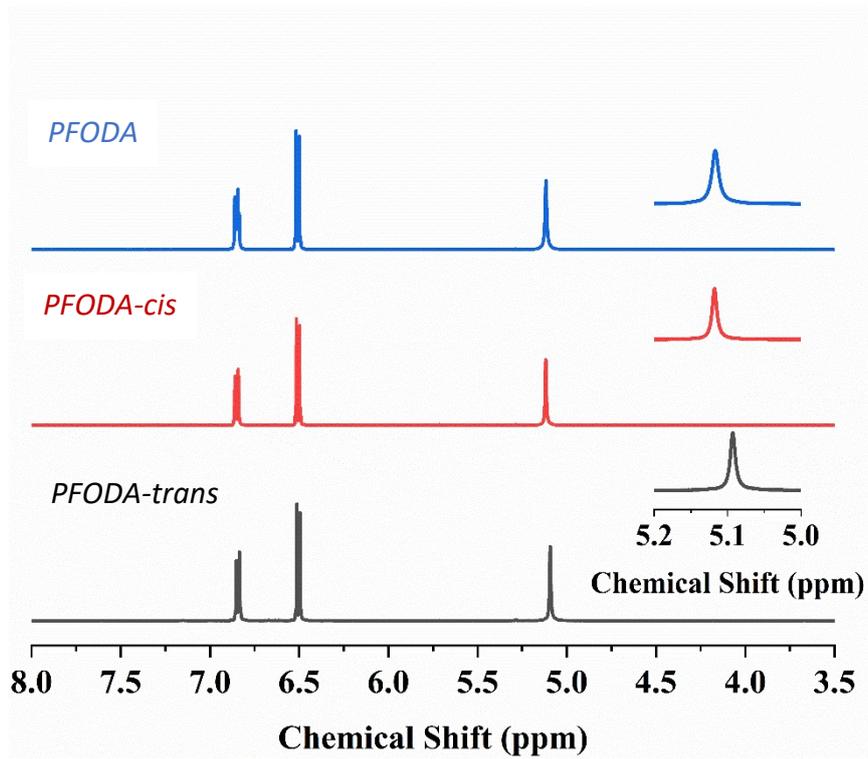


Figure S3 ¹H NMR spectra of PFODA and its isomers

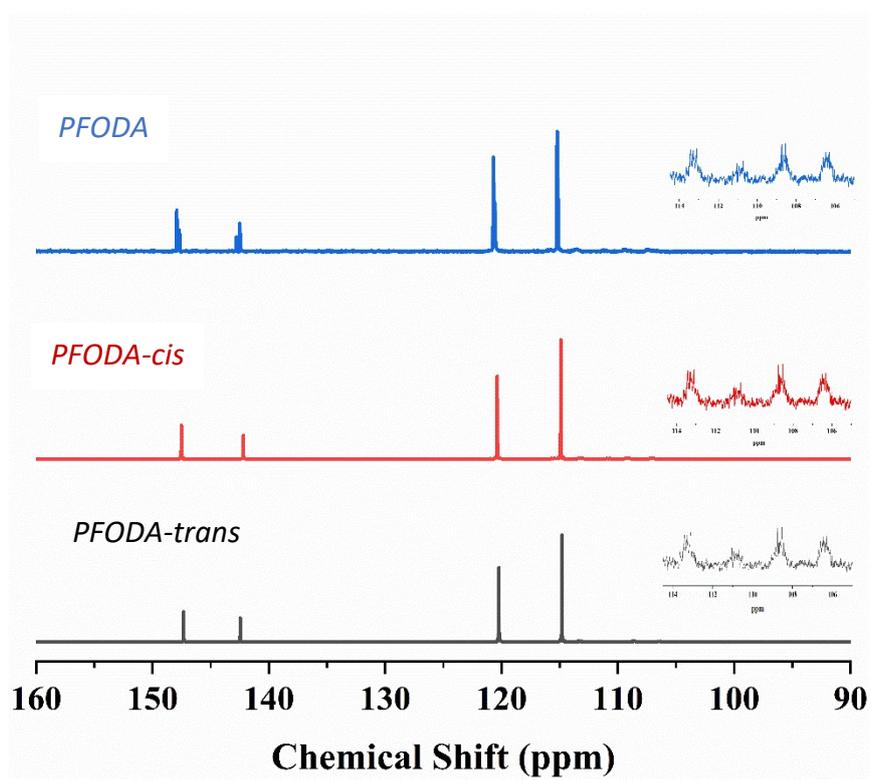


Figure S4 ^{13}C NMR spectra of PFODA and its isomers

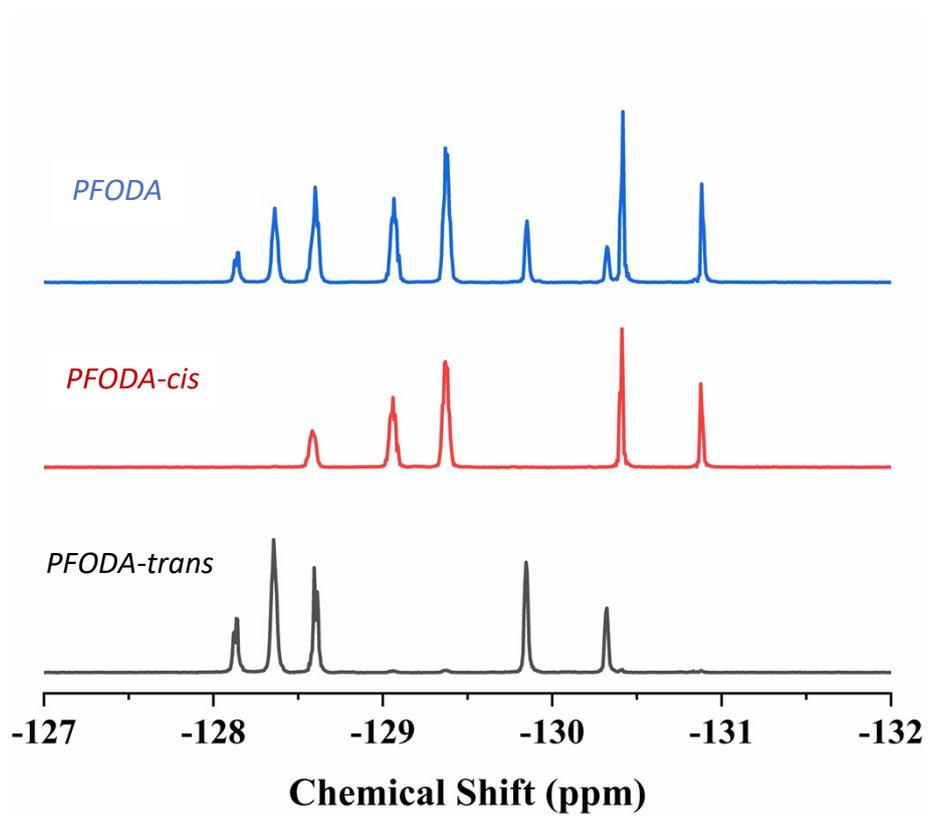


Figure S5 ^{19}F NMR spectra of PFODA and its isomers

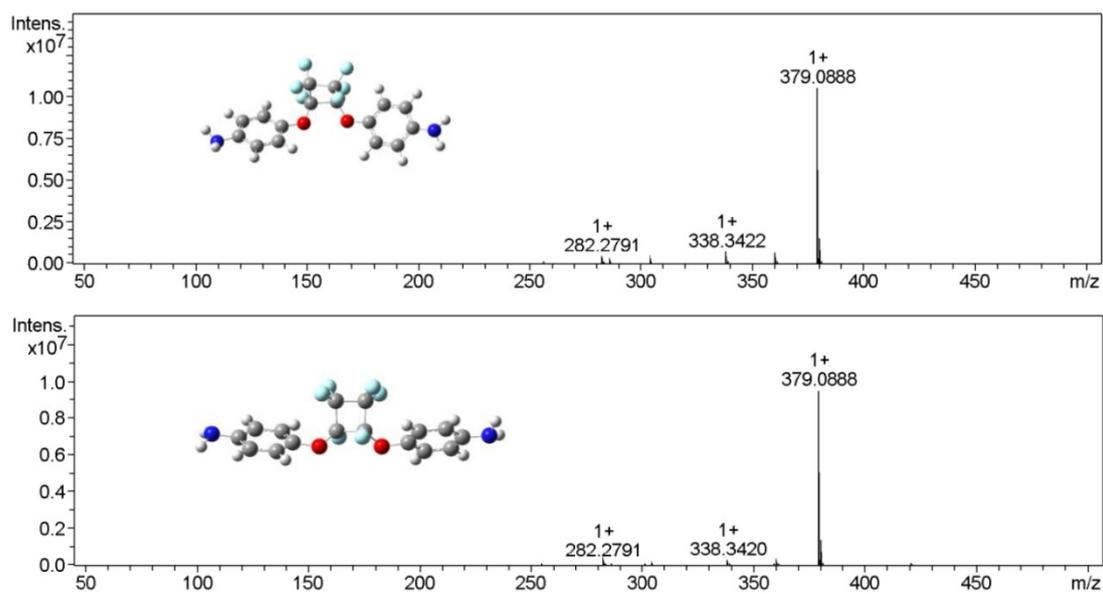


Figure S6 LC-MS of PFODA-trans and PFODA-cis

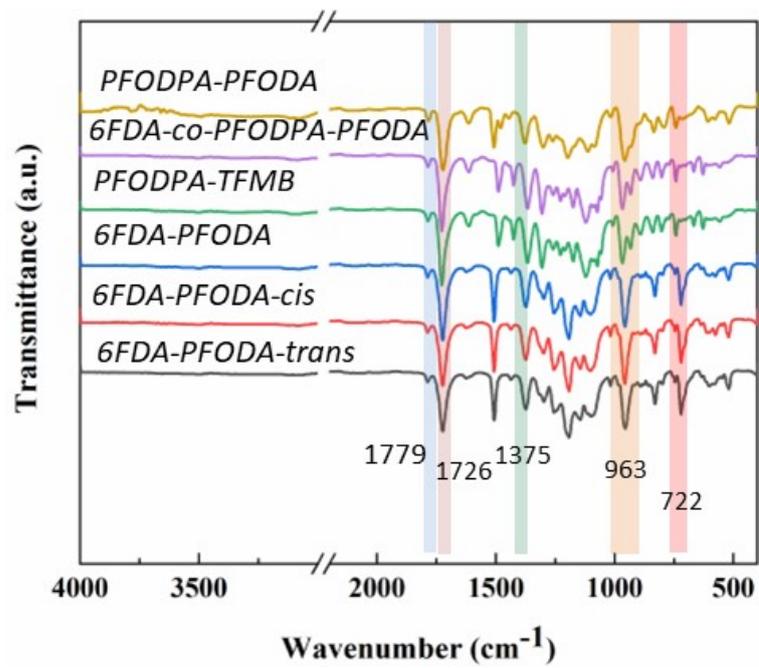


Figure S7 FT-IR spectra of polyimides

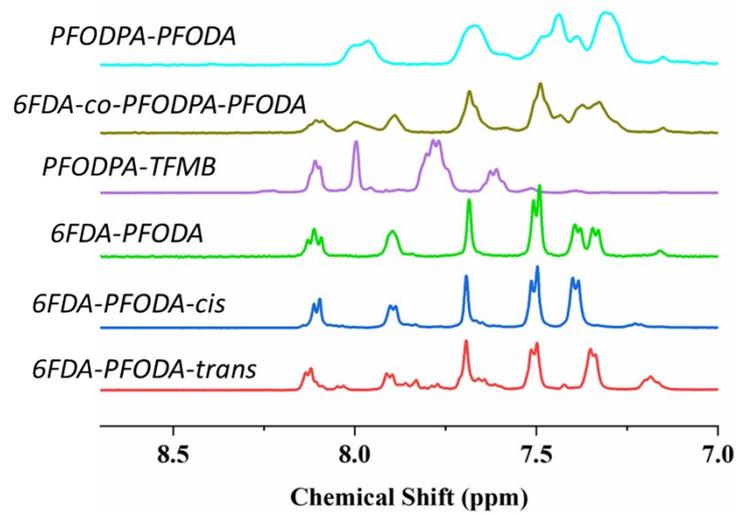


Figure S8 ¹H NMR spectra of polyimides

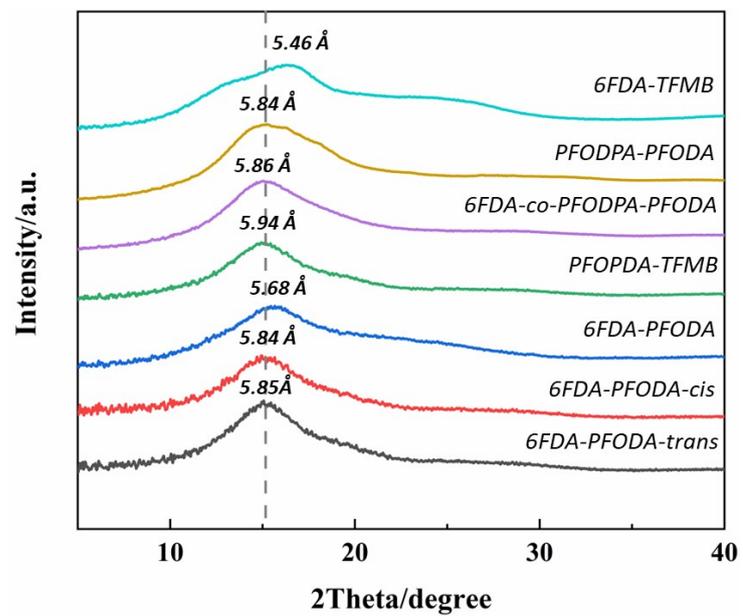


Figure S9 The WAXD patterns of polyimide films

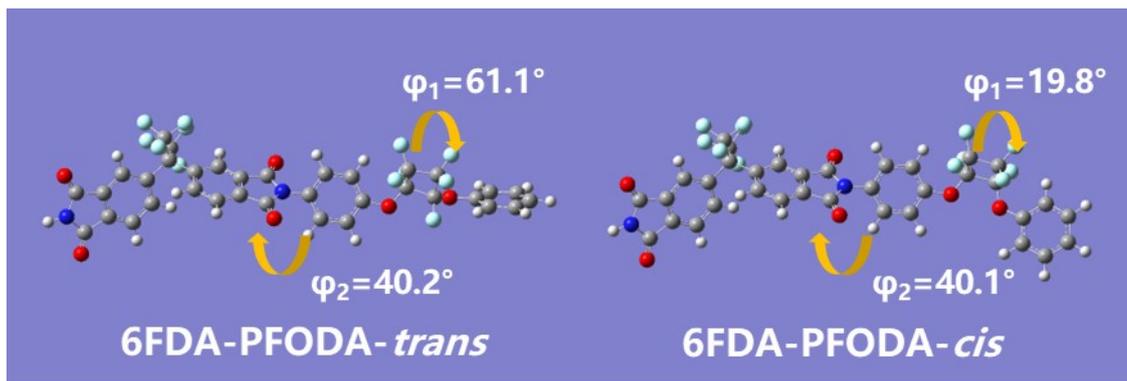


Figure S10 The optimized geometries of the 6FDA-PFODA-*trans* and 6FDA-PFODA-*cis* units

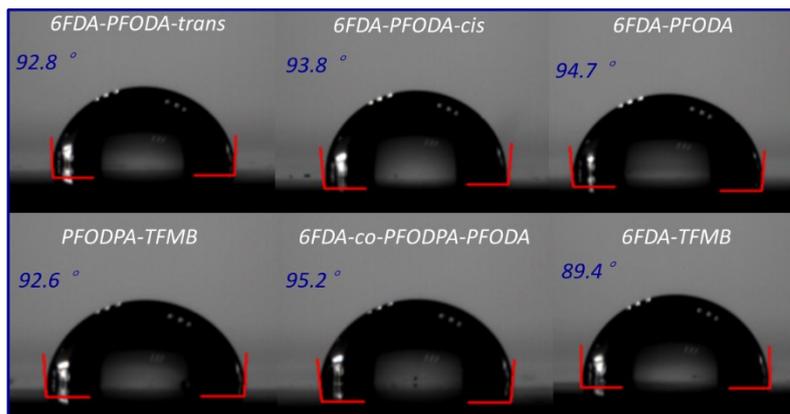


Figure S11 Water contact angles of polyimides

Table S1 Isomers conformation of PFODPA and PFODA and its lowest energy state

Dianhydride	Energy/hatree
	-1966.55
	-1966.55
Diamine	
	-1475.85
	-1475.85

Table S2 GPC and intrinsic viscosity data of polyimides

	6FDA- PFODA- <i>trans</i>	6FDA- PFODA-<i>cis</i>	6FDA- PFODA	PFODPA- TFMB	6FDA-<i>co</i>- PFODPA- PFODA	PFODPA- PFODA
M_n	48843	53988	87918	71883	35451	20889
M_w	80239	89909	162503	136048	65228	34054
PDI	1.71	1.66	1.84	1.89	1.84	1.64
[η] dL/g	0.69	0.75	0.92	0.87	0.45	0.35
ρ(g/cm³)	1.246	1.249	1.254	1.241	1.235	1.230

Table S3 Element analysis data of polyimides

	6FDA- PFODA-<i>trans</i>	6FDA- PFODA-<i>cis</i>	6FDA- PFODA	PFODPA- TFMB	6FDA-<i>co</i>- PFODPA- PFODA	PFODPA- PFODA
Repeat unit	C₃₅H₁₆F₁₂N₂O₆	C₃₅H₁₆F₁₂N₂O₆	C₃₅H₁₆F₁₂N₂O₆	C₃₅H₁₄F₁₂N₂O₈	C₇₀H₃₀F₂₄N₄O₁₄	C₃₆H₁₅F₁₂N₂O₈
C (Calculated)	55.65	56.69	55.44	55.01	55.4	53.8
C (Found)	53.40	53.40	53.40	53.20	52.30	52.00
H (Calculated)	2.21	2.43	2.05	1.86	1.99	1.83
H (Found)	2.03	2.03	2.03	1.73	1.86	1.81
N (Calculated)	3.56	3.50	3.69	3.76	3.52	3.46
N (Found)	3.56	3.56	3.56	3.47	3.49	3.37

Table S4 The solubility of polyimides

	6FDA- PFODA- <i>trans</i>	6FDA- PFODA- <i>cis</i>	6FDA- PFODA	PFODPA- TFMB	6FDA-<i>co</i>- PFODPA- PFODA	PFODPA- PFODA
NMP	++	++	++	++	++	++
DMAc	++	++	++	++	++	++
DMF	++	++	++	++	++	++
DMSO	++	++	++	++	++	++
m-cresol	++	++	++	++	++	++
Acetone	++	++	++	++	++	++
THF	++	++	++	++	++	++
CHCl₃	++	++	++	++	++	++
CH₂Cl₂	++	++	++	++	++	++

(2wt%), ++, dissolve at room temperature.

Table S5 Optical properties of polyimide films

	Cut off (nm)	^a T ₄₀₀ (%)	^b T ₅₅₀ (%)	L*	a*	b*	Haze	n	Thickness (μm)
6FDA- PFODA-<i>trans</i>	312	73.6	89.5	90.8	-2.0	2.1	0.42	1.558	13
6FDA- PFODA-<i>cis</i>	311	75.8	88.9	90.2	-2.2	3.4	0.58	1.562	13
6FDA- PFODA	334	66.8	88.4	90.9	-2.5	3.2	0.69	1.559	15
PFODPA- TFMB	335	71.1	85.7	90.8	-1.6	1.2	1.23	1.548	17
6FDA-<i>co</i>- PFODPA- PFODA	311	68.7	88.2	90.1	-2.0	6.8	1.44	1.545	16
6FDA-TFMB	326	80.2	89.8	92.1	-1.2	1.11	0.32	1.564	15

^{a, b} Optical transmittance at 400 nm and 550 nm. ^c Average transmittance in the range of 400 – 800 nm.