

ELECTRONIC SUPPORTING INFORMATION

Polyimides with Low Dielectric Constant and Dissipation Factor at High Frequency Derived from Novel Aromatic Diamine with Bistrifluoromethyl Pendant Groups

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I. Materials

3,5-Dimethoxyphenyl boronic acid (98%) and 3,5-bis(trifluoromethyl)bromobenzene (98%) were provided by Shanghai Haohong Scientific Co., Ltd. Potassium carbonate (K_2CO_3 , AR, 99%), ammonium chloride (NH_4Cl , 99%), sodium sulfate (Na_2SO_4 , 99%) sodium bicarbonate ($NaHCO_3$, 99%) and hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 98%) were purchased from Aladdin Industrial Corporation. Tetrahydrofuran (THF, 99%), petroleum ether (PE, 99%), ethyl acetate (EA, 99%) and anhydrous ethanol (EtOH, 99%) were received from Shanghai Lingfeng Chemical Reagent Co., Ltd. Dimethyl sulfoxide- d_6 , ($DMSO-d_6$, with 0.03% tetramethylsilane) was obtained from Shanghai Acme Biochemical Co., Ltd. Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, 99%), boron tribromide (BBr_3 , 99%), 4-chloronitrobenzene (98%), palladium on carbon (10 wt% loading, matrix activated carbon support, Pd/C), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, 98%), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, 98%), 4,4'-oxydiphthalic anhydride (ODPA, 98%), 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA, 98%), 4,4'-oxydianiline (ODA, 98%), N-methyl-2-pyrrolidone (NMP, 99%), N,N-Dimethylformamide (DMF, 99%), dichloromethane (DCM, 99%), Dimethyl sulfoxide, ($DMSO$, 99%) and N,N-Dimethylacetamide, ($DMAc$, 99%) were purchased from Energy Chemical Co., Ltd. Chloroform (TCM, 99%) was obtained from Merck Co., Ltd. All the anhydrides were dried in a 120 °C vacuum oven for 6 hours, and all other materials were used as received without extra treatments.

II. Characterization method

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE III 400 MHz spectrometer instruments and the compounds (about 20 mg) were dissolved in 600 μL DMSO- d_6 by using residual tetramethylsilane ($\delta\text{H} = 0.00$ ppm) as internal references. The high-resolution mass spectrometry (HRMS) was acquired by Q EXACTIVE to confirm the molecular weight of diamine monomer HFBODA. The high-performance liquid chromatography (HPLC) was obtained by Ultimate 3000 to estimate the purity of diamine monomer HFBODA. Fourier transform-infrared spectra (FT-IR) were detected from the Bruker Vertex 70 spectrometer with a scan range of 4000-600 cm^{-1} by using the room temperature attenuated total reflection (ATR) testing mode. The molecular weight of poly-amide acids (PAAs) and their polydispersity was measured by gel permeation chromatography (GPC, Thermo Fisher 2695 system) by using THF as an eluent at a flow rate of 1.0 mL/min at room temperature. The number average molecular weight (M_n) and weight average molecular weight (M_w) were calibrated by the standard curve of polystyrene. The ultraviolet visible (UV-vis) spectra was obtained on a UV-3600 from SHIMADZU (Japan) UV-VIS-NIR spectrophotometer, and the PI film was tightly attached to a 2.5 \times 7.5 cm transparent and colorless glass plate. The dielectric constant and dissipation factor of the cured samples at a high frequency of 10 GHz were estimated on the E5071C keysight ENA vector network analyzer at room temperature. The charge density of the imide group was calculated by natural bond orbital (NBO) in Gaussian. The mechanical properties of PI films were characterized by a dynamic mechanical analyzer (DMA Q850, TA Instruments, America) with a procedure of ranging from 1 N to 18 N (2 N/min) at room temperature. Thermomechanical analysis (TMA) was performed with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ ranging from 25 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ in nitrogen on the TMA-SDTA2+ (Mettler, Switzerland) instrument. The glass transition temperature (T_g) was detected by DSC 2500 (TA Instruments, America) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 30 $^{\circ}\text{C}$ to 350 $^{\circ}\text{C}$ in a nitrogen atmosphere. Thermo-gravimetric analysis (TGA) was performed in the nitrogen atmosphere on a TA SDT Q600 (America) apparatus at a heating rate of 10

°C/min from room temperature to 800 °C. Wide-angle X-ray diffraction (WXR) was performed on a D8 Advance diffractometer radiated by the CuK α of 0.15418 nm wavelength (Bruker, Germany) with a 2θ ranging from 10° to 70°. The obtaining d_{spacing} values were based on the Bragg's law: $2d \times \sin \theta = n\lambda$. Water contact angle (WCA) was characterized by the Dataphysics-OCA20 with the deionized water. The water absorption was obtained by weighing the mass change before and after 200 mg of dried PI films immersed in deionized water for 24 h. The water absorption of PIs was calculated by the formula: Water absorption (WA) = $(W_b - W_a)/W_a \times 100\%$, where W_a was the mass before immersion and W_b after immersion. The solubility of the synthesized PIs was tested with 5 mg PI film in 8 mL solvent at room temperature for 24 h. If it did not dissolve after 24 h, the film was heated to 60 °C for an additional 24 h to observe the phenomenon. The geometry and properties of the PIs were fully optimized through the use of Density Functional Theory (DFT) via the spin-unrestricted B3LYP functional.¹ Def2TZVPP basis sets have been applied for all models.² Also, the Grimme's D3 damping function has been applied in all models for dispersion interaction correction.³ All calculations were carried out by the Gaussian16 program.

III. Additional characterizations of monomers

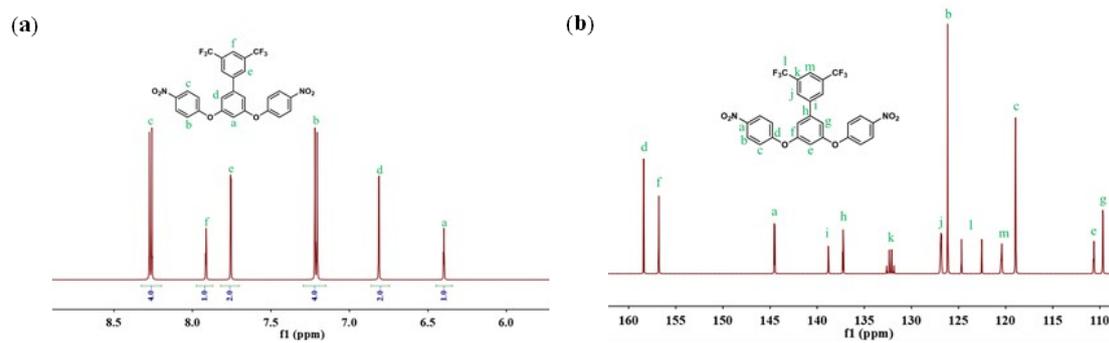


Fig. S1. NMR spectra of HFBODNO. (a) $^1\text{H-NMR}$ spectrum of HFBODNO and (b) $^{13}\text{C-NMR}$ spectrum of HFBODNO.

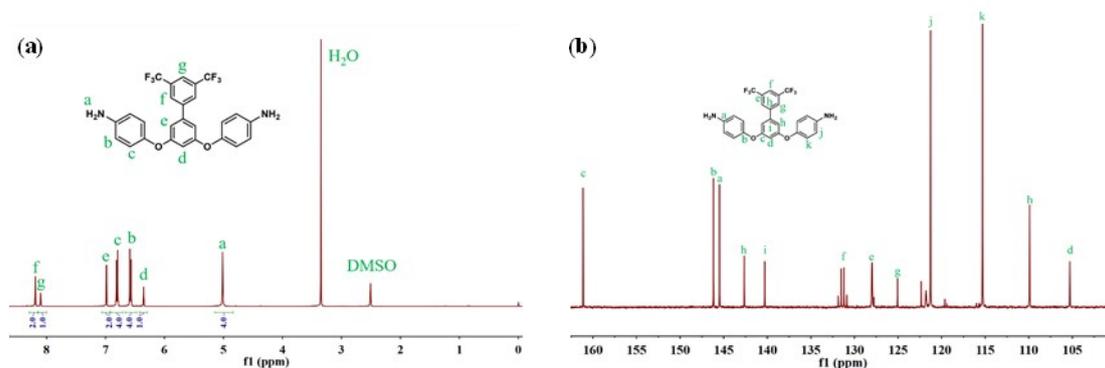


Fig. S2. NMR spectra of HFBODA. (a) $^1\text{H-NMR}$ spectrum of HFBODA and (b) $^{13}\text{C-NMR}$ spectrum of HFBODA.

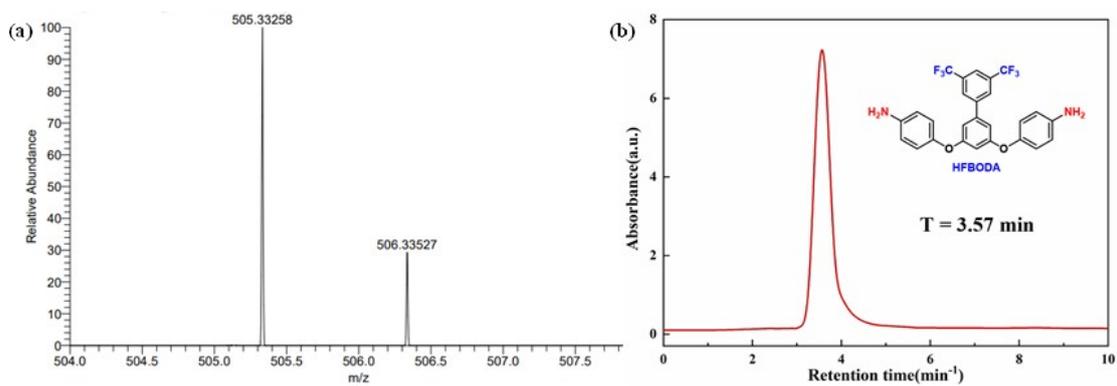


Fig. S3. Structure characterizations of HFBODA. (a) HRMS spectrum of HFBODA and (b) HPLC spectrum of HFBODA.

IV. Additional characterizations of the structure of PI films

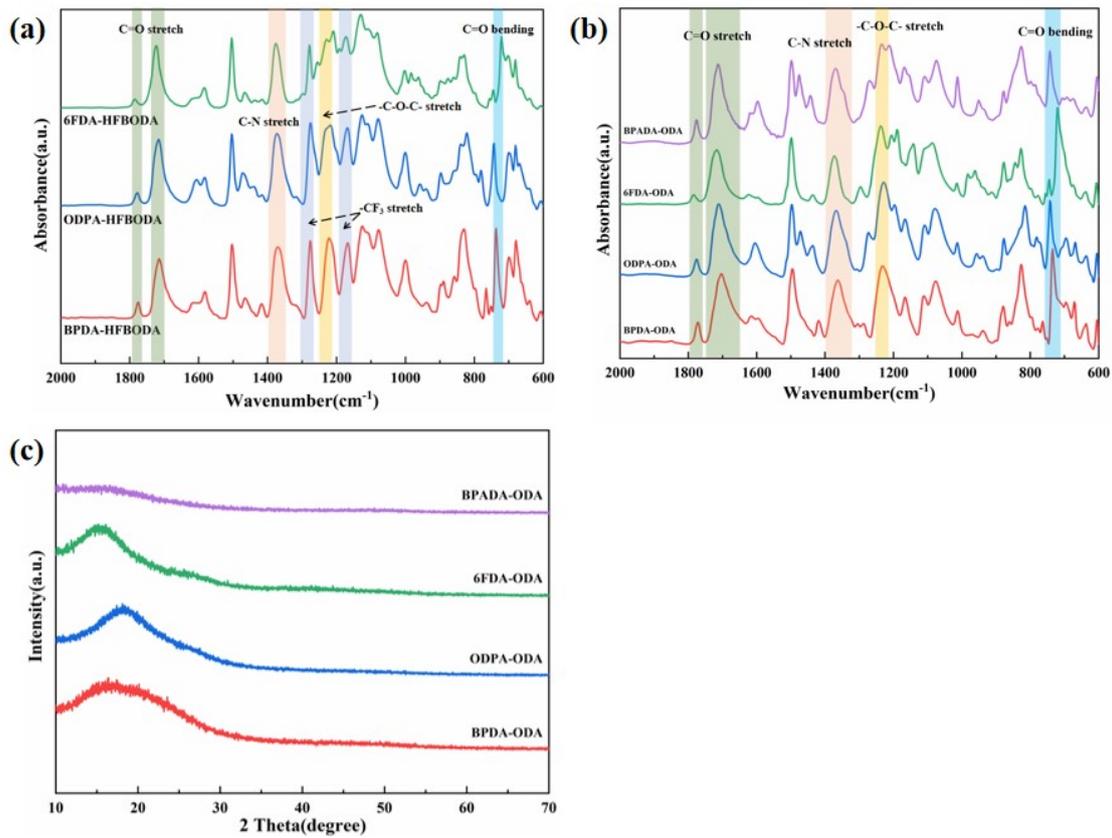


Fig. S4. Structure characterizations of PI films. (a) FT-IR spectra of HFBODA group, (b) FT-IR spectra of ODA group and (c) WXR patterns of ODA group.

V. Additional thermal properties and mechanical properties of PI films

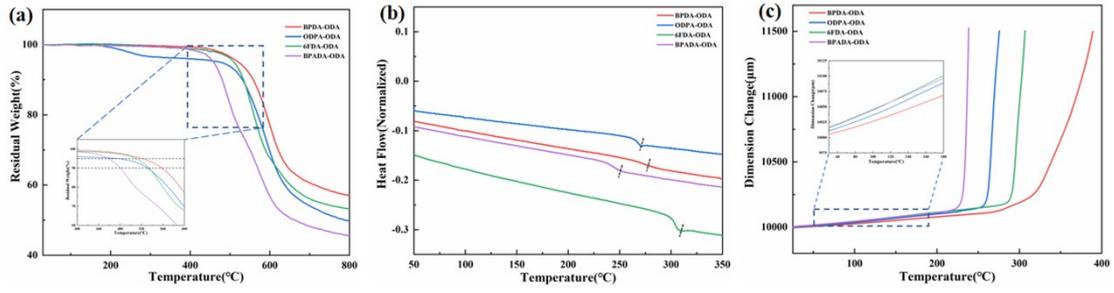


Fig. S5. Thermal properties of PI films from ODA group. (a) TGA curves of ODA group, (b) DSC curves of ODA group and (c) TMA curves of ODA group.

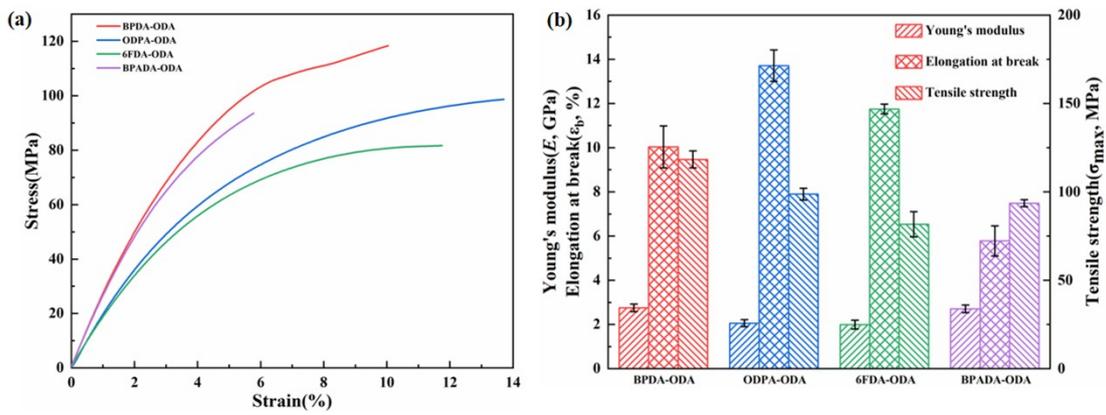


Fig. S6. Mechanical properties of PI films from ODA group. (a) typical stress-strain curves of ODA group and (b) column chart of mechanical parameters of ODA group.

VI. Additional theoretical calculations of the of PI films.

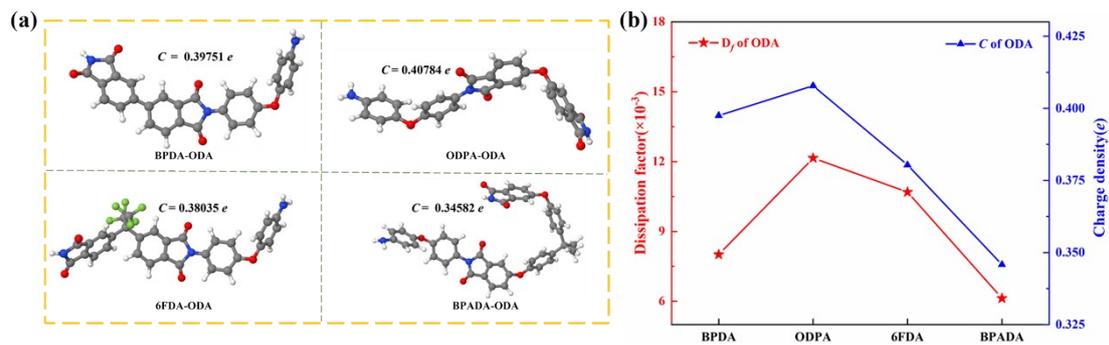


Fig. S7. (a) The charge density of the imide group of ODA group by NBO. (b) Correlating the dissipation factors of PIs from ODA group and the charge density of the imide group.

VII. Additional optical properties of PI films.

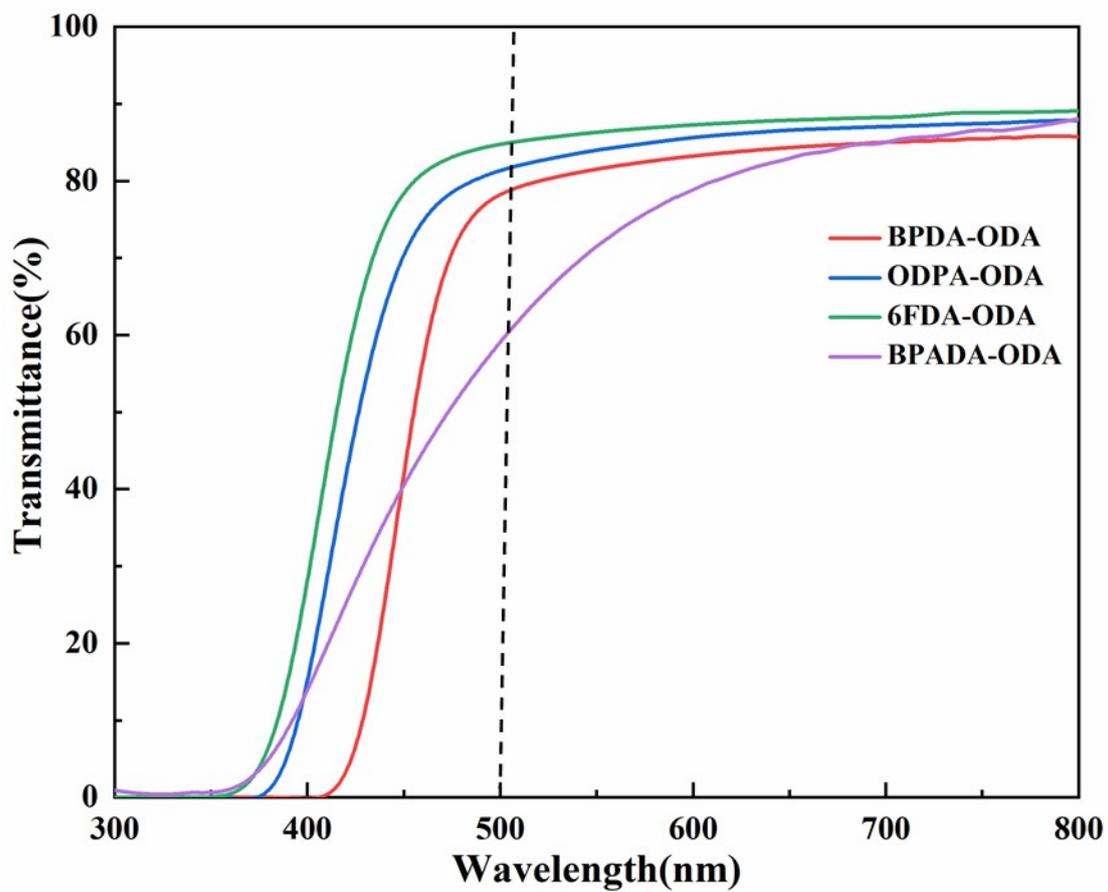


Fig. S8. UV-vis spectra of PIs based on ODA.

VIII. Additional detailed data of PI films.

Table S1. The dielectric properties of reported PI films.

Ref	Sample	Dielectric properties at 10 GHz	
		D_k	D_f
4	2-6FDA	2.38	0.0082
5	FAPI-70	2.93	0.0059
6	6FDA-BAPP	2.82	0.0052
6	BPADA-BAPHF	2.85	0.0053
This work	6FDA-HFBODA	2.63	0.0037
This work	BPADA-HFBODA	3.20	0.0023

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