Supporting information

Synergistic Regulation of Thermal-Optical Properties in Polyimides via Amide Bonds and Trifluoromethyl Groups: From Molecular Design to Flexible CNT TFTs Application

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13C NMR spectroscopy (400 MHz, DMSO-d_6)

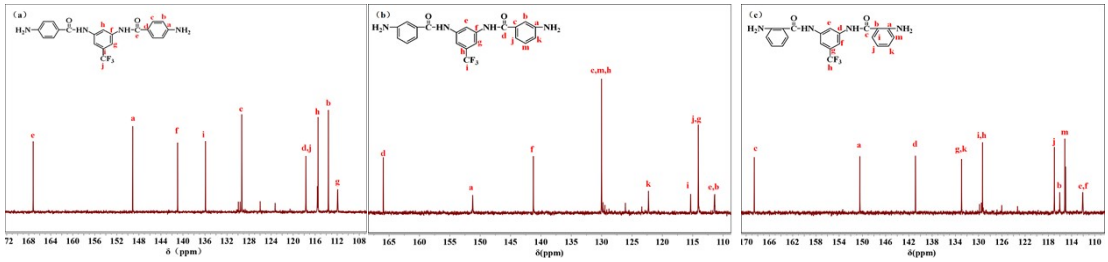

Figure S1 13C NMR spectroscopy of the synthesized monome:(a)3F-P、(b)3F-M and (c)3F-O.

High Liquid Chromatography-Mass Spectrometry

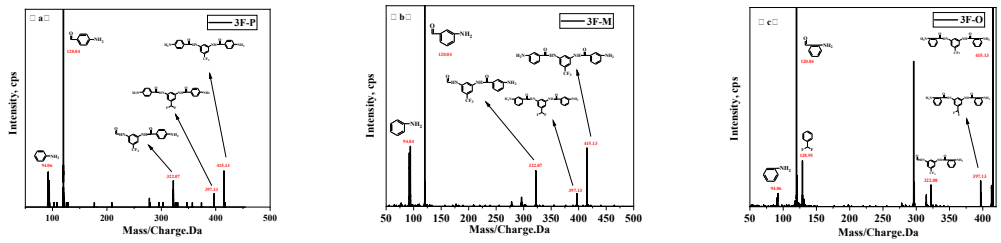

Figure S2 High Liquid Chromatography-Mass Spectrometry of the synthesized monome:(a)3F-P、(b)3F-M and (c)3F-O.

Melting Point By DSC

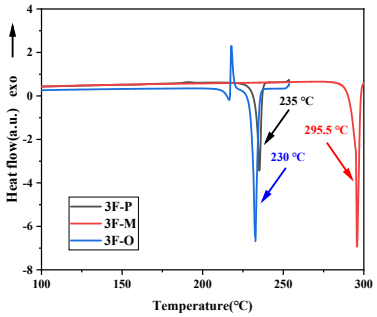

Figure S3 DSC Melting Point Curve of Diamine Monomers

Polyimide Dissolution Curve

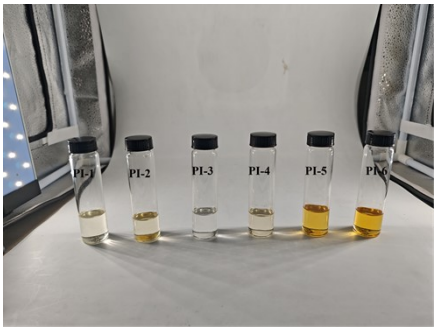

Figure S4 PI dissolution curve

Density Functional Theory Calculation Details

The repeating unit of polyimide was constructed using BIOVIA Material Studio 2019 software, which served as the model compound for calculation. DFT theory was

performed using the DMol3 module, applying GGA/PW91. The electronic exchange condition was set to even-valued plus polarization DNP4.4. After structural optimization was completed and virtual frequencies were removed, the lowest-energy optimized structure was obtained. Molecular orbital energies for the repeating unit were calculated by selecting orbitals in the "Properties" tab, and torsion angles were obtained using the measurement tool.

Molecular Dynamics Simulation

The repeating unit of PI was constructed and optimized. Literature suggests that PI models with 10-20 repeating units can produce reasonable simulation results.[1] Based on this, molecular chain models of PI-1, PI-2, PI-3, PI-4, PI-5, PI-6were established with each containing 10 repeating units. Following geometry optimization, the Amorphous Cell module was utilized to generate cubic simulation boxes. Three chains of each PI type were inserted into the boxes with an initial density of 0.5 g/cm^3 to prevent chain entanglement and overlap.Referring to the literature[2, 3], a series of molecular dynamics simulations were conducted using the Forcite module with the following procedures: (1) The system was compressed through a 200 ps MD simulation in the NPT ensemble at 0.1 GPa and 298 K to achieve densities close to experimental values. (2) Annealing cycles between 298 K and 600 K were performed in the NVT ensemble to eliminate unreasonable conformations. Five annealing cycles were executed with each cycle lasting 100 ps. (3) The system was equilibrated by performing a 200 ps MD simulation in the NPT ensemble at 0.0001 GPa and 298 K. (4) A production run of 500 ps was carried out in the NVT ensemble for data acquisition.

All simulations employed the COMPASS II force field. The Ewald summation method was applied to calculate electrostatic interactions. The atom-based cutoff method was used to handle van der Waals interactions. The Nosé thermostat and Berendsen barostat were adopted for temperature and pressure control respectively.

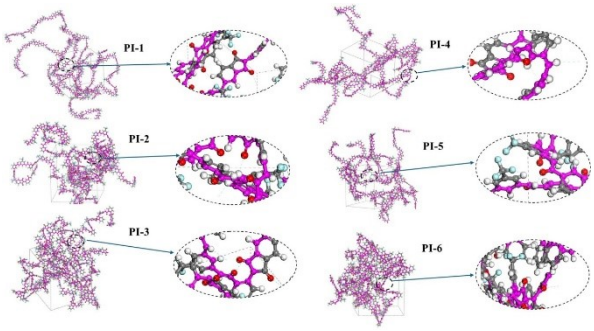

Figure S5 Simulation diagram of hydrogen bond.

Characterization Methods.

Attenuated total reflectance (ATR) FT-IR spectra were acquired using a Thermo Scientific Nicolet iS5 spectrometer over the range of 675 to 4000 cm^{-1}. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV III 400 MHz spectrometer using dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent.High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) was conducted to verify the molecular weights and structural integrity of the target diamine monomers (3F-P, 3F-M, 3F-O). The specific operation is as follows: Take an appropriate amount of solid sample, dissolve it in methanol, and filter it through a 0.45 μm organic filter membrane before injection.The ultra-high performance liquid chromatography (UPLC) system was Shimadzu LC-40D. The mobile phase was a methanol-water mixture. The injection volume was 5 μl, the column temperature was maintained at 40°C, and the flow rate was set to 0.3 ml/min.The mass spectrometer was a SCIEX X500R QTOF. An electrospray ionization (ESI) source was operated in positive ion mode. The ion source temperature was 500°C, the capillary voltage was set to 3.5 kV, and the curtain gas flow rate was 10 L/min. The nebulizer pressure was 40 psi, and the mass scan range was m/z 50~500. Soluble polyimide (PI) precursors' number-average (Mn) and weight-average (Mw) molecular weights were analyzed via gel permeation chromatography (GPC) using a Waters GPC 1515 system with an Agilent PLgel 5μm MIXED-C column. Chromatographic-grade N,N-dimethylformamide (DMF) served as the eluent at 1 mL/min flow rate under room temperature conditions. Calibration was conducted with narrow-polydispersity polystyrene standards. Glass Transition Temperature (T_g,DSC) were measured by SETARAM DSC141 instrument. TGA was performed on a Netzsch STA 449 F5 instrument. Samples (~5 mg) were heated from 40°C to 850°C at a rate of 10°C/min under a nitrogen flow of 30 mL/min. TMA was conducted on a TMA Q400 instrument. The coefficient of linear thermal expansion (CTE) in the film plane was calculated as the average value over the temperature range of 50–250°C from the second heating scan. Optical transmittance of PI films in the wavelength range of 200~800 nm was measured using a Shimadzu UV-2550 spectrophotometer. Dielectric constant (D_k) and dielectric loss (D_f) were measured at high frequency (microwave) using an AET ADMS01Nc dielectric constant analyzer equipped with silver electrodes. Samples measured 10 mm (L) × 10 mm (W) × 20 μm (T). DMA was performed on an EPLEXOR 500N dynamic mechanical analyzer. The peak in the loss tangent (tan δ) curve was reported as the dynamic mechanical T_g.

Reference

1. H. Lei, S. Qi and D. Wu, Polymer, 2019, 179, 121645.
2. Y. Li, J. Zhao, F. Zhao, F. Li, C. Dai, C. Chen, Z. Yang and G. Tu, ACS Applied Polymer Materials, 2024, 6, 10738-10749.
3. M. Heuchel and D. Hofmann, Desalination, 2002, 144, 67-72.