Supporting Information

Functional Polyimides based on diamine containing diarylethylene moieties and their photochromic mechanism studies

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Materials and Instrumentation

Materials. 2-Chloro-5-methylthiophene, glutaryl chloride, aluminium chloride, anhydrous dichloromethane, zinc, anhydrous tetrahydrofuran, n-Butyllithium (2.4 M solution in hexanes), tributyl borate, 4-bromoaniline, tetrakis (triphenylphosphine) palladium, 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA), 4,4'-(hexafluoroisopropylidene) diphthalic Anhydride (6FDA) and N-methyl-2-pyrrolidone (NMP) were purchased from Aladdin Chemical Co., Ltd. and used as received.
4,4-Oxydiphthalic anhydride (ODPA) and anhydrous N, N-dimethylformamide (DMF) were purchased from J&K Chemical Co., Ltd. and used as received.
All other reagents were analytical grade and used as received from commercial sources, unless otherwise mentioned.

Synthesis

(1) Synthesis of Dione:
In a 250 mL two neck round bottle filled with argon, anhydrous $AlCl_3$ (16.0g, 120 mmol) and anhydrous DCM (100 mL) were added. 2-Chloro-5-methylthiophene and glutaryl chloride were dissolved in DCM and added dropwise to this two-neck bottle and stirred at room temperature for 3 hours. The black mixture was poured into ice water and hydrochloric acid were added till no gas came out. The solution was extracted with DCM, the organic phrase was purified with silica gel with PE: DCM=3:1, the final product was 6.81 g light yellow Dione, with 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.09-2.03 ppm (m, 2H), 2.66 ppm (s, 6H), 2.88-2.85 ppm (m, 4H), 7.19 ppm (s, 2H). MS (EI): m/z=359.99 [M^+].

(2) Synthesis of DTE2Cl:
In a dry 250 mL two neck round bottle filled with argon, Zinc (20 g) and anhydrous THF (80 mL) were added, stirred at -5^{o}C. $TiCl_4$ (19.43 mL, 128.71 mmol) was added dropwise to this bottle and after completion, the mixture was heated to reflux for 3 hours and cooled to room temperature. Dione (6.8 g, 18.79 mmol) dissolved in 30 mL anhydrous THF was added and afterwards, the reactants were heated to reflux for 12 hours. After that, K_2CO_3 saturated aqueous solution were added at room temperature, filtered and extracted with DCM, the organic phase was purified with silica gel using PE, the final product was 5.58 g colorless crystal, with 90.3% yield.
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.88 ppm (s, 6H), 2.05-1.99 ppm (m, 2H), 2.73-2.70 (m, 4H), 6.58 ppm (s, 2H). MS (EI): m/z=327.77 [M^+].

(3) Synthesis of DTEDA:
In a dry 250 mL two neck round bottle filled with argon, DTE2Cl (5.50 g, 16.72 mmol) and anhydrous THF (30 mL) were added, the reactants were placed in -78^{o}C and stirred, n-Butyllithium (16.72 mL, 2.4 M solution in hexanes) were added dropwise in 10 min, after reaction for 1 hour, tributyl borate (13.56 ml, 50.17 mmol) were added and stirred for 1 hour. The product was used without purification. 4-bromoaniline (6.91 g, 40.14 mmol) were added

to previous mixture, with $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol) and 2M K_2CO_3 aqueous solution (60 mL), the reaction was protected by argon and refluxed for 12 hours. After that, the reaction was cooled to room temperature and extracted by DCM, the organic phase was purified with silica gel using DCM. The final product was 4.44 g light yellow power, with 60% yield.
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.86 ppm (s, 6H), 2.10-1.95 ppm (m, 2H), 2.89-2.71 ppm (m, 4H), 5.24 ppm (s, 4H), 6.60-6.50 ppm (d, 4H), 6.96 ppm (s, 2H), 7.19 ppm (d, 4H).
^{13}C NMR (125 MHz, $CDCl_3$, δ): 14.42 ppm, 23.08 ppm, 38.56 ppm, 115.34 ppm, 122.21 ppm, 125.41 ppm, 126.56 ppm, 132.69 ppm, 134.56 ppm, 136.52 ppm, 140.12 ppm, 145.62 ppm.
Anal. Calcd. for $C_{27}H_{26}N_2S_2$: C, 73.19; H, 5.87; N, 6.33; S,14.46. Found: C, 73.40; H, 6.09; N, 6.17; S, 13.63.
IR (KBr, ν, cm^{-1}): 3463, 3361, 2948,2915, 2846, 1616, 1517, and 1286.
MS (EI):m/z= 442.38 [M+].

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-plus 300 spectrometer and a Varian Unity Inova 500 NB spectrometer, respectively. The ^{1}H NMR and ^{13}C NMR were measured in deuterated dimethyl sulfoxide (DMSO-d_6) and chloroform-d respectively with tetramethylsilane (TMS) as an internal standard. Mass spectra were performed on a Thermo EI mass spectrometer (DSQ II). Elemental analysis data were recorded on a Thermo Elemental Analysis Flash 4000. Infrared spectra (IR) were analyzed by a Brucker Tensor 27 Fourier-transform infrared (FT-IR) spectrometer. The intrinsic viscosities (η_{inh}) of the polyimides were obtained at a solid content of 0.1 wt% in NMP at 30 °C on an Ostwald viscometer. Ultraviolet-visible (UV-vis) absorption spectra were obtained on a Hitachi UV-Vis spectrophotometer (U-3900). The PI solution spectra were measured at a concentration of approximate 0.05 $mmol \cdot L^{-1}$ before the absorbance was normalized. The fluorescence spectra of the PIs solutions at a concentration of approximate 0.02-0.05 $mmol \cdot L^{-1}$ were recorded using a Shimadzu RF-5301PC spectrometer. Thermogravity analysis (TGA) were carried out on a TA thermal analyzer (Q50) under nitrogen atmosphere at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204) at a heating rate of 10 °C/min.

Molecular simulation and analysis were carried out with the Gaussian 09 and the Multiwfn program package. The molecular geometry, molecular orbitals and dipole moment of the basic unit in the polyimide molecular structure were calculated and optimized by means of the density functional theory (DFT), using the Becke's three-parameter hybrid density functional method in conjunction with Lee-Yang-Parr's correction functional (B3LYP) method, and the 6-31+G(*d*) basic set. For all simulations, vibration frequencies were calculated analytically to ensure the minimum total energy of the optimized molecular geometry.

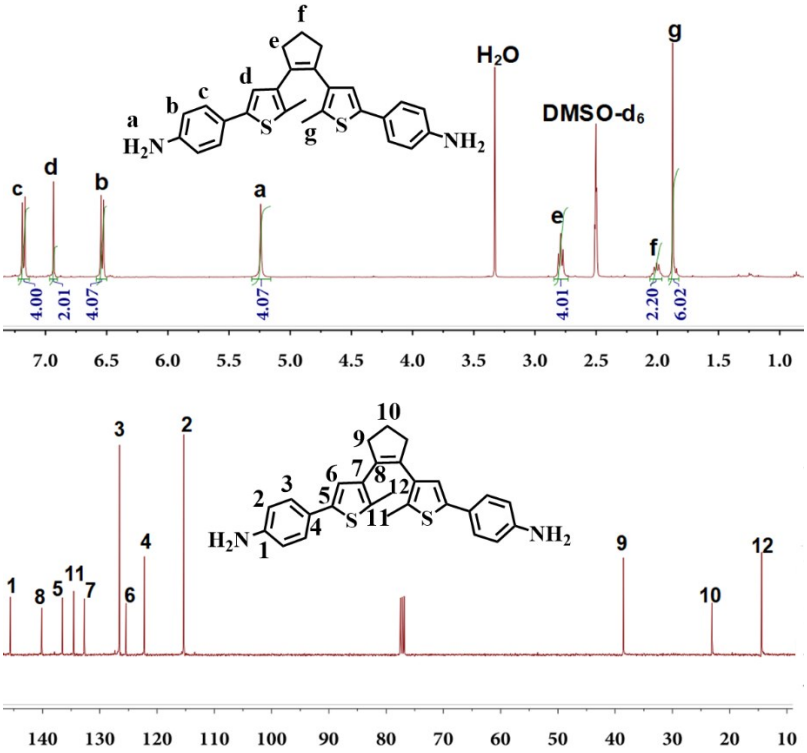

Fig.S1 ^{1}H NMR and ^{13}C NMR spectra of the diamine DTEDA

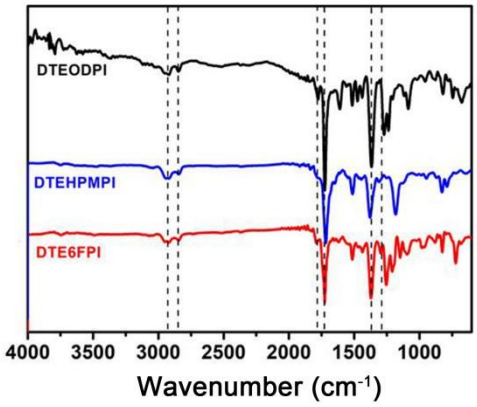

Fig.S2 FTIR spectra of the polyimides

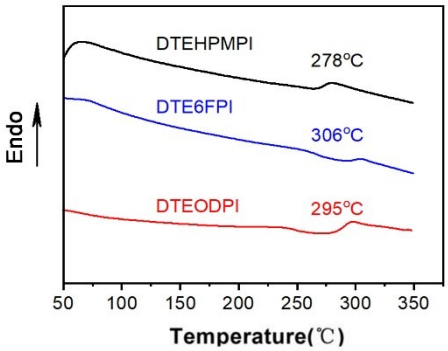

Fig. S3 DSC curves of three PIs.

Table S1 Solubility of the polyimides

Polyimide	NMP	DMF	DMAc	DMSO	$CHCl_3$	THF
DTE6FPI	++	++	++	++	++	++
DTE6FPI (film)	+	-	-	+	-	-
DTEHPMPI	++	++	++	++	+	+
DTEHPMPI (film)	+	-	-	+	-	-
DTEODPI	+	+	+	+	-	-
DTEODPI (film)	+	-	-	+	-	-

4 mg sample in 2 mL solvent; PI films were 300°C treated for 0.5 h before solubility test; ++: soluble at room temperature; +: soluble when heated; -: insoluble when heated