Synthesis and Properties of High-Performance Functional Polyimides Containing Rigid Nonplanar Conjugated Tetraphenylethylene Moieties

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ABSTRACT: A simple diamine (TetraPEDA) containing rigid nonplanar conjugated tetraphenylethylene (TetraPE) moieties was designed and synthesized through Wittig–Horner and Suzuki coupling reactions. Four kinds of high-performance functional polyimides (PI) were thus prepared by the polymerization of TetraPEDA and four dianhydrides, respectively. Because of the introduction of the aromatic rigid nonplanar TetraPE structure, the PI exhibited special fluorescent characteristics, as the maximum fluorescence emission of the four PI was observed at 425–505 nm in NMP solution and at 470–491 nm in film state. Also these organo-soluble PI showed outstanding properties, such as low dielectric constant (even without fluorinated substituent), light color, high glass transition temperatures (382–443 °C) and

INTRODUCTION Polyimides (PI) are widely used in microelectronics and aerospace industries as materials for electronic packaging and electrical insulation, because of their excellent thermal and thermo-oxidative stability, solvent and chemical resistance, electrical, and mechanical properties.¹⁻³ Functional PI and their applications are emerging research areas in recent years. Their application in the field of flexible electronics and displays,⁴ flexible and thin film photovoltaics (PV),^{5,6} xerography,^{7,8} light-emitting diodes,⁹ and so forth have been explored and attracted growing interest, especially in the field of polymer memories devices.¹⁰ Kang,^{11,12} Hsiao,¹³ and Ree¹⁴⁻¹⁵ have developed series of functional PI containing both electron-donor (D) and electron-acceptor (A) in the same macromolecule, which showed typical resistive switching behaviors and significant advantages over inorganic silicon- and metal-oxide-based memory materials. Compared to other polymer memory materials, functional PI exhibit not only the advantages of rich structure, flexibility, low-cost, and three-dimensional stacking capability, but also excellent thermal stability, dimensional stability, and favorable physical and chemical properties. However, these applications are limited by the infusible and insoluble nature and dark color (yellow to brown) of the PI, which mainly result

thermal stability in air ($T_{d5\%}$ up to 565 °C), and excellent mechanical properties. The polymer memory devices with the configuration of indium tin oxide/Pl/aluminum (ITO/Pl/Al) exhibited distinct volatile memory characteristics of static random access memory, with an ON/OFF current ratio of 1×10^4 to 1×10^5 . These functional Pl showed attractive potential applications in the field of high performance flexible polymer photoconducting devices or fluorescent polymer memory devices. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1302–1314

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from the rigid backbones and strong interchain packing, as well as the formation of charge transfer complex (CTC) between the electron-donating diamine moiety and the electron-accepting dianhydride moiety in polyimide molecular chain.¹⁶⁻¹⁷ In this regard, many structural modifications of the polymer backbone have been utilized to modify the properties of PI,18-20 mainly focusing on the organo-solubility,²¹ colorlessness, and high transparency.²² Considerable efforts have been made by introducing flexible linkages, fluorinated substituent, unsymmetrical units or bulky pendent groups into the polymer backbones.²³⁻²⁸ Among these strategies, introduction of fluorinated substituent such as hexafluoroisopropylidene linkages, perfluoroalkyl groups, and pendent trifluoromethyl groups has been considered as one of the most promising methods. However, its application is limited because fluorochemicals are too expensive to be widely used. Strategies of introducing flexible linkages, unsymmetrical units, or bulky pendent groups have shown certain benefits to improve the solubility and color of the polymers, but usually led to reduction of thermal stability and mechanical properties of PI.

The tetraphenylethylene (TetraPE) motif has attracted considerable attention by virtue of its rich electrochemical 29,30

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FIGURE 1 3D structure of TetraPEDA and its polyimide.

and excited state properties^{31,32} as well as its extensive usage as an electron transfer catalyst in a variety of polymerization,³³ aggregation enhanced emission.³⁴ In TetraPE, an iconic aggregation-induced emission (AIE) chromophore, fast rotation of the phenyl rings and partial twisting of the C=C bond quench its fluorescence in dilute solutions.³⁵⁻³⁷ In TetraPE aggregates, short intermolecular interactions obstruct the rotation of the phenyl groups and permit deactivation by fluorescence. The unique luminescence behavior of TetraPE and other rotors has been harnessed for the development of biological sensors,³⁸ solid-state lighting materials,^{39,40} and luminescent polymers.^{35–37,41,42} Derivatives of TetraPE have been incorporated into organic polymers and oligomer with the resulting materials displaying fluorescence profiles that can be perturbed according to the overall density of TetraPE units within the polymer/oligomer and the environment surrounding the bulk material.43,44

In this work, a novel diamine (TetraPEDA) containing TetraPE moiety was designed and synthesized through Wittig-Horner and Suzuki coupling reactions. The 3D chemical structure of TetraPEDA and its polyimide are shown in Figure 1. The TetraPEDA has a special twisted steric structure (as shown in the red circle), where the four benzene rings are nonplanar, and the direct coupling of the six benzene rings through the ethylene group builds the large conjugated structure. When such kind of structure is introduced into the polyimide main chain, the nonplanar steric structure minimizes the strong interaction and tight stacking of the molecular chains. As a result, the increase in free volume of the polymers favors solubility improvements in organic solvents as well as lowering of the dielectric constant. In addition, the large nonplanar conjugated structure may evoke special photoelectric properties, affording a convenient method to build novel functional PI. With TetraPEDA moieties as electron donors (D) and the dianhydride moieties as electron acceptors (A), the polyimide D-A molecules may build electronic transition between the ground and excited states and could be manipulated by the induced charge transfer (CT) from donor (D) to acceptor (A) under applied electric fields. For this reason, the PI are expected to exhibit

bistable conductance switching effects, applicable to data storage, such as polymer memory devices.⁴⁵ Finally, the rigid nature of this hexaphenylethylene structure is expected to maintain a relatively high glass transition temperature, excellent thermal stability, and mechanical properties. Such kind of design philosophy can also be extended to the design and synthesis of other high performance functional polymers, such as aromatic polyamides, polyesters, and so forth, to obtain good solubility and processability while maintaining their excellent overall properties.

EXPERIMENTAL

Materials

Diphenylmethane, *n*-butyllithium, 4-amino-phenylboronic acid, tetrakis(triphenylphosphine) palladium, 4,4'-dibromobenzophenone, and Aliquat 336 (tricaprylyl-methylammonium chloride) were purchased from Alfa-Aesar company and used as received. 3,3',4,4'-biphenyltetra-carboxylic acid dianhydride (BPDA), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA), 4,4'-(hexafluoroiso-propylidene) diphthalic anhydride (6-FDA), and pyromellitic dianhydride (PMDA) were purchased from National Pharmaceutical Group Chemical Reagent Co., and were heated at 140 °C under vacuum for 12 h prior to use. Analytical grade dimethyl formamide (DMF) was purified by distillation under an inert nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other solvents and reagents as analytical grade were purchased from Guangzhou Dongzheng Company and used without further purification.

Instrumentation

All nuclear magnetic resonance spectra (NMR) were recorded at room temperature using a Varian Unity Inova 500 NB spectrometer, operating at 499.774 MHz for ¹H with indirect detection probe and at 125.682 MHz for ¹³C with broadband probe. Samples were prepared as solution of 5-15 mg of each compound in 0.7 mL of deuterated dimethyl sulfoxide (DMSO), using tetramethylsilane (TMS) as the internal reference. Inverse gated decoupling was employed for quantitative carbon nuclei intensities at pulse angle of 248, acquisition time of 0.45 s, and relaxation delay of 2.9 s for about 5000 scans. Two-dimensional spectra were obtained by using standard Varian software and the parameters used were as follows: COSY spectra were collected with four transients for each of 256 increments and the spectral windows were 4096.5 Hz in both dimensions. Mass spectra were measured using a Thermo MAT95XP-HRMS spectrometer. Elemental analysis was carried out on a CHNS Elemental Analyzer. Infrared spectra were recorded by a BRUKER TENSOR 27 Fourier-transform infrared (FTIR) spectrometer. Gel permeation chromatography (GPC) was carried out on a Waters 717 plus autosampler and Waters 1515 Isocratic HPLC Pump. Two Waters columns, connected in series, were used with DMF as the eluent and calibrated with polystyrene standards having narrow polydispersity. UV-vis (UV) absorption spectra were recorded on a Hitachi UV-vis spectrophotometer (U-3900). Fluorescence spectra were measured using a Shimadzu RF-5301PC spectrometer with a slit width of 5 nm for PI and 3 nm for monomer respectively, for emission on 365 nm. Cyclic voltammetry (CV) measurements were carried out on a Shanghai Chenhua electrochemical workstation (CHI660C) in a three-electrode cell with a Pt disk working electrode, an Ag/AgCl reference electrode, and a glassy carbon counter electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1 M tetrabutyl-ammonium perchlorate $(n-Bu_4NClO_4)$ in N-methyl-2-pyrrolidone (NMP) at a scan rate of 100 mV/s using ferrocene as standard. The highest occupied molecular orbital (HOMO) energy levels were obtained using the onset oxidation potentials from the CV curves. The lowest unoccupied molecular orbital (LUMO)/HOMO energy gaps (ΔE_g) for the compounds were estimated from the onset absorption wavelengths of the UV absorption spectra. Thermogravimetric analyses (TGA) were performed with a TA thermal analyzer (Q50) under N₂/air (flowing rate of 40 mL/min) at a heating rate of 20 °C/min from 30 to 1000 °C. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204) at a heating rate of 25 °C/min from 30 to 450 °C under flowing nitrogen. The glass transition temperatures $(T_g \text{ values})$ were taken from the second heating trace after rapid cooling from 450 °C at a cooling rate of 40 °C/min and read at the midpoints of the transitions in the heat capacity. The dynamic mechanical (DMA) spectra of the samples were obtained by using NETZSCH DMA 242. The specimens were analyzed in tensile mode at a constant frequency of 1 Hz, static force of 0.1 N, dynamic force of 0.11 N, and a temperature range from 30 to 480 °C at a heating rate of 5 °C/min. Tensile test was performed on samples cut from 35 to 40 mm thick sheet and tested using U-CAN UT-2060 (Taiwan, China) instrument according to ISO standard 37-2005. The specimen size was 6 \times 100 mm^2 and Jaw separation was 50 mm. Jaw speed was first set at 2 mm/min, and then changed to 20 mm/min when elongation reached 1 mm. The dielectric constant was measured at frequencies between 100 Hz and 1 MHz at 20 °C and 50% relative humidity, using Solartron SI 1260 Impedance/Gain Phase Analyzer together with two custom-built copper electrodes (10.2 imes 10.2 mm²). The amplitude of the a.c. electric field was about 1 V/ cm. The samples were thin films in size of 12 \times 12 mm². Silver paste was coated onto both side surfaces of the PI film to ensure excellent contact between the electrodes and PI film.

Synthesis of 1-Bromo-4-(1-(4-bromophenyl)-2,2diphenylvinyl) benzene (TetraPEDBr)

Diphenylmethane (6.18 mL, 36.8 mmol) and anhydrous tetrahydrofuran (100 mL) were mixed in a 500-mL flask and continuously stirred for 40 min under argon at 0 °C. A 2.2 M solution of *n*-butyllithium in hexane (21.7 mL, 47.74 mmol) was added into the flask. After stirring for 40 min at that temperature, 4-(4-bromophenyl) benzophenone (10 g, 21.7 mmol) was added and the reaction mixture was stirred for another 10 h allowing the temperature to rise gradually to room temperature. Then the reaction was quenched with an aqueous solution of ammonium chloride (100 mL) and the

mixture was extracted with dichloromethane. The organic layer was evaporated after drying with anhydrous sodium sulfate and the resulting crude product was dissolved in toluene (100 mL). Then p-toluenesulfonic acid (2.00 g, 11.6 mmol) was added, and the mixture was refluxed overnight at 110 °C under argon and cooled to room temperature. Finally, the mixture was concentrated and the crude product was purified by silica gel column chromatography using nhexane as eluent to yield a white powder (9.17 g, 86%). ¹H NMR (500 MHz, CDCl₃, δ): 6.84–6.88(d, 4H), 6.98–7.01(m, 4H), 7.10-7.13(m, 6H), 7.20-7.23 (d, 2H); ¹³C NMR (125 MHz, CDCl₃, δ): 120.69, 126.86, 127.89, 130.97, 131.10, 132.89, 138.35, 142.15, 142.26, 142.99; IR (KBr): v = 698(C—Br stretching), 1495 (C—C stretching), 1097–702 cm⁻¹ (Ar—H stretching); HRMS (ESI, m/z): $[M + H]^+$ calcd for C₂₆H₁₈Br₂: 490.23; found, 490. Anal. calcd for C₂₆H₁₈Br₂: C 63.7, H 3.7, N 0.000; found: C 63.35, H 3.735, N 0.000.

Synthesis of (4',4"-(2,2-Diphen-ylethene-1,1-diyl)dibiphenyl-4-amine) (TetraPEDA)

TetraPEDBr (7.3535 g, 15 mmol)) and 4-aminophenylboronic acid (5.202 g, 30 mmol) were dissolved in THF (100 mL), and then 2 M aqueous K_2CO_3 aqueous solution (45 mL) and 10 drops of Aliquat 336 were added. The mixture was stirred for 45 min under argon at room temperature. Then tetrakis(triphenyl-phosphine) palladium (Pd(Pph₃)₄) catalyst (catalytic amount) was added in and the reaction mixture was stirred at 75 °C for 24 h. After being cooled to room temperature, the product was concentrated and purified by silica gel column chromatography using dichloromethane/ *n*-hexane (vol/vol = 2/1). Yield of the product was about 85%. ¹H NMR (500 MHz, DMSO- d_6 , δ): 5.18 (s, 4H), 6.58– 6.63(d, 4H), 6.96-6.99(d, 4H), 7.00-7.03(d, 4H), 7.01-7.11(m, 2H), 7.11-7.15(t, 4H), 7.29-7.34 (m, 8H); ¹³C NMR (125 MHz, DMSO- d_6 , δ): 114.12, 124.27, 126.31, 126.53, 126.79, 127.74, 130.63, 131.17, 138.39, 139.74, 140.15, 140.50, 143.52, 148.26; IR (KBr): v = 1495 (C-C stretching), 1097-702 (Ar-H stretching), 3037 (C-H stretching), 1285 (C—N stretching), 1617 (δ N—H), 3368 cm⁻¹ (N—H stretching); HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{38}H_{30}N_2$: 514.66; found: 514. Anal. calcd for C38H30N2: C 88.68, H 5.876, N 5.44; found: C 88.15, H 5.962, N 5.508.

Synthesis of Polyimides

Synthesis of polyimide TetraPEDA-6FDA (PI-6FDA) was used as an example to illustrate the general synthetic route. To a solution of TetraPEDA (1.0293 g, 2 mmol) in 11.8 mL of purified DMF in a 50-mL flask, 6-FDA (0.8885 g, 2 mmol) was added in, achieving a solid content of approximately 15 wt %. The mixture was stirred at room temperature under argon for about 6 h to form a viscous poly(amic acid) (PAA) solution. The weight average molecular weight (M_w) and the polydispersity index (PDI) of the resultant PAA (PAA-6FDA) estimated from GPC were 3.29×10^5 and 1.58, respectively, measured in DMF at a concentration of 4 mg/mL at 50 °C. The PAA was subsequently coated uniformly on a clean and dry glass plate with a controlled film thickness, and then thermally imidized in a vacuum oven with temperature program of 100 °C (1 h)/200 °C (1 h)/300 °C (1 h)/350-400 °C



SCHEME 1 Synthesis routes of TetraPEDA.

(1 h) to produce PI (TetraPEDA-6FDA). The polyimide film was removed from the glass substrate after the oven cooled to room temperature. ¹H NMR (500 MHz, DMSO- d_6 , δ): 7.05–7.09(d, 4H), 7.10–7.19(m, 10H), 7.47–7.57(m, 8H), 7.70–7.77(d, 4H), 7.77–7.81(m, 2H), 7.92–7.97(d, 2H), 8.11–8.18 (d, 2H); IR (KBr): v = 1776 and 1718 (CO stretching), 1495 (CC stretching), 1097–702 cm⁻¹ (Ar—H stretching); Anal. calcd for C₅₇H₃₂F₆N₂O₄: C 73.58, H 4.013, N 3.205; found: C 74.18, H 3.495, N 3.035. All of the other PI (PI-BTDA, PI-BPDA, and PI-PMDA) were synthesized by using a procedure similar to that described above.

Fabrication and Characterization of the Memory Devices The memory devices were fabricated on an indium-tin oxide (ITO)-coated glass, with the configuration of ITO/PI/Al. Before the fabrication, the ITO glass was precleaned by ultrasonication with water, acetone, and isopropanol each for 20 min. A PAA solution in DMF (10 mg/mL) was spin-coated onto the clean ITO glass at a spin speed of 2000 rpm for 45 s and then thermal imidization was performed as mentioned above. The thickness of the thin film was determined to be around 80-110 nm. Finally, an 80-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of 0.2 \times 0.2 mm² in size) at a pressure of 10^{-7} Torr with a uniform depositing rate of 3–5 Å/s. The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer equipped with a Keithely 4205-PG2 arbitrary waveform pulse generator. ITO was used as the cathode, and Al was set as the anode during the voltage sweep. The probe tip was a tungsten wire (10 μ m in diameter) attached to a tinned copper shaft with a point radius < 0.1 μm (GGB Industries, Inc.).

Molecular Simulation

Molecular simulations of the PI were carried out with the Gaussian 03 (revision E.03) program package. Equilibrium ground state geometry and electronic properties of basic unit of the PI were optimized by means of the density functional theory (DFT) method at the B3LYP level of theory



FIGURE 2 (a) ¹H NMR, (b) ¹³C NMR, (c) H-H COSY, (d) C-H QC, and (e) C-H BC spectra of TetraPEDA in DMSO-d_e.

Materials Views

TABLE 1 Thermal and Photophysical Properties of TetraPEDA

		$T_{d} (^{\circ}C)^{b}$			λ_{\max}^{em} (nm)	
Compd	τ _g (°C) ^a	5%	10%	λ_{\max}^{abs} (nm) ^c	THF^d	Powder
TetraPEDA	144	368	389	393	485	463

^a Measured by DSC at a heating rate of 25 °C/min.

 $^{\rm b}$ Measured at a heating rate of 20 $^\circ\text{C/min}$ under N_2

 c TriPEDA concentration of 1 \times 10 $^{-5}$ mol/L in THF.

 $^{\rm d}$ Measured in THF solution at a concentration of 1 \times 10 $^{-5}$ mol/L.

(Beckes-style three-parameter DFT using the Lee-Yang-Parr correlation functional) with the 6-31 G(d) basic set.

RESULTS AND DISCUSSION

Synthesis and Characterization of TetraPEDBr and TetraPEDA

The synthesis of TetraPEDA is illustrated in Scheme 1, where dibromide (TetraPEDBr) is prepared under Wittig-Horner reaction conditions from the reaction of diphenylmethane with 4,4-dibromobenzo-phenone, followed by the Suzuki reaction with 4-aminophenyl-boronic acid to yield the desired diamine TetraPEDA. ¹H NMR and ¹³C NMR, mass spectra, FTIR, and elemental analysis were employed to identify the structures of the synthesized dibromide intermediate product and diamine monomer. The ¹H and ¹³C NMR spectra of TetraPEDBr are shown in Supporting Information Figure S1, whereas panels (a) and (b) in Figure 2 illustrate the ${}^{1}\mathrm{H}$ and ¹³C NMR spectra of TetraPEDA. Assignments of each carbon and proton were assisted by the two-dimensional (2D) COSY, C-H QC, and C-H BC NMR spectra shown in Figure 2(c-e). The spectral results were in agreement with the proposed molecular structure of TetraPEDA, and the ¹H NMR spectra confirmed that the diamine was successfully synthesized by the mentioned three-step reactions by the



FIGURE 3 PL spectra of TetraPEDA (1 \times 10⁻⁵ M) in THF with varying amounts of water (vol %). (The inset depicts the changes of PL peak intensity with water fraction, and the pictures are UV irradiation excited at 365 nm.)



SCHEME 2 Synthesis of polyimides.

resonance signals at around 5.2 ppm corresponding to the amino protons.

The thermal and photophysical properties of the synthesized compound TetraPEDA (Table 1) analyzed by TGA and DSC revealed that TetraPEDA had good thermal stability. The 5% and 10% weight-loss temperatures of TetraPEDA in nitrogen were 368 and 389 °C, respectively, and its glass transition temperature (T_{g}) was about 144 °C.

Figure 3 shows the photoluminescence (PL) spectra of Tetra-PEDA (10^{-5} M) in THF solution with varying amounts of water (vol %). Because of the rigid aromatic non-coplanar 3D structure and large conjugated properties, the novel diamine displayed the expected photophysical properties and remarkable aggregation-induced emission enhancement (AIEE) properties.^{46,47} The maximum UV absorption wavelength of TetraPEDA was 393 nm in THF, which can be attributed to the π - π ^{*} transition of the π electronic system delocalized along the hexaphenylethylene conjugated moieties. When TetraPEDA was excited at the maximum absorption wavelength, its maximum PL emission in THF solution and powder state appeared at wavelength of 485 and at 463 nm, respectively, indicating a significant blue-shift in the maximum emission for powder TetraPEDA compared to TetraPEDA in solution. The PL intensity of the TetraPEDA increased with the addition of water (poor solvent for Tetra-PEDA). It reached the maximum when water content was 90%. However, the overall PL intensities of TetraPEDA (1 imes 10^{-5} M) in THF with addition of water were much higher than that without the addition of water, suggesting the AIEE properties of TetraPEDA.

Synthesis and Characterization of the Polyimides

Four kinds of PI were prepared in a conventional two-step procedure by the reaction of equal molar amounts of diamine TetraPEDA with commercially available aromatic



FIGURE 4 (a) Chemical structure of PI-6FDA, (b) 1H NMR, and (c) H-H COSY spectra of PI-6FDA in DMSO-d₆.

tetracarboxylic dianhydrides (PMDA, BPDA, BTDA, and 6FDA) in DMF to form precursor PAAs, followed by thermal cyclodehydration, as shown in Scheme 2. The chemical structures of the PI derived from TetraPEDA were confirmed by FTIR spectra in Supporting Information Figure S2. Compared

to the spectra of TetraPEDA, the characteristic absorption at 3368 and 1617 cm⁻¹ (N—H stretching) disappeared in the spectra of PI, meanwhile the characteristic absorption peaks of the imide group at 1776 cm⁻¹ (asymmetrical stretching of carbonyl) and 1718 cm⁻¹(symmetrical stretching of

ABLE 2 Molecular Weight of the	PAAs and the Solubility	Behaviors of the C	orresponding Polyimides
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	GPC ^a		Solvent ^b						
Polymer	$M_{ m w} imes10^5$	PDI	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol		
PI-6FDA	3.29	1.58	++	++	++	++	+		
PI-BPDA	2.68	1.87	++	+	+-	++	+-		
PI-BTDA	3.46	1.60	+	+	+	+	+-		
PI-PMDA	2.31	1.93	++	+	+	+-	+-		
Kapton			_	_	_	_	-		

 a With respect to polystyrene standards, DMF as the eluent at flow rate of 1 mL/min and test temperature of 50 $^\circ\text{C}.$

 $^{\rm b}$ Solubility: ++, Soluble at room temperature; +, partially soluble at room temperature, soluble on heating(90 °C); +-, partially soluble on

heating (90 °C); –, insoluble even on heating. The solubility was determined by adding 10 mg of PI in 1 mL of solvent.



	т	т	<i>T</i> _{d5%} (°C)		<i>T</i> d10%	₀ (°C)	Char Vield	
Polymers	/ _g (°C) ^a	(°C) ^b	N_2	Air	N_2	Air	(wt %) ^c	
PI-6FDA	371	382	540	534	559	554	69	
PI-BPDA	408	422	567	565	584	588	69	
PI-BTDA	377	390	546	542	567	571	67	
PI-PMDA	434	443	546	516	571	555	64	

 TABLE 3 Thermal Properties of the PIs

^a Measured by DSC at a heating rate of 25 °C/min.

^b Measured by DMA at 1 Hz and at a rate of 4 °C/min.

^c Residual weight percentage at 800 °C in nitrogen.

carbonyl), and the C—N bond at around 1373 cm⁻¹ were clearly shown. This indicated the successful reaction between TetraPEDA and the four dianhydrides, and the complete imidization reaction of the PAA. Moreover, the desired formation of all polymers was confirmed by ¹H NMR, and the spectra of PI-6FDA as an example are shown in Figure 4.

The molecular weight of the PAAs was determined by GPC and the qualitative solubility behavior of the corresponding PI is summarized in Table 2. The $M_{\rm w}$ of the PAAs ranged from 2.31×10^5 to 3.46×10^5 , with PDIs ranging from 1.58 to 1.93, indicating the synthesized PI had a very high molecular weight and a narrow molecular weight distribution. It is well-known that aromatic PIs generally show poor solubility in organic solvents, especially for those derived from rigid monomers, such as PMDA, BTDA, BPDA, PPD, and ODA. As shown in Table 2, commercial aromatic polyimide (Kapton film) was insoluble in all the test solvents even on heating, while the four synthesized PI were soluble in polar solvents such as N-methylpyrrolidone (NMP), dimethylacetamide (DMAc), DMSO, DMF, and *m*-cresol, even without fluorinated substituent. The enhanced solubility can be attributed to the introduction of the twisted nonplanar conjugated TetraPE group into the main chain of polyimide macromolecule. Such a structure may increase the steric hindrance moieties, and thus reduce the interactions between the molecular chains. The excellent solubility makes these polymers as potential candidates for practical application in microelectronics by spin- or dip-coating processes.

	250	300 Тетре	350 erature /	$^{400}_{/}$ $^{400}_{C} \rightarrow$	450
					4
	0.2				4
tan	0.4			$' \downarrow \uparrow$	434
↑ &	0.6	— PI-PMDA			
	0.8	— PI-BTDA		$\wedge \wedge$	
	1.0	— PI-6FDA PL BPD A	382	390	422

FIGURE 5 DMA curves of the PI films.

The thermal properties of the PIs were investigated by TGA, DSC, and DMA, and the results of TGA analyses (Table 3 and Supporting Information Fig. S3) revealed that all the polymers exhibited good thermal stability with insignificant weight loss up to 500 °C in nitrogen or air. The 5% and 10% weight-loss temperatures ($T_{d5\%}$ and $T_{d10\%}$) of the polymers in nitrogen were in the range of 571-592 and 594-610 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 69% at 800 °C, and the high char yields can be ascribed to the high aromatic content of the polymer. The $T_{\rm g}$ values of the polymers (Table 3) measured from DSC thermograms were in the range of 371-434 °C, or measured from DMA curves (Fig. 5) were ranged 382-443 °C. The different values of T_g measured by DSC and DMA may be attributed to the different heating stories and the distinct natures of these two testing methods. The thermal stability and T_{g} of the synthesized PI are much higher than those of the reported Al-PIs (T_{d5%}: 425–457 °C, T_g: 220–322 °C),⁴⁸ because of the aromatic nature of TetraPEDA. Moreover, all the polymers showed no clear melting endothermic peaks up to the decomposition temperatures on their DSC thermograms (not shown here), and this is in agreement with the wide-angle X-ray diffraction (WAXD) results (see Supporting Information Fig. S4), demonstrating the amorphous

Polyimide	In solutions (nm) ^a			Films (nm)				
	λ_{\max}^{abs}	λ ^{abs}	λ_{\max}^{PL} b	λ_0^c	λ_{\max}^{abs}	λ ^{abs}	λ_{\max}^{PL} b	E_{g}^{d}
PI-6FDA	321	383	425	418	412	456	471, 483, 493	3.24
PI-BPDA	309	391	426	427	424	472	470, 483, 493	3.17
PI-BTDA	342	393	505	432	425	504	473, 484, 494	3.15
PI-PMDA	362	403	494	430	424	520	471, 483, 493	3.08

TABLE 4 Optical Properties of the Polyimides

^a Polymer concentration is 1×10^{-2} mg/mL in NMP.

^b Excited at absmax in both solid and solution states.

^c The cutoff wavelengths (λ_0) from the transmission UV-vis absorption spectra of polymer films (thickness about 10 μ m).

 d Calculated from polymer solution (1 \times 10 $^{-2}$ mg/mL in NMP) using the equation: $E_g=$ 1,240/ $\lambda_{onset}.$



FIGURE 6 UV-vis transmission spectra of the PI films in thickness of ${\sim}10~\mu\text{m}.$

nature of these PI based on the rigid nonplanar conjugated TetraPE moieties.

Mechanical properties of functional PI are rare reported in the literatures, maybe due to the brittle characteristic. However, the PI in this work could afford flexible and tough films via solution casting and these films were subjected to tensile testing, yielding the tensile strength and tensile modulus in the range of 85.6-108.5 MPa and 1.9-2.9 GPa, respectively (Supporting Information Table S1). The excellent mechanical properties are of vital importance to the practical application of these functional PI. Additionally, in comparison with the commercial Kapton films (dielectric constant of 3.49), the PI showed low electrical properties with the dielectric constant in the range of 2.58-3.11 (Supporting Information Fig. S5). The high T_{o} s, excellent thermal stability, favorable mechanical properties, and electrical properties of the soluble PIs are probably due to the aromatic rigid nonplanar TetraPE structure in the PI main chains, and are expected to meet the requirements of heat resistance, high processing, and application temperatures in the microelectronics industry.

Optical Properties of the Polyimides

The optical and electrochemical properties of the PI (Table 4) were investigated by UV-vis and PL spectroscopy, in both the solution and solid state (film). The transmission UV-vis spectra of the polyimide films observed in the visible region showed the cut off wavelengths (λ_0) were in the range of 418-432 nm (Fig. 6). These polyimide films were in lightcolor with good transparency (more than 85% transmittance in the visible region), compared with conventional PI such as Kapton, which is deep brown (Supporting Information Fig. S6) and shows very low transparency in the visible region with λ_0 of 513 nm.⁴⁹ Other reported functional PI containing triphenylamine (TPA) moieties also appeared as dark red brown to deep brown, with λ_0 higher than 500 $\text{nm.}^{50,51}$ The improvement in color and transparency of the TetraPEDAbased PI may be due to the large aromatic rigid nonplanar conjugated structure directly connected with the imide unit, which may induce a high steric hindrance and low inductive



FIGURE 7 Absorptivity of the PIs in NMP solution (1 \times 10 $^{-2}$ mg/mL).

effect and thus effectively suppress the formation of intermolecular CTC of polymer chains.

The absorptivity spectra of PI measured in NMP solution (1 \times 10⁻² mg/mL) exhibited the maximum absorption wavelength (λ_{max}^{abs}) at around 309–362 nm (Fig. 7), which can be attributed to the π - π ^{*} transition of the π electronic system delocalized along the hexaphenylethylene conjugated moieties. The absorption edge of the PI extended to about 383-403 nm, from which the band gaps ($E_{\rm g}$, the difference between HOMO and LUMO) of the four PI were estimated at 3.24, 3.17, 3.15, and 3.08 eV, respectively (Table 4). Compared to the diamine TetraPEDA (λ^{abs}_{max} 393 nm), the four PI showed λ_{\max}^{abs} with a blue-shift of 72 nm, 84 nm, 51 nm, and 31 nm for PI-6FDA, PI-BPDA, PI-BTDA, and PI-PMDA, respectively. This observation indicated that the chemical structure of the dianhydride affected the electron-withdrawing (acceptor) property of the imide group in the TetraPEDAbased PIs. On the other side, the maximum absorption peaks of PI-6FDA, PI-BPDA, PI-BTDA, and PI-PMDA films were 412, 424, 425, and 424 nm, respectively, with the absorption



FIGURE 8 Absorptivity of the polyimide films.



FIGURE 9 PL of the polyimide films in thickness of \sim 10 μ m.

edges extending to 456–520 nm (Fig. 8). The different absorption behaviors of the PI in solid states versus in solution indicated that the chemical and steric structure of the dianhydrides and the aggregation structure of the polymers may affect the optical properties of the PI.

Aromatic PI with fluorescent characteristic are rarely reported in the literature. It has been reported that the PI containing fluorescent chromophore, such as oxadiazole⁵² and TPA⁵³ derivatives, usually show quenching of PL, which is due to the re-absorption by the CT complexing between the donor structure and the acceptor imide units. In this work, as aforementioned, the hexaphenylethylene moiety was an efficient fluorescence chromophore, and the synthesized TetraPEDA exhibited an intense emission peak at 485 nm in THF and 463 nm in solid state. After introducing of TetraPEDA into the polyimide main chain, the obtained aromatic PI also showed obvious fluorescent characteristics, exhibiting the maximum fluorescence emission (λ_{max}^{PL}) at around 425-505 nm in NMP solution and around 470-494 nm in film state (Fig. 9 and Table 4), respectively. The retaining of fluorescent characteristic in the PI system can be mainly attributed to the rigid nonplanar and large conjugated structure in the main chain, which can lower the intermolecular CT effect between the electron-donating diamine moiety and the electron-accepting dianhydride moiety and consequently, can effectively avoid the quenching of PL caused by reabsorption through the CTC. These highperformance fluorescent aromatic PI may have great potential application in the field of optics and microelectronics.

Electrochemical Properties of the Polyimides

The CV of the synthesized PI in NMP was measured at a scan rate of 100 mV/s using tetrabutylammonium perchlorate (*n*-Bu₄NClO₄, 0.1 M) as the supporting electrolyte and ferrocene as standard (Supporting Information Fig. S7). The onset oxidation ($E_{\text{onset}}^{\text{OX}}$) of the four PI exhibited at 0.75, 0.81, 0.69, and 0.77 eV, respectively. The external ferrocene and ferrocenium (Foc/Foc⁺) redox standard $E_{1/2}$ was measured to be 0.56 V vs. Ag/AgCl in NMP. By assuming that the HOMO level for the Foc/Foc⁺ standard was -4.8 eV with respect to the zero vacuum level, the HOMO energy levels for the four PI were determined to be -4.98, -5.04, -4.92, and -5.00 eV, respectively. Furthermore, the LUMO energy levels of the PI were estimated to be -1.86, -2.03, -2.04, and -2.24 eV (Supporting Information Table S2). The HOMO and LUMO energy levels of the synthesized PI were comparable to those of reported functional PI,^{10,52,54} so the synthesized PI can be expected to exhibit the similar electrical switching behavior and to be used in polymer memory devices.

Electrical Switching Effects and Memory Performances of the ITO/Polyimide/Al Device

The electrical switching behavior of the PI can be demonstrated by the current-voltage (*I-V*) characteristics of ITO/ PI/Al sandwich device, as shown in Figure 10. Figure 11 exhibits the typical *I-V* curves of the electrical switching and memory devices fabricated with PI-6FDA, PI-BPDA, PI-BTDA, and PI-PMDA. During the first positive sweep from 0 to 6–10 V (with Al as the anode and ITO as the cathode), the four devices were initially in the low-conductivity (OFF) state and then switched to the high-conductivity (ON) state at 2.7, 4.2, 4.7, and 6.5 V with an ON/OFF current ratio on the order of 1×10^4 to 1×10^5 . The polymeric memory devices can store data based on the high-conductivity (ON) and low-conductivity (OFF) responses to the external applied voltages. And the driving voltages of the memory devices are related with the chemical structure of the dianhydride monomers.

For the case of PI-BPDA [Fig. 11(b)], the device was initially in the OFF state ("0" signal in data storage) with a current range of 1×10^{-10} to 1×10^{-12} A as the voltage swept from 0 to 4.2 V (first sweep). When the voltage increased further, an abrupt increase in the current was induced at a threshold voltage of about 4.2 V, being indicated by a transition from the OFF state to ON state ("1" signal in data storage). This electronic transition from OFF state to ON state in the first sweep can serve as the "writing" process, with the ON/OFF current ratio of the studied memory device as high as 1×10^5 , suggesting a low misreading rate for memory applications. In addition, the device could be kept in the ON



FIGURE 10 Schematic diagram of the memory device.



FIGURE 11 Current density-voltage (I-V) characteristics of ITO/PI/AI devices.

state during the subsequent second sweep from 7 to 0 V, and the third sweep (from 0 to -7 V) was conducted after turning off the power for about 2 min. Moreover, the device could be reprogrammed, starting from the OFF state, to the ON state again with an accurate threshold voltage of -4.0 V and being kept in the ON state (the third and fourth sweeps). It suggests that the ON state could be retained for a short period of time after the removal of power and would relax to the original OFF state eventually. And the positive switching phenomena in the negative sweep were also observed.

Figure 12 shows the retention times and stress tests of both the ON and OFF states of the PIs. Initially, the memory devices started to turn ON or OFF to a high or low conductivity state. Under a constant stress of -1 V, no obvious degradation in current was observed for both ON and OFF states for at least 2 h during the test and the PI memory devices were stable for at least 10^8 continuous read pulses of -1 V. The "remanent," yet volatile nature of the ON state, as well as the randomly accessible ON and OFF states in each ITO/PI/ Al device, are similar to the data remanence behavior of a static random access memory (SRAM).⁵² In a SRAM, the memory can be written into or read out in any order, regardless of the memory location last accessed, and the stored data can be retained temporarily after the power has been turned off. However, the memory is volatile and the data will eventually disappear if the memory remains in the power-off state.

Proposed Switching Mechanism by the Theoretical Analysis

To better understand the possibility of CT processes and the switching behavior of the synthesized PI and their memory devices, the electronic properties of the PIs at the ground state were studied by DFT. The molecular orbital and dipole moment of the basic repetitive units (BRU) of the PI were calculated by DFT/B3LYP/6-31G(d) level with the Gaussian 03 program package. Figure 13 shows the charge density isosurfaces of the basic unit of the PI with the most energetically favorable geometry. The HOMO isosurfaces were mainly located on the diamine moiety, while the LUMO, LUMO1, and LUMO2 were mainly located on the dianhydride moieties. For the higher LUMO orbital, such as LUMO3, LUMO4, and LUM05, the four PI showed different distribution of the electron cloud at the molecular orbital, indicating that the chemical and steric structure of the four dianhydrides and their electronic effects obviously affected the electronic transition behavior of the polymers.

In this work, PI-BPDA was chosen as an example to illustrate the mechanism of field-induced conductivity of the PI, as





FIGURE 12 Retention time on the ON and OFF states of the ITO/PI/AI devices under a constant readout voltage (-1 V).



FIGURE 13 Electronic density contours of molecular orbital of the basic repetitive units of the four PI.



FIGURE 14 Molecular orbital (left) of the basic repetitive units PI-BPDA and the transitions (right) from ground state to the CT state induced by the electric field.

shown in Figure 14. The calculated energy levels are comparable to the HOMO (-5.04 eV) and LUMO2 (-2.03 eV)energy levels of PI-BPDA, measured by CV (Supporting Information Table S2). The HOMO locating on the hexaphenylethylene moiety may act as a donor (D), while the first three LUMOs locating on the phthalimide moiety may act as an acceptor (A). At the threshold voltage, electrons at the HOMO with sufficient energy transit to LUMO4 within the hexaphenylethylene moiety (Donor) to give rise to excited state. Excitation of the donor could lead to a decrease in ionization potential and consequently promote intra- or intermolecular CT at the excited state. CT can occur indirectly from the LUMO4 to the LUMO2 or LUMO1, then to LUMO of the acceptor, or directly from the HOMO to the LUMO2, LUMO1 and LUMO at the exited state, to form a conductive complex. These proposed processes have been supported by the electronic absorption spectrum of PI-BPDA (Fig. 7 and Table 4). The maximum absorption and absorption edge at about 307 nm (4.04 eV), 340 nm (3.65 eV), and 391 nm (3.17 eV) corresponded to the transitions from HOMO to LUMO4 (3.98 eV, highest probability), HOMO to LUM02 (3.48 eV), and HOM0 to LUM01 (2.74 eV), respectively. Once the conductive CT states are formed under an applied electric field, they will facilitate electrical conduction under both biases and the device cannot be switched off by applying a reverse bias of the same magnitude. Nevertheless, the polymer will relax to its original conformation sometime after removal of the applied electric field. As the potential barrier disappears, the CT state will dissociate via back electron transfer from the phthalimide

moiety to the hexaphenylethylene moiety, and consequently show SRAM characteristic.

CONCLUSIONS

In summary, a novel, simple but efficient diamine (Tetra-PEDA) with TetraPE rigid nonplanar conjugated moiety was successfully prepared via Witting-Honer and Suzuki reactions. A series of PI produced by the polymerization of Tetra-PEDA and four dianhydrides respectively exhibited special fluorescent and resistive switching (ON-OFF) characteristic, low dielectric constant, exceptional thermal stability, and excellent mechanical properties, mainly due to their rigid nonplanar conjugated structure. The PI also showed enhanced solubility in common organic solvents, light color, and high transparency. The memory devices with the configuration of ITO/PI/Al exhibited distinct volatile memory characteristics of SRAM. The theoretical analysis showed that the chemical and steric structure of the dianhydride may affect the distribution of the electron cloud at the molecular orbital, and the CT mechanism could be used to explain the memory characteristics of the PI.

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