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

Yi-Wu Liu^{a,b†}, Li-Shuang Tang^{a†}, Lun-Jun Qu^a, Si-Wei Liu^a, Zhen-Guo Chi^a, Yi Zhang^{a*}, and Jia-Rui Xu^a

^a PCFM Lab, GD HPPC Lab, Guangdong Engineering Technology Research Centre for High-performance Organic and Polymer Photoelectric Functional Films, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China

^b Key Laboratory of Advanced Packaging Materials and Technology of Hunan Province, School of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou 412007, China

Electronic Supplementary Information

Abstract A diamine (WuFDA) containing vertical rigid non-planar conjugated fluorene moiety and low polarizability group (C–F) was designed and synthesized through three steps of reactions (halogenated reaction, Suzuki coupling reaction, and reduction reaction). Four kinds of high performance functional polyimides (WuFPI-6F, WuFPI-BP, WuFPI-BT, and WuFPI-PM) were thus prepared by the condensation polymerization of WuFDA with four commercial dianhydride 6FDA, BPDA, BTDA, and PMDA, respectively. The polyimides exhibited low dielectric constant, excellent thermal stability, outstanding solubility, good film-forming property, and mechanical properties. The dielectric constants of the polyimides were in the range of 2.28–2.88 ($f = 10^4$ Hz). The 5% weight-loss temperatures ($T_{d5\%}$) in nitrogen were in the range of 555–584 °C, and the glass transition temperatures (T_g) were in the range of 408–448 °C. The weight loss of WuFPI-BP maintaining at 450 and 500 °C for half an hour was only 0.33% and 1.26%, respectively. All the WuFPIs could be dissolved in almost all organic solvents, even chloroform. The tensile strength and tensile modulus of these films were in the ranges of 78.6–85.7 MPa and 3.1–3.2 GPa, respectively. In addition, the polyimides displayed light color with special fluorescent and resistive switching (ON-OFF) characteristics; the maximum fluorescence emission was observed at 422–424 nm in NMP solution and at 470–548 nm in film state. The memory devices with the configuration of indium tin oxide/WuFPIs/aluminum (ITO/WuFPIs/Al) exhibited distinct volatile memory characteristics of static random access memory (SRAM), with an ON/OFF current ratio of 10^5 – 10^6 . These functional polyimides showed attractive potential applications in the field of high performance flexible polymer photoelectronic devices or polymer memory devices.

Keywords Functional polyimide; Fluorene derivative moieties; Fluorescence polymer; Low dielectric constant; Thermal stability

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INTRODUCTION

Polyimides have been widely used as the materials for electronic packaging and electrical insulation in microelectronics industries by virtue of their excellent thermal, mechanical, and dielectric properties.^[1,2] In recent years, functional polyimides and their applications are emerging research areas, especially in the fields of polymer electronic memories,^[3–9] flexible display,^[10] flexible photovoltaic device,^[11,12] high-performance interlayer dielectric,^[13,14] and the upcoming fifth generation mobile communication technology (5G technology).^[15,16] Compared to other polymer functional materials, polyimides exhibit not only the advantages of rich structures, flexibility, 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 insoluble and infusible nature and dark color (yellow to brown) of the polyimides, which mainly result from the rigid backbone and the 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.^[17] In this regard, many types of the structural modifications of the polymer backbone have been utilized to functionalize polyimides,^[18–22] mainly focusing on their organo-solubility,^[23–25] colorlessness, and high transparency.^[26,27] Considerable efforts have been made by introducing flexible linkages, fluorinated substituent, unsymmetrical units or bulky pendent groups into the polymer backbones.^[28–32] 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,

* Corresponding author: E-mail ceszy@mail.sysu.edu.cn

† These authors contributed equally to this work.

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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 transparency of the polymers, but usually lead to the reduction of thermal stability and mechanical properties of polyimides. Thus, the design and synthesis of multifunctional polyimides with transparency, solubility, and high thermostability are of great interests.

In this work, 9,9-diphenyl-9H-fluorene was chosen as a functional core to build a diamine (WuFDA) with special spatial stereoscopic structure, as shown in Fig. 1(a). Two phenylamine groups in WuFDA are connected with the conjugate fluorene plane through carbon atom which has a sp^3 hybridized orbital; the conjugated fluorene plane is almost vertical to the two phenylamine planes, thus forming a totally non-planar structure. The conjugated fluorene plane was further extended by the direct connection with fluorobenzene groups at 2,7-position. When such kind of structure was introduced into the polyimide main chain (Figs. 1c and 1d), WuFPIs showed multifunctional properties with exceptional overall properties. These polyimide films exhibited ultralow dielectric constant (with the lowest k value of 2.28), bistable resistive switching effects (with ON/OFF current ratio of 10^5 – 10^6), as well as light color and transparency (transmittance over 80% in the visible region). More importantly, these polyimides had excellent solubility in common solvents and exceptional thermal stability, with glass transition temperature (T_g) over 400 °C, 5 wt% loss temperature higher than 555 °C in N_2 and 548 °C in air, and a residual higher than 69% at 800 °C in N_2 . Therefore, they could well meet the requirements of high temperature process, like PVD or PECVD, and highly efficient roll-to-roll process, and thus can be used in large-area, thin-film optoelectronic devices.

EXPERIMENTAL

Materials

2,7-Dibromofluorene, 1-fluoro-4-nitrobenzene, hydrazine monohydrate ($NH_2NH_2 \cdot H_2O$), potassium *tert*-butoxide (*t*-BuOK), palladium 10% on carbon (10% Pd/C), Aliquat336

(tricaprylylmethylammonium chloride), and tetrakis(triphenyl-phosphine)palladium ($Pd[P(C_6H_5)_3]_4$) were purchased from Alfa-Aesar company and used as received. 3,3',4,4'-Biphenyltetracarboxylic acid dianhydride (BPDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), pyromellitic dianhydride (PMDA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were purchased from Alfa-Aesar company 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.

Synthesis of 2,7-Dibromo-9,9-bis(4-nitrophenyl)-9H-fluorene (WuBrDN)

2,7-Dibromofluorene (32.401 g, 0.1 mol), 1-fluoro-4-nitrobenzene (42.33 g, 0.3 mol), and potassium *tert*-butoxide (11.221 g, 0.1 mol) were mixed in a 500-mL flask and DMF (300 mL) were added. The mixture was stirred for 24 h under argon at 120 °C. After reaction, the product was concentrated and purified by silica gel column chromatography using dichloromethane/*n*-hexane (*V/V*, 1/2). Yield of the product was about 92%. IR (KBr, ν , cm^{-1}): 1518 ($-NO_2$ stretching), 1100–700 (Ar–H stretching), 701 (C–Br stretching). ^1H -NMR (500 MHz, $DMSO-d_6$, δ , ppm): 8.15 (d, $J = 9$ Hz, 4H), 8.00 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 1.6$ Hz, 2H), 7.69 (dd, $J = 8.2, 1.8$ Hz, 2H), 7.42 (d, $J = 9$ Hz, 4H); ^{13}C -NMR (125 MHz, $DMSO-d_6$, δ , ppm): 150.62, 150.35, 146.77, 137.89, 131.99, 128.97, 128.76, 123.99, 123.34, 121.85, 64.98. MS (EI, m/z): 568 (50) [M^+], 566 (100) [M^+], 564 (50) [M^+], Calcd. for $C_{25}H_{14}Br_2N_2O_4$ or $C_{25}H_{14}^{81}Br_2N_2O_4$, 563.9315; HRMS (EI, m/z): [M^+] Calcd. for $C_{25}H_{14}Br_2N_2O_4$, 563.9315; Found, 563.9317. Anal. Calcd. for $C_{25}H_{14}Br_2N_2O_4$ (wt%): C, 53.03; H, 2.49; N, 4.95; Found: C, 53.50; H, 2.88; N, 4.84.

Synthesis of 2,7-Bis(4-fluorophenyl)-9,9-bis(4-nitrophenyl)-9H-fluorene (WuFDN)

WuBrDN (11.324 g, 0.02 mol) and 4-fluorobenzeneboronic acid (6.996 g, 0.05 mol) were dissolved in THF (150 mL) and mixed in a 250-mL flask. Then 2 mol·L $^{-1}$ aqueous K_2CO_3 solution (75 mL) and 10 drops of Aliquat336 were

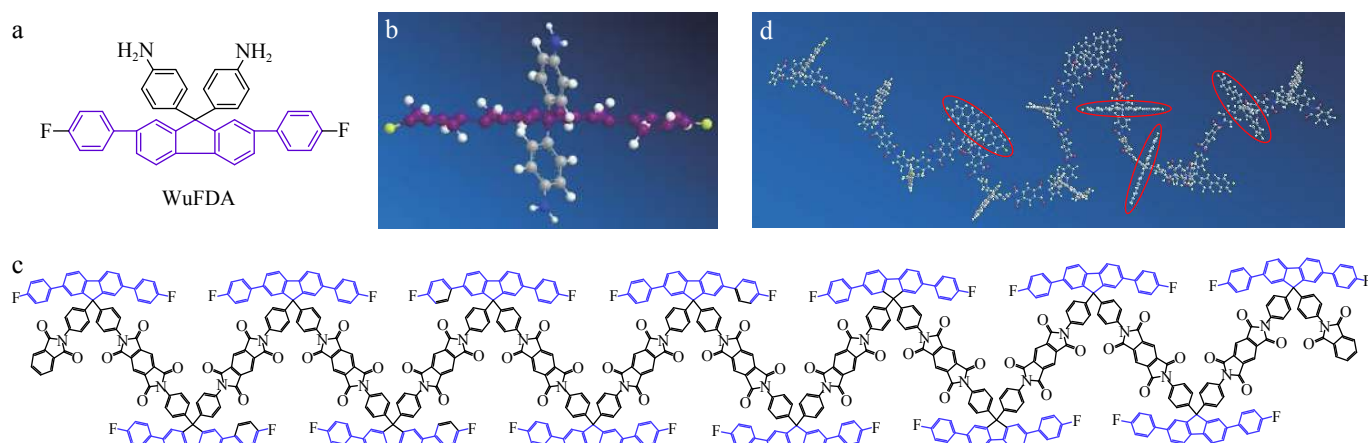


Fig. 1 (a, c) Chemical structures and (b, d) 3D structures of (a, b) diamine WuFDA and (c, d) polyimide WuFPI-PM

added. The mixture was stirred for 45 min under argon at room temperature. Then the tetrakis(triphenylphosphine) palladium ($\text{Pd}(\text{PPh}_3)_4$) catalyst (catalytic amount) was added and the reaction mixture was stirred at 75 °C for 24 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography using dichloromethane/*n*-hexane (*V/V*, 1/1). Yield of the product was about 85%. IR (KBr, ν , cm^{-1}): 1600 ($-\text{NO}_2$ stretching), 1230 (C–F stretching), 1100–700 (Ar–H stretching). ^1H -NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.15 (d, $J = 9$ Hz, 4H), 8.12 (d, $J = 8.5$ Hz, 2H), 7.80–7.77 (m, 4H), 7.73–7.69 (m, 4H), 7.54 (d, $J = 9$ Hz, 4H), 7.28–7.23 (t, 4H). ^{13}C -NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 161.88 (d, $^1J = 243.9$ Hz), 151.84, 149.48, 146.48, 139.40, 138.42, 135.94, 129.23, 128.99 (d, $^3J = 6.9$ Hz), 127.53, 124.02, 123.42, 121.90, 115.76 (d, $^2J = 21.4$ Hz), 65.06. MS (EI, m/z): 597(35) [$\text{M}^+ + \text{H}$], 596(100) [M] $^+$. Calcd. for $\text{C}_{37}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_4$, 596.1541; HRMS (EI, m/z): [M] $^+$ Calcd. for $\text{C}_{37}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_4$, 596.1542; Found, 596.1541. Anal. Calcd. for $\text{C}_{37}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_4$ (wt%): C, 74.49; H, 3.72; N, 4.70; Found: C, 74.66; H, 3.96; N, 5.00.

Synthesis of 4-(9-(4-Aminophenyl)-2,7-bis(4-fluorophenyl)-9H-fluoren-9-yl)benzenamine (WuFDA)

A mixture of WuFDN (11.9316 g, 0.02 mol), 10% Pd/C catalyst (0.5 g), hydrazine monohydrate (16 mL), and ethanol (400 mL) was placed in a three-necked flask and heated at 85 °C for 24 h. The mixture was then filtered to remove the Pd/C catalyst. After cooling to room temperature, the precipitated crystals were isolated by filtration, recrystallized from ethanol twice, ground into powder, and dried under vacuum. Yield of the product was about 92%. IR (KBr, ν , cm^{-1}): 3340 (N–H stretching), 1620 (δ N–H), 1275 (C–N stretching), 1100–700 (Ar–H stretching). ^1H -NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.97 (d, $J = 7.6$ Hz, 2H), 7.67–7.64 (m, 6H), 7.60 (dd, $J = 9.3, 5.4$ Hz, 2H), 7.29–7.25 (t, 4H), 6.93 (d, $J = 8.5$ Hz, 4H), 6.49 (d, $J = 9$ Hz, 4H), 4.97 (s, 4H). ^{13}C -NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 161.78 (d, $^1J = 243.3$ Hz), 153.55, 147.13, 138.44, 138.23, 136.67, 132.60, 128.57 (d, $^3J = 8$ Hz), 128.31, 125.84, 123.79, 120.88, 115.70 (d, $^2J = 21.3$ Hz), 113.72, 63.90. MS (EI, m/z): 537(45) [$\text{M}^+ + \text{H}$], 536(100) [M] $^+$. Calcd. for $\text{C}_{37}\text{H}_{26}\text{F}_2\text{N}_2$, 536.2059; HRMS (EI, m/z): [M] $^+$ Calcd. for $\text{C}_{37}\text{H}_{26}\text{F}_2\text{N}_2$, 536.2059; Found, 536.2058. Anal. Calcd. for $\text{C}_{37}\text{H}_{26}\text{F}_2\text{N}_2$ (wt%): C, 82.82; H, 4.88; N, 5.22; Found: C, 82.86; H, 4.96; N, 5.30.

Synthesis of Polyimides

The synthesis of WuFPI-BT was used as an example to illustrate the general synthetic route. To a solution of WuFDA (1.0732 g, 2 mmol) in 13.9 mL of purified DMF in a 50-mL flask, BTDA (0.6445 g, 2 mmol) was added in one portion. Thus, the solid content of the solution was approximately 15 wt%. The mixture was stirred at room temperature under argon for about 6 h to afford a viscous poly(amic acid) (PAA) solution. The weight-average molecular weights (M_w) values and the polydispersities (PDI) of the resultant PAA (WuFPAA-BT) estimated from GPC were 27.5×10^4 and 1.79, respectively, measured in DMF at a concentration of 4 $\text{mg} \cdot \text{mL}^{-1}$ at 50 °C. The PAA solution was then uniformly coated on a clean and dry glass (film

thickness can be controlled), and subjected to thermal imidization in vacuum drying oven to give the WuFPI-BT. The temperature program was as following: 100 °C (1 h), 200 °C (1 h), 300 °C (1 h), 400–450 °C (1 h). Then the polyimide film was removed from the glass substrate after the oven was cooled to room temperature. IR (KBr, ν , cm^{-1}): 1785 and 1725 (C=O stretching), 1100–700 (Ar–H stretching). ^1H -NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.19 (s, 2H), 8.01–8.13 (d, 6H), 7.798 (s, 2H), 7.66–7.75 (m, 6H), 7.35–7.54 (m, 8H), 7.216 (s, 4H). Anal. Calcd. for $\text{C}_{54}\text{H}_{28}\text{F}_2\text{N}_2\text{O}_5$ (wt%): C, 78.83; H, 3.43; N, 3.40; Found: C, 78.03; H, 3.67; N, 3.72. WuFPI-6F, WuFPI-BP, and WuFPI-PM were synthesized by using a similar procedure to WuFPI-BT.

RESULTS AND DISCUSSION

Synthesis and Characterization of WuBrDN, WuFDN, and WuFDA

The synthesis of WuFDA was described in the experimental section and also shown in Scheme S1 (in electronic supplementary information, ESI).^[33] WuBrDN was first prepared from 2,7-dibromofluorene and 1-fluoro-4-nitrobenzene by halogenated reaction. Secondly, as-obtained WuBrDN was further reacted with 4-fluorobenzenboronic acid by a Suzuki reaction to give WuFDN. Then WuFDN was reduced to afford diamine WuFDA containing vertical rigid non-planar conjugated fluorene moieties and low polarizability group (C–F). NMR, mass spectroscopy, FTIR spectroscopy, and elemental analysis were used to identify the structures of the synthesized intermediate products and diamine monomers. The ^1H -NMR, ^{13}C -NMR, H–H COSY, C–H QC, and C–H BC spectra of WuBrDN and WuFDN are shown in Figs. S1 and S2 (in ESI). Figs. 2(A) and 2(B) illustrate the ^1H - and ^{13}C -NMR spectra of WuFDA. 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 Figs. 2(C), 2(D), and 2(E), and these spectra agreed well with the proposed molecular structure of WuFDA. The ^1H -NMR spectra confirm that the diamine was successfully synthesized by the mentioned three-step reactions as suggested by the resonance signals at around 5 ppm corresponding to the amino protons. Mass spectra of monomers are shown in Table S1 and Figs. S3–S8 (in ESI).

Synthesis and Characterization of the Polyimides

The polyimides were prepared in a conventional two-steps procedure by the reaction of equal molar amounts of diamine WuFDA with commercially available aromatic tetracarboxylic dianhydrides (6FDA, BPDA, BTDA, and PMDA) in dimethyl formamide (DMF) to form precursor poly(amic acid)s, followed by thermal cyclodehydration, as shown in Scheme 1. The chemical structures of WuBrDN, WuFDN, WuFDA, and the polyimides were confirmed by FTIR spectra, as shown in Fig. 3. Compared to WuFDA, the characteristic absorption bands at 3340 and 1624 cm^{-1} (N–H stretching) disappeared. Meanwhile, the characteristic absorption peaks of the imide group at 1785 (asymmetrical stretching of carbonyl) and 1725 cm^{-1} (symmetrical

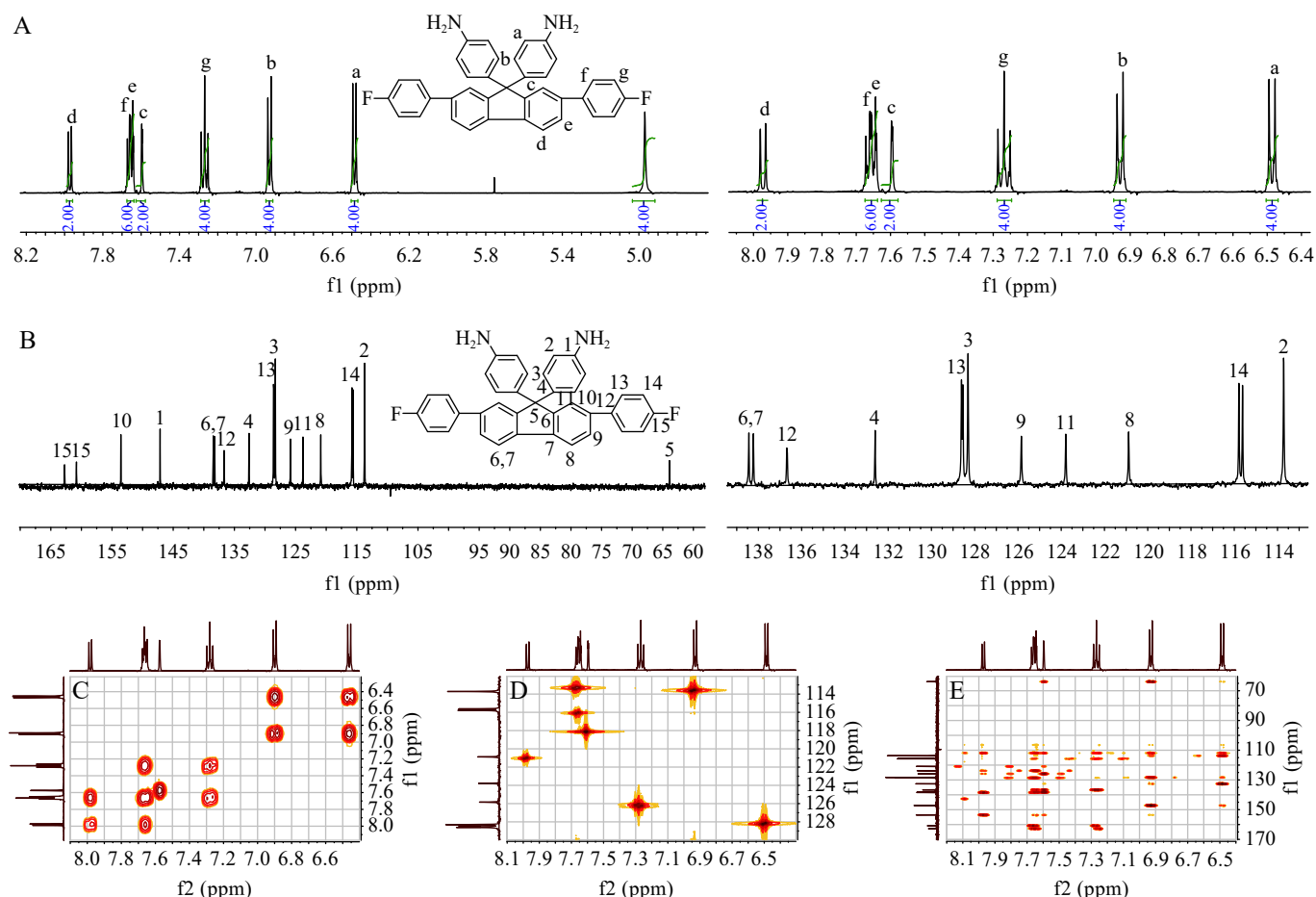
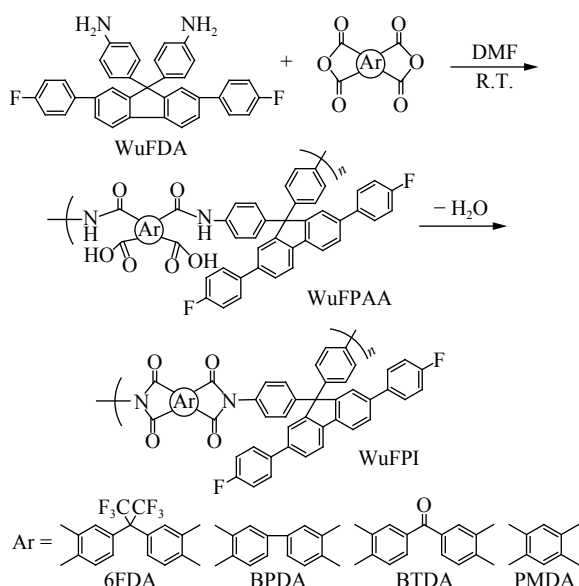


Fig. 2 (A) ^1H -NMR, (B) ^{13}C -NMR, (C) H-H COSY, (D) C-H QC, and (E) C-H BC spectra of WuFDA in DMSO-d_6



Scheme 1 Synthesis of the WuFPIs

stretching of carbonyl), and the C—N bond at around 1277 cm^{-1} are clearly shown in the FTIR spectra of the polyimides, indicating the successful reaction between WuFDA and four dianhydrides, and the complete imidization of PAA. The desired formations of the WuFPIs were also confirmed

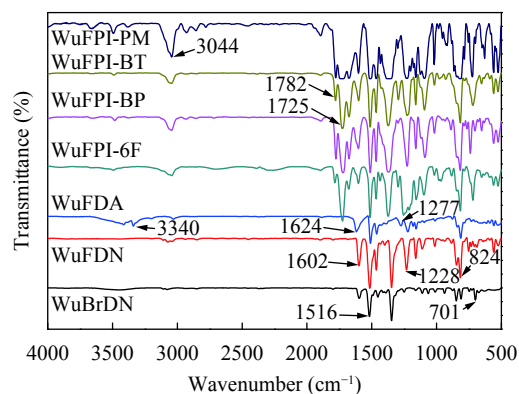


Fig. 3 FTIR spectra of WuBrDN, WuFDN, WuFDA, and the WuFPIs

by ^1H -NMR and H-H COSY, as shown in Figs. S9–S11 (in ESI).

The molecular weights of four PAAs were determined by GPC. The solubility behavior of the polyimides was tested qualitatively. Both results are shown in Table 1. M_w s of the four PAAs were in the range of 23.0×10^4 – 29.8×10^4 , with a polydispersity index of 1.76–2.34, respectively, which mean that the synthesized polyimides had a very high molecular weight and a narrow molecular weight distribution. The WuFPIs were soluble in polar solvents such as *N*-

Table 1 GPC results of the PAAs and solubility of the WuFPIs

Sample	GPC ^a		Solubility ^b						
	$M_w \times 10^{-4}$	PDI	NMP	DMSO	DMAc	DMF	<i>m</i> -cresol	THF	CHCl ₃
WuFPI-6F	26.9	1.97	++	++	++	++	++	++	++
WuFPI-BP	23.0	2.34	++	+	++	++	+	+	+
WuFPI-BT	27.5	1.79	++	+	+	+	+	+-	+-
WuFPI-PM	29.8	1.76	+	++	++	++	+	++	++

^a With respect to polystyrene standards, with DMF as the eluent; flow rate: 1 mL·min⁻¹, test temperature: 50 °C; ^b Solubility: ++: soluble at room temperature; +: partially soluble at room temperature, soluble on heating (90 °C). The solubility was determined by testing 10 mg of PI in 1 mL of solvent.

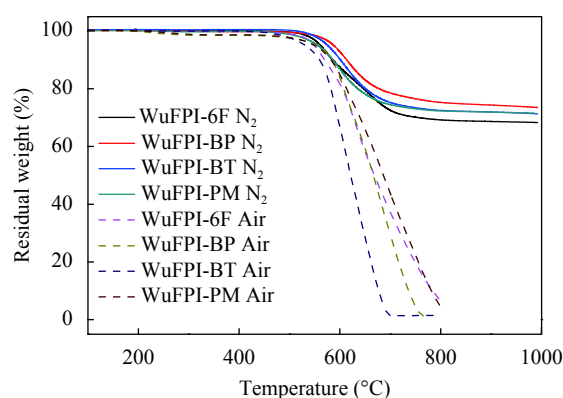
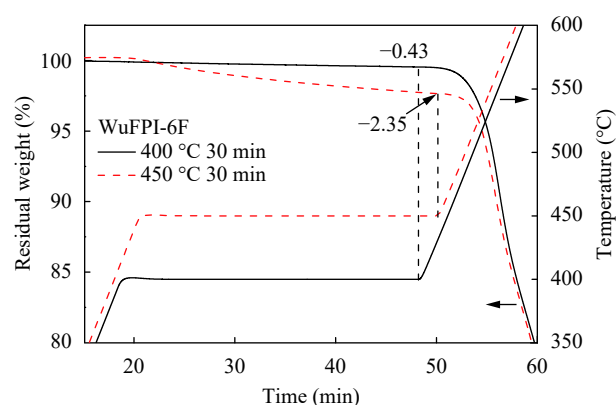
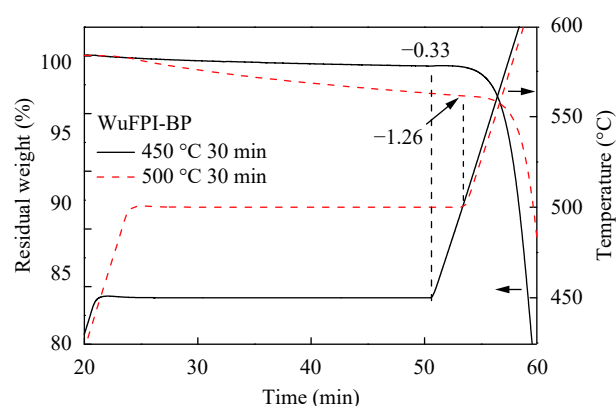
methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), DMF, *m*-cresol, and THF; they could even be completely dissolved in chloroform at room temperature. The enhanced solubility can be attributed to the introduction of twisted non-planar conjugated fluorene and fluorin group into the side chain of polyimide macromolecule. Such vertical structure would increase the steric hindrance moieties, thus weakening the interaction between molecular chains. The excellent solubility of these polymers made them potential candidates for practical application in microelectronics by spin- or dip-coating processes.

Thermal and Mechanical Properties of the Polyimides

TGA and DSC were employed to investigate the thermal properties of the PIs. The results are summarized in Table 2. TGA results revealed that all the polymers exhibited good thermal stability with insignificant weight loss up to 550 °C in nitrogen (Fig. 4). The 5% and 10% weight-loss temperatures ($T_{d5\%}$ and $T_{d10\%}$) of the polymers in nitrogen were recorded in the range of 555–584 and 579–610 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 69% at 800 °C. The high char yields can be ascribed to their high aromatic content. More importantly, these polymers show excellent thermal stability at high temperature. For example, the weight losses of WuFPI-6F films at 400 and 450 °C for half an hour were only 0.43% and 2.35%, respectively (Fig. 5), and those of the WuFPI-BP films at 450 and 500 °C for half an hour were only 0.33% and 1.26%, respectively (Fig. 6). Soluble polyimides with excellent thermal stability were rarely reported in the literature. T_g s of all the polymers could be easily measured by DSC thermograms and were observed in the range of 408–433 °C (Fig. S12 in ESI). All the polymers showed no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. These results also complied with the amorphous nature of these polyimides due to the rigid non-planar conjugated fluorin and fluorene moieties (Fig. S13 in ESI).

The polyimide films also showed good mechanical properties (Table 3), with tensile strength and tensile modulus in

the range of 73.9–85.7 MPa and 2.8–3.2 GPa, respectively, and the elongation at break higher than 6.7%. The high T_g s, excellent thermal stability, and good mechanical properties of the soluble PIs are probably due to the aromatic rigid non-

**Fig. 4** TGA curves of the WuFPI films**Fig. 5** TGA curves of the WuFPI-6F films**Fig. 6** TGA curves of the WuFPI-BP films**Table 2** Thermal properties of the PI films

Sample	T_g ^a (°C)	$T_{d5\%}$ (°C)		$T_{d10\%}$ (°C)		Char yield ^b (wt%)
		N ₂	Air	N ₂	Air	
WuFPI-6F	408	555	548	579	568	69
WuFPI-BP	433	584	563	610	591	75
WuFPI-BT	414	583	555	610	586	71
WuFPI-PM	448	581	550	614	580	73

^a Measured by DSC at a heating rate of 25 °C·min⁻¹; ^b Residual weight percentage at 800 °C in nitrogen

planar fluorene structure in the PI main chains, and are expected to meet the requirements of heat resistance and high processing and application temperatures in the micro-electronics industry.

Table 3 Mechanical properties of the PI films

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
WuFPI-6F	85.7	3.1	9.3
WuFPI-BP	78.6	3.2	8.7
WuFPI-BT	77.5	3.0	8.4
WuFPI-PM	73.9	2.8	6.7

Optical Properties of the Polyimides

The optical and electrochemical properties of the polyimides were investigated by UV-Vis and PL spectroscopy, both in the solution and solid state (films). The results are summarized in Table 4. Fig. 7 shows the transmission UV-Vis spectra and photos of WuFPI-6F and WuFPI-BP films in the visible region. The cut-off wavelengths (λ_0) of the synthesized polyimides were in the range of 368–454 nm. These polyimide films were light-color with good transparency (more than 80% transmittance in the visible region) compared with the conventional polyimides such as Kapton, which is deep brown and shows very low transparency in the visible region ($\lambda_0 = 513$ nm).^[8] The functional polyimides containing triphenylamine (TPA) moieties reported before had dark red brown to deep brown color, with a λ_0 higher than 500 nm.^[34,35] The improvement in color and transparency of the WuFPIs may be due to the large aromatic rigid non-planar conjugated structure directly connected with the imide unit, which can inhibit the formation of charge transfer complex (CTC) of polymer chains effectively through higher steric hindrance and lower inductive effect.

Fig. S14 (in ESI) shows the absorption spectra of polyimides measured in NMP solution (0.2 mg·mL⁻¹). The polyimides exhibited a maximum absorption peak at around 315–346 nm, which can be attributed to the π - π^* transition of the π electronic system delocalized along the fluorene conjugated moieties. The absorption edge of the polyimides extends to about 363–367 nm, from which the band gap (E_g , the difference between the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level) of four polyimides are estimated to be 3.38–3.42 eV, as shown in Table 4. Compared to that of the diamine WuFDA (285 nm), WuFPIs showed red-shift, indicating that the chemical structure of dianhydrides did influence the electron-withdrawing (acceptor) property of the im-

ide group in these WuFDA-based PIs. In film state, as shown in Fig. S15 (in ESI), the maximum absorption peaks of the PI films were in the range of 371–431 nm and the absorption edges were extended to 425–525 nm. Different absorption behavior of the polyimides in solid states confirmed that chemical and steric structure of the dianhydrides and the aggregation structure did affect the optical properties of the polyimides.

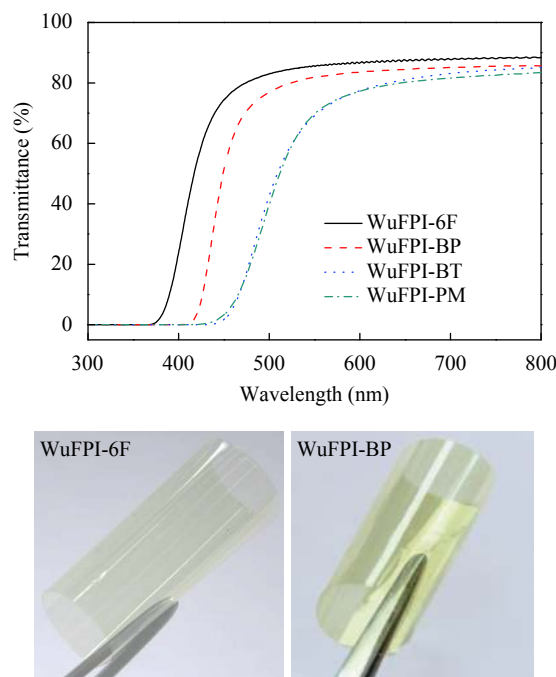


Fig. 7 UV-Vis transmission spectra of PI films (~10 μ m) and photographs of WuFPI-6F and WuF-BP films (~60 μ m)

It has been reported that polyimides containing fluorescent chromophores, such as oxadiazole^[36] and TPA^[37] derivatives, usually show PL quenching, which is due to the re-absorption by the charge transfer complexing between donor and the imide acceptor. In this study, as mentioned above, the fluorene moiety was efficient fluorescence chromophores that let WuFDA exhibit an intense emission peak at 467 nm in THF and 392 nm in solid state.^[33] When introduced into the polyimide main chain, the formed aromatic polyimides also showed obviously fluorescent characteristic, and the fluorescence emission maxima appeared at around 422–424 nm in NMP solution (Table 4) and around 470–548 nm in film state (Fig. S16 in ESI). The fluorescent characteristic in the WuFPIs system mainly derived from the ri-

Table 4 Optical properties of the PI films

Sample	In solutions (nm)			λ_0^c	Films (nm)			E_g^d
	$\lambda_{\max}^{abs}$	$\lambda_{\text{onset}}^{abs}$ ^a	$\lambda_{\max}^{PL}$ ^b		$\lambda_{\max}^{abs}$	$\lambda_{\text{onset}}^{abs}$	$\lambda_{\max}^{PL}$ ^b	
WuFPI-6F	315	363	422	368	371	425	470	3.42
WuFPI-BP	346	367	424	406	420	467	472	3.38
WuFPI-BT	346	364	422	454	421	516	548	3.41
WuFPI-PM	345	363	423	453	431	525	537	3.42

^a Polymer concentration was 0.2 mg·mL⁻¹ in NMP; ^b Excited at absorption maxima for both solid and solution states; ^c The cut-off wavelengths (λ_0) from the transmission UV-Vis absorption spectra of polymer films (thickness about 10 μ m); ^d Calculated from polymer solution (0.2 mg·mL⁻¹ in NMP) by the equation, $E_g = 1240/\lambda_{\text{onset}}$

gid non-planar and large conjugated structure in the side chain, which can increase the steric hindrance of polyimide macromolecules, lower the CTC effect between the electron-donating diamine moiety and the electron-accepting dianhydride moiety, and thus decrease the optical loss and improve the optical properties (light colour, high transparency, etc.). The four polyimides showed similar λ_{max} s in solution but quite different values in film state. This is because in polymer system, the aggregation of polymer chains will greatly affect their emission properties, and the strong intermolecular charge transfer effect due to the strong intermolecular interactions will greatly quench the fluorescence of polyimides.^[38,39] Compared with WuFPI-BT and WuFPI-PM, due to the existence of the trifluoromethyl group in WuFPI-6F and the biphenyl group in WuFPI-BP, the intermolecular interactions between the polyimide macromolecules were greatly weakened, thus the polyimide films of WuFPI-6F and WuFPI-BP exhibited stronger fluorescence than that of the WuFPI-BT and WuFPI-PM films (Fig. 8). The fluorescence quantum yields of WuFPI-BP and WuFPI-6F in NMP solution were 10.3% and 12.1%, respectively, and those in film state were 1.47% and 1.59%, respectively. The novel high performance, organo-soluble, photoluminescent polyimide films show great potential application in the field of optics and microelectronics.

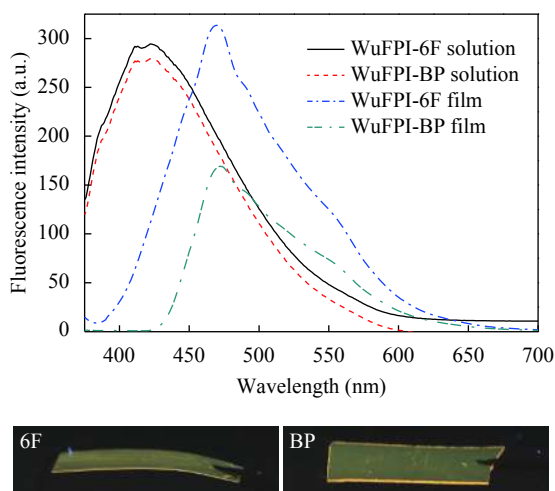


Fig. 8 PL of the PIs in NMP solution ($0.2 \text{ mg} \cdot \text{mL}^{-1}$) and film state (photographs: WuFPI-6F and WuFPI-BP under 365 nm UV light)

Dielectric Properties and Morphology of the Polyimides

Dielectric properties of the WuFPI films were measured at the frequencies between 100 Hz and 1 MHz at 20 °C and 50% relative humidity using a Solartron SI 1260 impedance/gain phase analyzer (Solartron Group Ltd, UK). A commercialized DuPont™ Kapton® polyimide film was examined as well. In comparison with the commercial Kapton films ($k = 3.49$, $f = 10^4 \text{ Hz}$), the polyimides showed much lower dielectric constants in the range of 2.28–2.88 ($f = 10^4 \text{ Hz}$) (Fig. 9), which means that the introduction of non-planar, rigid fluorene moieties into the side-chain of polyimide is beneficial to lowering the dielectric constant. Among them, WuFPI-6F had the lowest dielectric constant. As can be seen in Fig. S13 (in ESI), WuFPI-6F exhibited the

smallest 2θ for the XRD profiles, and the corresponding d -spacing (calculated according to Bragg's law: $n\lambda = 2d\sin\theta$) was 0.584 nm. The largest d -spacing of WuFPI-6F in the four polyimides may be due to the spatial steric resistance effect of the trifluoromethyl groups. Compared with the reported intrinsic low- k polyimides (Fig. 10, corresponding structures are shown in Table S2 in ESI), WuFPI-6F possessed not only a higher T_g but also a lower k value than most of the literature date. WuFPI-PM showed the highest thermal stability with a k value lower than 2.6.^[14,22,40–49]

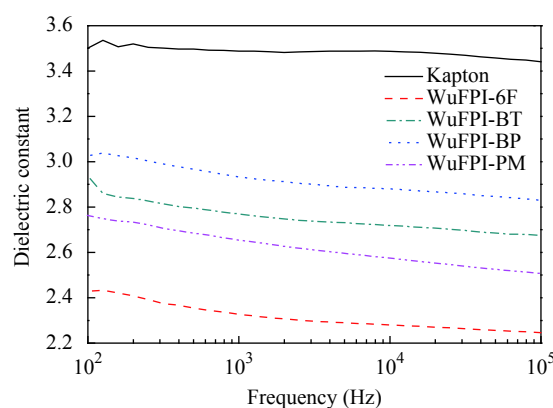


Fig. 9 Relationship between dielectric constant and frequency of the polyimides and Kapton film

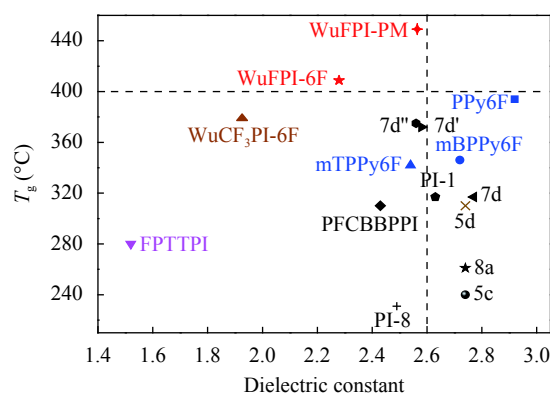


Fig. 10 The comparison of k and T_g of WuFPI-6F, WuFPI-PM, with the reported intrinsic low k polyimides (related structures and references shown in Table S2 in ESI^[14,22,40–49])

To better understand the mechanism behind low dielectric properties, positron annihilation lifetime spectroscopy (PALS) was used to study the free-volume of WuFPI-6F films, which has the lowest k value among the four PI films. The o -Ps lifetime curves of WuFPI-6F and Kapton films are shown as examples (Fig. 11). The data of o -Ps lifetime are collected in Table 5. Compared with the Kapton film, WuFPI-6F had long-life component τ_3 , which was about 2.89 ns in our experiment. The mean hole radius was calculated to be 0.355 nm, and the diameter of the free volume was about 0.71 nm.^[14] That means, the introduction of the rigid, non-planar conjugated side group that is vertical to the main chain did help to increase the free volume of polymers, thus decreasing their dielectric constants. The morphology of WuFPI-6F film was determined by SEM and AFM and

the results are shown in Fig. 12. The WuFPI-6F film had a compact structure (Fig. 12a); its surface was smooth and dense, with a surface roughness (R_q) of 0.239 nm (Figs. 12b and 12c). All these results indicated that the rigid, non-planar conjugate fluorene unit in the side-chain, which is

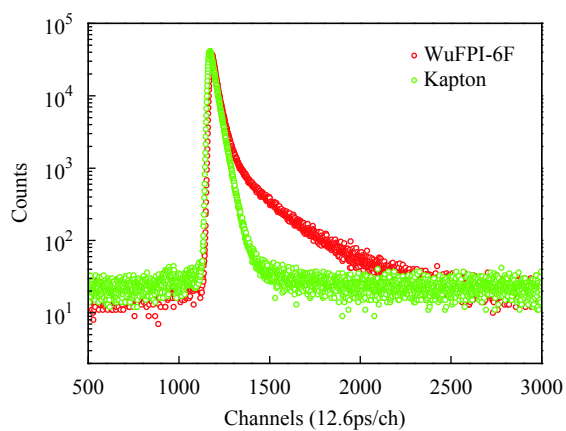


Fig. 11 Ps lifetime of polyimide films

Table 5 Analyzed data for the positron lifetime in the WuFPI-6F film and a DuPont Kapton polyimide film

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	r^a (nm)
WuFPI-6F	0.27	0.62	2.89	52.5	28.9	18.6	0.355
Kapton	0.29	0.41		34.5	65.6		

^a Calculated according to our previous work^[14]

perpendicular to the polymer main chain, could enlarge the free volume of the polyimide products. Such additional free volume served as intrinsic “holes” that existed in polymers. Hence, compared with the physical pore-forming strategy,^[50,51] it is beneficial to promoting the comprehensive properties of polymers.

Electrochemical Properties of the Polyimides

Fig. 13 shows the cyclic voltammetry (CV) results of the four synthesized polyimides in NMP at a scan rate of

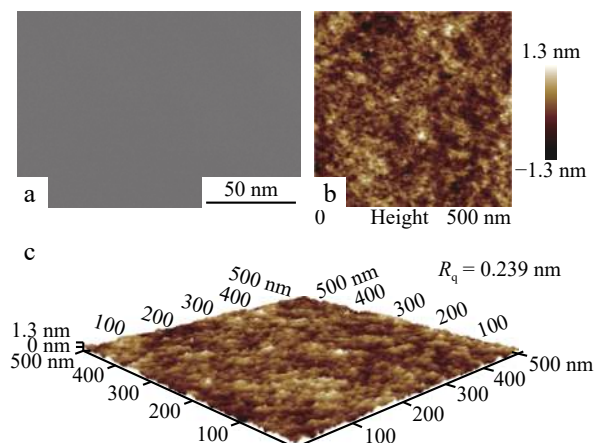


Fig. 12 (a) SEM, (b) AFM (2D), and (c) AFM (3D) images of WuFPI-6F film

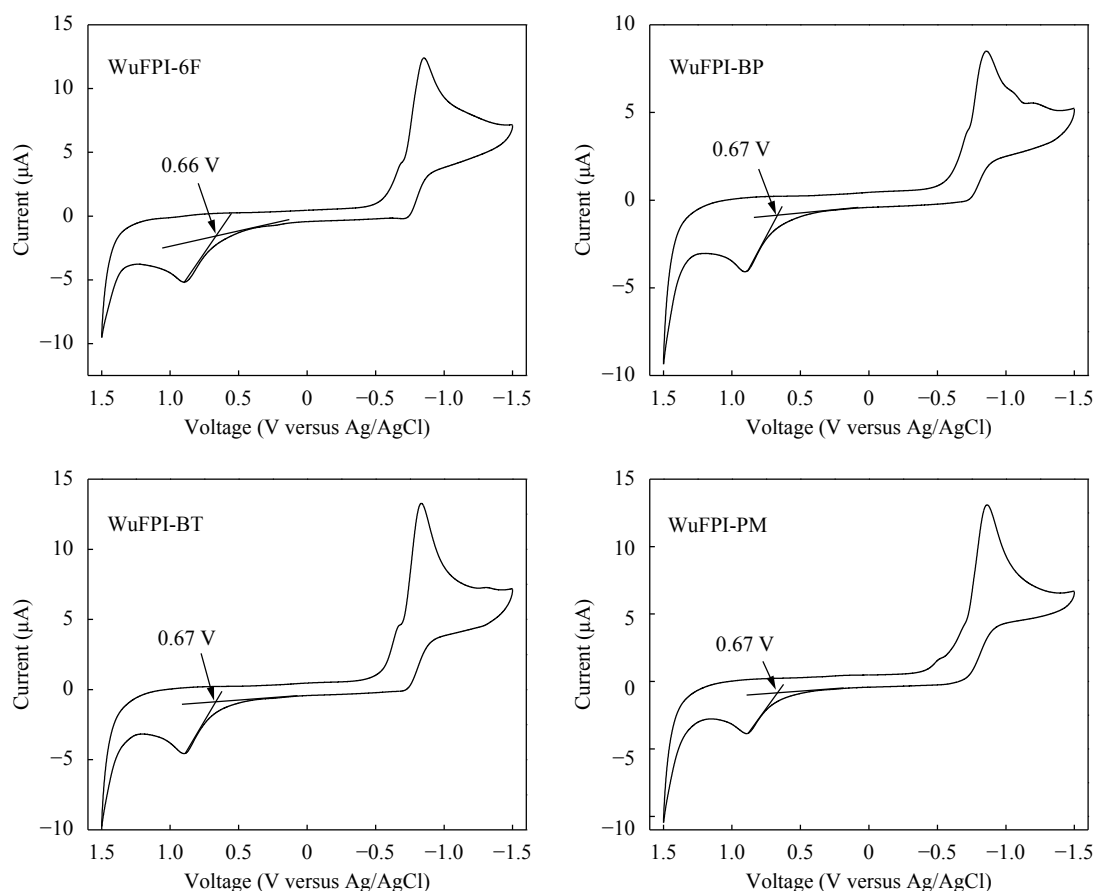


Fig. 13 Cyclic voltammograms of the WuFPIs in NMP

100 $\text{mV}\cdot\text{s}^{-1}$ using tetrabutylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$, $0.1\text{ mol}\cdot\text{L}^{-1}$) as the supporting electrolyte and ferrocene as standard. The onset oxidation ($E_{\text{onset}}^{\text{ox}}$) of the four polyimides was 0.66 or 0.67 eV, and the estimated HOMO level was -4.90 eV to -4.91 eV . The external ferrocene and ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ was measured to be 0.56 V versus Ag/AgCl in NMP. Assuming that the HOMO level for the Fc/Fc^+ standard was -4.8 eV with respect to the vacuum level, the HOMO energy level for the four polyimides was determined to be about minus $4.90\text{--}4.91\text{ eV}$. Therefore, the LUMO energy levels of the polyimides were estimated to be -1.48 eV to -1.53 eV , as shown in Table 6.

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

Fig. 14 presents the typical I–V curves of electrical switching and memory devices fabricated with the WuFPIs. During the first positive sweep from 0 V to $6\text{--}8\text{ V}$ (with Al as the anode and ITO as the cathode), the device was initially in the low-conductivity (OFF) state and switched to the high-conductivity (ON) state at $3.1, 4.3, 3.7,$ and 3.4 V with an ON/OFF current ratio about $10^5\text{--}10^6$. The polymeric memory devices store data based on the high-conductivity (ON) and low-conductivity (OFF) responses to the external applied voltages, and the driving voltage of the memory devices are related to the chemical structure of dianhydride monomers. The PIs showed the best stability at the OFF and ON status, where their conductivity was slightly changed with the applied voltage before and after the switching behavior. For the case of WuFPI-6F (Fig. 14a), the device was initially in

Table 6 Electrochemical properties of the polyimides

Polyimide	E_g (eV)	$E_{\text{onset}}^{\text{ox}}$ (V)	HOMO (eV)	LUMO (eV)
WuFPI-6F	3.42	0.66	-4.90	-1.48
WuFPI-BP	3.38	0.67	-4.91	-1.53
WuFPI-BT	3.41	0.67	-4.91	-1.50
WuFPI-PM	3.42	0.67	-4.91	-1.49

the OFF state (“0” signal in data storage) with a current on 10^{-11} A level as the voltage swept from 0 V to 3.1 V (first sweep). When the voltage increased further, it induced an abrupt increase in current at a threshold voltage of about 3.1 V , as indicated by the transition from OFF state to ON state (“1” signal in data storage). The ON/OFF current ratio of the studied memory device was as high as 10^6 , which led to a low misreading rate for memory applications. This electronic transition from OFF state to ON state in the first sweep serves as the “writing” process. In addition, the device could be kept in the ON state during the subsequent second sweep from 6 V to 0 V (second sweep). The third sweep (sweep from 0 V to -6 V) was conducted after turning off the power for about 2 min . The device could be reprogrammed, starting from the OFF state to the ON state again with an accurate threshold voltage of -3.2 V , and staying in the ON state (the third and fourth sweeps). It suggested 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. Positive switching phenomena during the negative sweep were also observed.

Fig. 15 shows the retention time and stress tests of both

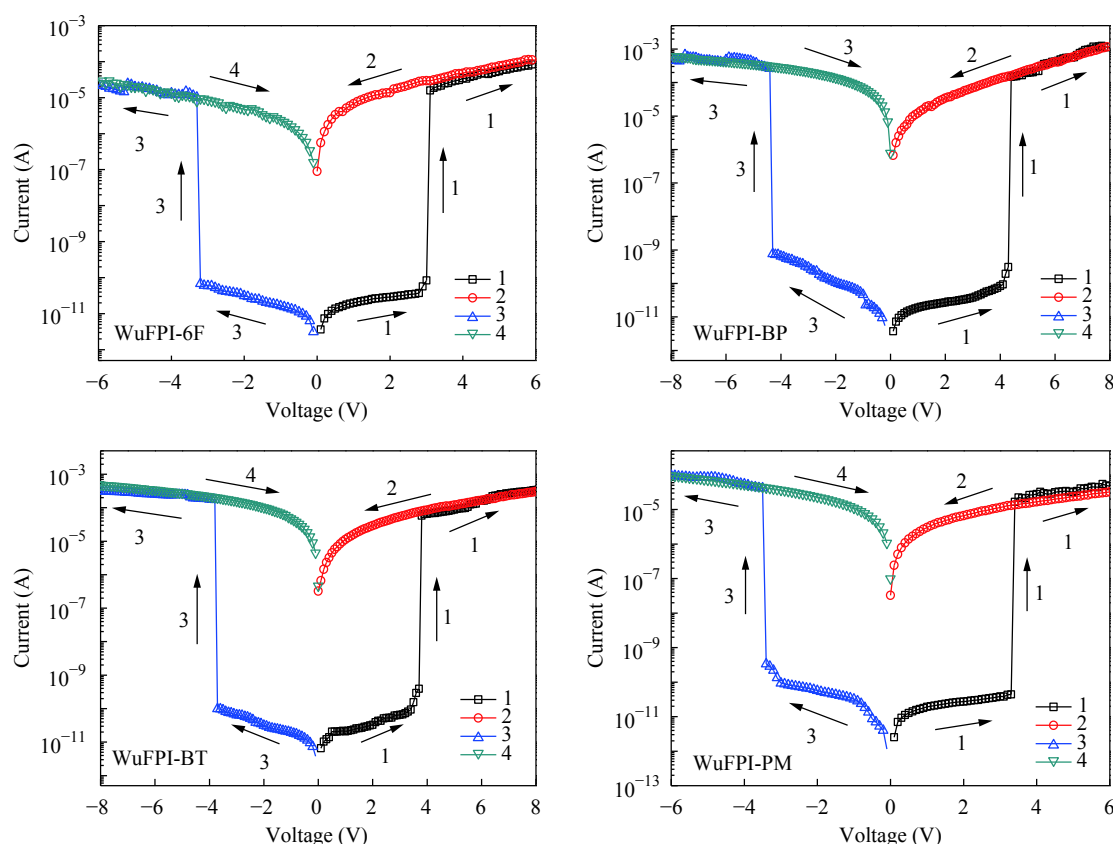


Fig. 14 Current density-voltage (I–V) characteristics of the ITO/WuFPIs/Al device

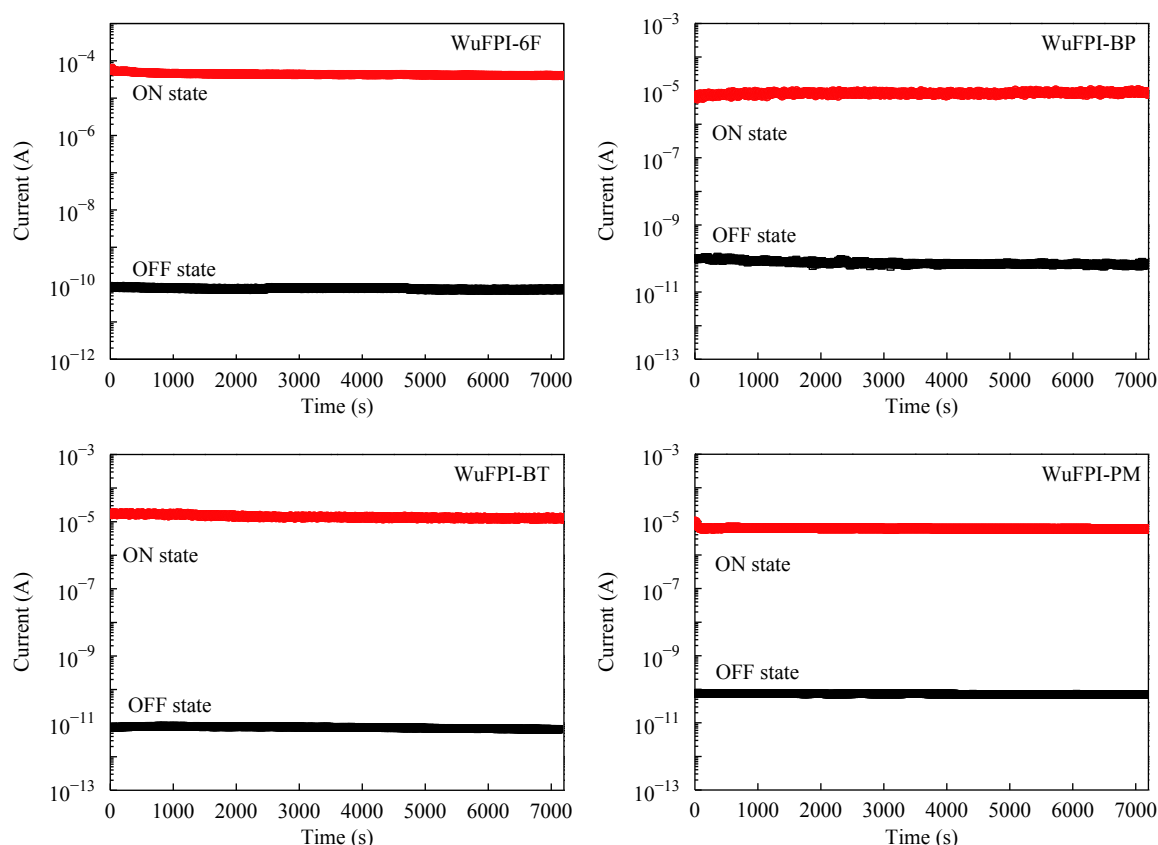


Fig. 15 Retention time on the ON and OFF states of the ITO/WuFPIs/Al devices under a constant readout voltage (-1 V)

ON and OFF states of the WuFPIs. Initially, the memory devices started to turn ON or OFF to give 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/WuFPIs/Al device, is similar to the data remanence behavior of a static random access memory (SRAM).^[36] 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.

CONCLUSIONS

A fluorene-based diamine (WuFDA) with the vertical rigid non-planar conjugated moiety was successfully prepared *via* halogenated reaction, Suzuki coupling reaction, and reduction reaction. A series of polyimides produced by the dipolymerization of WuFDA and four dianhydrides, respectively, exhibited low dielectric constant, excellent thermal stability, solubility, film-forming ability, and mechanical properties. In addition, these PIs prepared possessed many functions, such as the special fluorescent and resistive switching (ON-OFF) characteristics, mainly due to their rigid non-planar conjugated structure and C—F group. The rigid

non-planar conjugated fluorene structure and the C—F group also showed the enhanced solubility in common organic solvents, light color, and high transparency. The memory devices with the configuration of ITO/WuFPIs/Al exhibited distinct volatile memory characteristics of SRAM. Among the four WuFPIs, WuFPI-6F with a T_g of 408 °C had the lowest dielectric constant as well as the best fluorescent properties, solubility and transparency, which showed great potential applications in high performance flexible polymer photoelectronic devices.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2225-0>.

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