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Multi-functional polyimides containing tetraphenyl fluorene moieties: fluorescence and resistive switching behaviors[†]

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Two novel aromatic polyimides (PIs), **TPF27OPI** and **TPF99OPI**, with a tetraphenyl fluorene (TPF) unit as the electron donor (D) and a 4,4'-oxydiphthalic dianhydride (ODPA) unit as the electron acceptor (A) were synthesized and characterized. Both of the as-synthesized PIs showed obvious photoluminescence properties, and compared with **TPF27OPI**, where the fluorene unit is located in the polymer main chain, **TPF99OPI** with a fluorene unit in the side chain showed stronger fluorescence and a fluorescence blue shift in the film state. The memory device with a sandwich configuration of ITO/**TPF27OPI**/Al showed the nonvolatile "write once, read many" (WORM) switching behavior, while that of ITO/**TPF99OPI**/Al exhibited "static random access memory" (SRAM) switching behavior. Both of the devices exhibited a stable ON/OFF current ratio above 10⁴ and a long operation time, following 10⁴ pulse reading cycles with no obvious degradation in current. The mechanism of the resistive switching behaviors was discussed using the experimental and molecular simulation results. These multi-functional polyimides showed attractive potential applications in the field of polymer optoelectronic devices and memory devices.

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Introduction

With the increasing development of information technology in the past decade, low turn-on voltage, fast reading speed and high data storage density have been the indispensable conditions of the semiconducting memory devices.^{1,2} Compared with the inorganic materials, organic and polymeric materials with lowcost potential, easy processability and large capacity for data storage have been promising materials and will be applied in the next generation of the semiconductor industry.³ The reported organic or polymeric materials for electronic memory device applications include conjugated organic molecules,⁴ complex organic molecules,⁵ copolymers,⁶ polymer nanocomposites,⁷ and functional polyimides,⁸ *etc.*

Polyimides (PIs) with optoelectronic functions have attracted more and more attention as new functional materials compared with the traditional inorganic materials and polymeric materials

Sun Yat-sen University, Guangzhou 510275, China. E-mail: ceszy@mail.sysu.edu.cn; Fax: +86 20 84112222; Tel: +86 20 84112222 with low glass transition temperature.⁹ PIs not only exhibit outstanding thermal stability, high mechanical strength, good solubility and flexibility, but also excellent structural designability. Moreover, unlike encoding "0" (charge OFF) and "1" (charge ON) in a memory cell in silicon-based memory devices, polymeric memory devices are characterized by bistable resistive switching behaviors with a low applied voltage and a high current "ON/OFF" ratio.¹⁰ Recently, functional PI-based memory devices have been demonstrated to exhibit different kinds of resistive switching behaviors from non-volatile memory properties, such as write once-read many memory (WORM)¹¹ and FLASH memory,¹² to volatile memory properties, such as dynamic random access memory (DRAM).¹⁴

Although various PI-based memory devices with different resistive switching behaviors have been prepared, the structureproperty relationship of PI and their electronic memory mechanisms are still unclear.¹⁵ Currently, the intramolecular and intermolecular charge-transfer (CT) interactions between the electron donor (D, diamine moiety) and acceptor (A, dianhydride moiety) in polyimide moieties play an important role in the memory performances and have been considered as a main factor to influence the resistive switching behaviors under the applied voltage.¹⁶ However, most previously reported PI-based memory devices possess different molecular structures, and a fine structure-property relationship is rarely systematically established.

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[†] Electronic supplementary information (ESI) available: NMR spectra of the monomers and the polyimides; FTIR spectra, WAXD patterns, thermal properties and transmittance of polyimides; SEM and fitted curves of the memory device. See DOI: 10.1039/c7tc01807j

Herein, we report two novel diamines, 4,4'-(9,9-diphenyl-9Hfluorene-2,7-diyl)dianiline (TPF27DA) and 4,4'-(2,7-diphenyl-9H-fluorene-9,9-diyl)dianiline (TPF99DA), with the same molecular weight containing a tetraphenyl fluorene (TPF) unit core. Based on the two diamines, two aromatic polyimides, TPF27OPI and TPF99OPI, were prepared and characterized. Both of the as-prepared PIs showed obvious photoluminescence properties, and compared with TPF27OPI (maximum emission wavelength, EM_{max} = 506 nm), where the fluorene unit is located in the polymer main chain, TPF99OPI with a fluorene unit in the side chain showed stronger fluorescence with a blue shift in the film state ($EM_{max} = 492 \text{ nm}$). And the resistive switching behaviors, conducted by a simple sandwich device configuration consisting of spin-coated PI films between the ITO bottom electrode and the Al top electrode, were also characterized. The ITO/TPF27OPI/Al device showed WORM switching behavior, while the ITO/TPF99OPI/Al device exhibited SRAM switching behavior. Both of the PI-based memory devices exhibited a stable ON/OFF current ratio above 10⁴ and a long operation time, following 10⁴ pulse reading cycles with no obvious degradation in current. In order to clarify the switching mechanism of the devices, theoretical calculations performed using the density functional theory (DFT) method at the B3LYP level with the 6-31G(d) basic set were also applied to analyze the geometry effect and electronic transitions of the studied polyimides.

Results and discussion

Synthesis and characterization of the diamines

The diamine **TPF27DA** was synthesized *via* the Suzuki–Miyaura reaction, and the diamine **TPF99DA** was synthesized according to our previous work,¹⁷ as shown in Scheme 1. ¹H NMR, ¹³C NMR, mass spectra, IR spectra and elemental analysis techniques were used to confirm the chemical structure of the intermediates and the diamines, as shown in the Experimental section and Fig. S1 and S2 (ESI[†]). The proton signal of **TPF27DA** is at around 5.25 ppm, and that of **TPF99D** is at around 4.95 ppm (Fig. 1). The infrared absorptions at around 3345 cm⁻¹ and 3420 cm⁻¹, and 3370 cm⁻¹ and 3460 cm⁻¹, respectively, which are characteristic of the amino groups, indicating that the diamines were successfully synthesized, as shown in Fig. S3 (ESI[†]). The resonance of the proton signals at 5.25 ppm for **TPF27DA** is much higher than that for



Scheme 1 Synthesis routes of diamine monomers.



Fig. 1 ¹H NMR spectra of the diamines

TPF99DA (4.95 ppm), which is due to the conjugation of the amino group with the TPF unit, and will have an obvious effect on the photoluminescence of the diamines and the polyimides.

The absorption and photoluminescence spectra of the diamines were characterized both in solution and in the solid state, as shown in Fig. 2. The absorption peaks at 355 nm and 310 nm of TPF27DA and **TPF99DA**, respectively, resulted from the π - π * transition of the conjugated fluorene with a benzene ring, which had a red-shift in polar solvents (Fig. 2(a) and Fig. S4, ESI⁺). However, the absorption peak at 336 nm of TPF99DA resulted from intramolecular charge transfer, which was weakened by increasing the solvent polarity (Fig. S5, ESI[†]). When excited at the maximum excitation wavelength of 362 nm, TPF27DA showed a strong royal purple emission peak at 421 nm, while that of TPF99DA was red-shifted and had a bright blue-green emission peak at 473 nm when excited at 341 nm in THF solution (Fig. 2(b)). In the solid state, TPF27DA exhibited a strong blue emission peak at 432 nm (Fig. 2(c)), while that of TPF99DA exhibited a strong emission peak at 420 nm. It is interesting to find that the Stokes shift of TPF99DA is much larger than that of TPF27DA. Thus we calculated the frontier orbitals for the two diamine molecules (Fig. S6, ESI⁺). The results show that the HOMO and LUMO of TPF27DA have higher overlapping integrals, while those of TPF99DA are totally separated. These phenomena indicate that the special large conjugated and non-coplanar structure of TPF99DA forms a typical D– π –A molecule with a strong internal charge transfer (ICT) nature, according to our previous reports.^{17,18} In other words, ICT is much easier to be formed in the case of TPF99DA. In fact, the Stokes shift of TPF99DA (Fig. S8, ESI⁺) is much larger than that of TPD27DA (Fig. S7, ESI⁺) in different solutions, indicating that TPF99DA tends to have stronger ICT properties.

Synthesis and characterization of the polyimides

The polyimide films (**TPF27OPI** and **TPF990PI**) were prepared by reaction of the as-synthesized diamine and the commercial 4,4-oxydiphthalic anhydride (ODPA) through traditional polycondensation, as shown in Scheme 2. Mixing of the monomers produced a viscous polyamic acid (PAA) solution in DMF, then the PAA solution was casted on a clean dry glass plate followed by programmed thermal imidization. In Fig. 3, the infrared absorptions at 1780 cm⁻¹ (asymmetric C=O stretching) and 1720 cm⁻¹ (symmetric C=O stretching) for **TPF27OPI** and at 1782 cm⁻¹ and 1724 cm⁻¹ for **TPF990PI**, respectively, correspond

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Fig. 2 The optical spectra of the diamines in THF solution and in the solid state.





to the imide ring, and no amide bands are found. **TPF27OPI** was insoluble in traditional solvents, such as NMP, DMSO, DMF, *etc.*, even upon heating. And **TPF99OPI** was partially soluble upon heating (90 °C). The thermal properties of the polyimides were measured using TGA and DSC, as shown in Fig. S9 and S10 (ESI†). Both of the polyimides had a high glass transition temperature (T_g), for **TPF27OPI** at 340 °C and for **TPF990PI** at 338 °C, respectively. And they also showed good thermal stability with a 5% weight loss temperature ($T_{d5\%}$) for **TPF27OPI** at 602 °C and for **TPF990PI** at 586 °C, respectively. Their excellent thermal properties could ensure the electronic memory devices can be prepared at high temperature and maintain high stability in applications.

The optical properties of the polyimide films were studied by UV-vis and photoluminescence spectroscopy. The absorption spectra of the polyimide films are similar to those of the diamines, as shown in Fig. 4(a) and Fig. S11 (ESI⁺). For the yellow **TPF27OPI** film, the absorption edge wavelength (λ_{edge}) and the maximum absorption peak (λ_{max}^{abs}) are 377 nm and 340 nm, respectively, while for the light-colored **TPF990PI** film, the λ_{edge} is 362 nm, and there are two distinct absorption peaks located at 333 nm and 318 nm, respectively. The λ_{max}^{abs} of TPF27OPI and TPF99OPI at 340 nm and 333 nm is suggested to be related to the imide ring centered $n-\pi^*$ transitions. However, the absorption peak at 318 nm is suggested to be related to the π - π * transition centered at the big conjugated fluorene structure. In addition, the optical energy band gaps (E_{g}) of the **TPF27OPI** and **TPF99OPI** are estimated to be 3.29 eV and 3.43 eV, respectively, according to the Planck equation ($E_g = 1240/\lambda_{edge}$).

The photoluminescence of the two polyimides is obviously different, as shown in Fig. 4(b). For **TPF27OPI**, the maximum

emission wavelength (EM_{max}) is at 506 nm, and it emits a considerably low intensity yellow-green light, when excited by the maximum excitation wavelength (EX_{max}) of 416 nm. However, the **TPF990PI** emits a considerably high intensity blue-green light with the EM_{max} at 492 nm, when excited at 388 nm (EX_{max}) . Fluorene is an efficient fluorescence emission group; for **TPF990PI**, the sp³ hybridized carbon atom (C-9) separated the conjugated fluorene structure from the polymer main chain, so it shows a non-conjugated structure in the main chain, which may enhance the luminescence, while for **TPF270PI**, the conjugated fluorene structure is at the main chain, which may quench the fluorescence of the conjugated fluorene structure because of the strong CT effect between the diamine moiety (electron donor) and the dianhydride moiety (electron acceptor).

The electrochemical behaviors of the as-prepared polyimides were investigated by cyclic voltammetry (CV) measurements, as shown in Fig. 4(c). The PI film casted on the ITO-coated glass slide acts as the working electrode, tetrabutylammonium perchlorate (TBAP, 0.1 mol mL⁻¹) in CH₃CN as the supporting electrode and Ag/AgCl as the reference electrode. **TPF27OPI** shows a maximum oxidation peak (E_{max}^{OX}) at 1.90 V and the onset oxidation voltage (E_{onset}^{OX}) is 1.48 V, while the E_{max}^{OX} of **TPF99OPI** is 1.86 V and the E_{onset}^{OX} is 1.54 V. Note that the oxidation voltage of ferrocene (external standard) is 0.38 V, and thus the estimated highest occupied molecular orbital (HOMO) energy levels of **TPF27OPI** and **TPF99OPI** are calculated as -5.90 V and -5.96 V, respectively, based on the reference energy level of ferrocene (4.80 eV below the vacuum level). Meanwhile, the lowest unoccupied



Fig. 4 (a) Absorption spectrum of the polyimide films; (b) fluorescence spectroscopy of the polyimide films; (c) cyclic voltammetry (CV) of PI cast films on an ITO-coated glass slide in CH_3CN (scan rate: 50 mV s⁻¹).

molecular orbital (LUMO) energy levels of the PIs are -2.61 eV and -2.53 eV, respectively. Both the optical and the electrochemical properties of the polyimides are summarized in Table 1. These results indicate that the location of the tetraphenyl fluorene unit in the macromolecular main chain has a certain impact on the HOMO and LUMO energy levels of the polyimides, which in turn may have an impact on the switching behaviors of the memory devices.

Memory device characteristics of the polyimides

The configurations of sandwich memory devices with the as-synthesized PIs as the active layer were fabricated successfully, as shown in Scheme 3. The resistive switching behaviors of the ITO/**TPF27OPI**/Al and ITO/**TPF99OPI**/Al devices, with Al as the anode and ITO as the cathode, were investigated using the current-voltage (*I*-*V*) characteristics.

For the ITO/**TPF27OPI**/Al device, the thicknesses of the polyimide layer and the Al electrode were estimated to be around 60 nm and 100 nm (Fig. S12–S14, ESI†), respectively. Fig. 5(a) exhibits the typical *I–V* curves of the device (recorded device units of $0.5 \times 0.5 \text{ mm}^2$) at a scan rate of 0.05 V s^{-1} . In the first positive voltage sweep from 0 V to 5 V, the device was initially in the OFF state ("0" signal in memory data storage) with a low current in the range of 10^{-14} – 10^{-9} A, until an abrupt increase is observed in the current range at around 1.7 V with a higher conductivity (10^{-5} – 10^{-4} A, ON state), which was defined as the switching threshold voltage. This electronic transition from the OFF state to the ON state in the first sweep serves as

Table 1	Optical and electrochemica	al properties of t	he polyimides
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	UV-vi	s (nm)	_r OX	номо	O^a (eV)	LUMO	b^{b} (eV)	$E_{\rm g}^{\ c}$ (e	eV)
Polyimides	λ_{\max}^{abs}	λ_{edge}	E_{onset} (eV)	Exp.	Calc. ^d	Exp.	Calc. ^d	Exp.	Calc.
TPF27OPI TPF99OPI	340 333	377 362	$\begin{array}{c} 1.48\\ 1.54 \end{array}$	$-5.90 \\ -5.96$	$-5.42 \\ -5.44$	$-2.61 \\ -2.53$	$-2.51 \\ -2.54$	3.29 3.43	2.91 2.90

^{*a*} The HOMO energy levels were determined from the CV measurement onset oxidation voltage ($E_{\text{onset}}^{\text{OX}}$) using ferrocene as the external reference (4.8 eV below the vacuum level): HOMO = $-[E_{\text{onset}}^{\text{OX}} - E_{\text{ferrocene}} + 4.8]$ (eV). $E_{\text{ferrocene}}$ is determined to be 0.38 V vs. Ag/AgCl. ^{*b*} Determined from the equation: LUMO = E_{g} + HOMO. ^{*c*} Estimated from the UV-vis absorption edge wavelength (λ_{edge}) using the Planck equation: $E_{\text{g}} = 1240/\lambda_{\text{edge}}$. ^{*d*} The data were obtained by quantum calculation of the basic units of the PIs based on DFT/B3LYP/6-31G(d) using the Gaussian 09 program.



Scheme 3 Schematic diagram of the memory device.

the "writing" process ("1" signal in memory data storage). After this transition, the device could remain in the ON state, observed during the subsequent positive scan from 5 V to 0 V (the second sweep). The next dual sweeps were performed after turning the power off for usually less than 3 minutes, and the subsequent negative scan from 0 V to -5 V (the third negative sweep) did not turn the device from the ON state to the OFF state, and the device could also retain the ON state in the fourth sweep, indicating that the device was non-erasable. The long retention ability of the ON state determines the "write once, read many" (WORM) functionality of the ITO/**TPF27OPI**/Al device.

In addition, other parameters such as stability and read cycles are also important for the performance of the memory device. Fig. 5(b) shows the effects of the operation time on the memory device. At the constant voltage of 1 V, both the ON state and the OFF state of the device were observed to have no obvious degradation in current in 1 hour. The ON/OFF current ratio is roughly as high as 10^4 at 1 V. As shown in Fig. 5(c), the ON and OFF states were also stable up to 10 000 read pulses of 1 V (1 ms in period, 0.5 ms in duration width), indicating the excellent stability of the memory device.

However, the ITO/**TPF99OPI**/Al sandwich device exhibits completely different switching behavior, as shown in Fig. 6(a). During the first positive voltage sweep from 0 V to 5 V, the device is also initially at a low current, but a sharp increase in current was observed at a switching threshold voltage around 2.0 V, indicating the transition of the device from the OFF state to the ON state. In the subsequent second sweep from 5 V to 0 V,



Fig. 5 (a) Current–voltage (*I–V*) characteristics of the ITO/**TPF27OPI**/Al sandwich device with an initial positive voltage sweep. (b) Effects of operation time on the ON and OFF states of the memory devices under a constant 1 V bias voltage. (c) Effects of 1 V read pulse (1 ms in period, 0.5 ms in duration width) on the ON and OFF states of the sandwich device.

the ON state could still be retained. However, the device relaxed to the OFF state after the power was turned off for about 3 minutes. In the third sweep from 0 V to -5 V, a sharp increase in current was also observed at a switching threshold voltage of about -2.0 V, indicating that the transition of the device from the OFF state to the ON state occurs again. In the next sweep (the fourth sweep from -5 V to 0 V), the ON state was also stable. It was exhibited that the ON and OFF states were randomly accessible and volatile in the memory device, which was similar to the data storage behavior of a static random access memory (SRAM) functionality.

The stability of the device and the ON/OFF current ratio were measured as a function of the operation time, as shown in Fig. 6(b). No obvious degradation in current was observed for the OFF state and the ON state during the testing process, and the device maintained an ON/OFF current ratio as high as 10^5 at 1 V. Fig. 6(c) shows the stimulus effect of the read pulse on the OFF state and the ON state. The PI-based memory device was stable up to at 10 000 continuous read pulses of 1 V at least, and the OFF state and the ON state were not changed significantly.

Molecular simulations and the proposed electronic transition mechanism

To have a clear understanding of the charge transfer process and the corresponding switching behavior of the present polyimide-based memory devices, the electronic structure, molecular orbitals, electrostatic potentials, and energy levels of the synthesized polyimides were investigated by molecular simulations. The basic units (BUs) of **TPF27OPI** and **TPF99OPI** were selected as the model compounds, for the sake of model simplicity and practical availability for simulations.

Although XRD patterns (Fig. S15, ESI[†]) indicate that the two polyimides are amorphous, according to the simulation results, the BU of **TPF27OPI** is more planar than that of **TPF990PI**, as shown in Fig. 7. The twisted conformation of the ether bond on the dianhydride and the dihedral angle between the imide rings are similar. The most different dihedral angles between fluorene and the connected benzene rings of the BUs of two PIs for **TPF270PI** are 37° and 41°, but those for **TPF990PI** are 91° and 145°. These indicate that **TPF990PI** is more twisted than **TPF270PI** in spatial structures. The rigid planar structure of **TPF270PI** is more conducive to electron transport than the twisted structure of **TPF990PI**.

Fig. 8 shows the simulation results for the BUs of **TPF27OPI** and **TPF990PI** based on DFT/B3LYP/6-31G(d) using the Gaussian 09 program. The HOMOs of the model compounds are located on the diamine side (as the donor, D), whereas the LUMOs are located on the ODPA side (as the acceptor, A). These features will facilitate the charge transfer from the diamine side to the ODPA side to form charge-transfer (CT) complexes in the polyimide system under the applied voltage. For **TPF27OPI**, the calculated HOMO and LUMO energies of the model compound are -5.42 eV and -2.51 eV, and the E_g is 2.91 eV, which are basically consistent with the experimental results obtained from the UV-vis and CV



Fig. 6 (a) Current–voltage (*I–V*) characteristics of the ITO/**TPF99OPI**/Al sandwich device with an initial positive voltage sweep. (b) Effects of operation time on the ON and OFF states of the memory devices under a constant 1 V bias voltage. (c) Effects of 1 V read pulse (1 ms in period, 0.5 ms in duration width) on the ON and OFF states of the sandwich device.



Fig. 7 The optimized geometries for the BUs of PIs.



measurements (HOMO: -5.90 eV, LUMO: -2.61 eV, E_g : 3.29 eV), while for the **TPF990PI** model, the HOMO energy is -5.44 eV and the LUMO energy is -2.54 eV, respectively, and the E_g is 2.91 eV, basically consistent with experimental results (HOMO: -5.96 eV, LUMO: -2.53 eV, E_g : 3.43 eV). Both of them indicate the rationality of the theoretical quantum calculations and the corresponding experimental results.

Calculated oscillator strength (OS) and transition assignment of the BUs of PIs are also summarized, as shown in Table 2, which indicates the slight differences in the processes of the electronic transition and might afford to explain the different switching behaviors of the two PI-based memory devices. For the **TPF27OPI** system, the HOMO (-5.42 eV) to the LUMO (-2.51 eV) transition is almost impossible with an oscillator strength of 0.0006, but LUMO+2 (0.9577), LUMO+3 (0.2536) and LUMO+4 (0.5186) are more likely to form transitions with a larger value of the oscillator strength. This indicates that the accumulated electrons are more inclined to be excited to LUMO+2 (-1.63 eV) rather than the LUMO (-2.51 eV) under sufficient energy. However, for the **TPF990PI** system, the accumulated View Article Online

Table 2 The oscillator strengths (OS) and the assignment of S_0 to S_0 transitions in the BUs of PIs^a

PI	S_i	OS	Orbitals	Contribution
TPF27OPI	4	0.9577	HOMO \rightarrow LUMO+2	0.91
			HOMO \rightarrow LUMO+3	0.09
	9	0.2536	HOMO \rightarrow LUMO+3	0.14
			HOMO \rightarrow LUMO+4	0.03
	10	0.5186	HOMO \rightarrow LUMO+3	0.05
			HOMO \rightarrow LUMO+4	0.53
			HOMO \rightarrow LUMO+5	0.10
TPF99OPI	1	0.0001	HOMO \rightarrow LUMO	0.81
			HOMO \rightarrow LUMO+1	0.19
	2	0.0005	$HOMO \rightarrow LUMO$	0.19
			HOMO \rightarrow LUMO+1	0.81
	8	0.1170	HOMO \rightarrow LUMO+2	0.03
			HOMO \rightarrow LUMO+3	0.04
			HOMO \rightarrow LUMO+4	0.93

^a Prohibited transitions are not listed.

electrons are more inclined to be excited from the HOMO (-5.44 eV) to LUMO+4 (-1.27 eV) with an oscillator strength of 0.1170 rather than the LUMO (-2.44 eV) with an oscillator strength of 0.0001. The energy for electron transition of the BUs of **TPF27OPI** (3.79 eV, from the HOMO to the LUMO+2) is less than **TPF990PI** (4.17 eV, from the HOMO to the LUMO+4), which is consistent with the experimental results of the threshold voltage (1.7 V < 2.0 V) of PI-based memory devices.

The energy level diagrams of the polyimides and the memory devices are also shown in Fig. 9. Distinctly lower energy barriers between the two electrodes (work function: ITO = -4.80 eV and Al = 4.28 eV) and the HOMO energy levels of the polyimides (**TPF27OPI**: -5.90 eV and **TPF99OPI**: -5.96 eV) are observed. Theoretically, an applied electronic field exceeding 1.10 eV (the barrier between the ITO electrode and the HOMO of **TPF27OPI**) and 1.16 eV (the barrier between the ITO electrode and the HOMO of **TPF99OPI**) will provide lower energy for hole injection than the barrier between the Al electrode and the LUMO of the PIs. This suggests that **TPF27OPI** and **TPF99OPI** function more likely as p-type materials, and indicates that the hole injection from the ITO electrode into the HOMO is more favorable than the electron injection from the Al electrode into the LUMO during the charge injection process.

In addition, to better illustrate the process from the OFF state to the ON state, the *I*–*V* curves in both states are analyzed



Fig. 9 Energy level diagrams of the PIs and the memory devices.



Fig. 10 Experimental (dots) and fitted (solid line) *I–V* curves for (a) the OFF state and (b) the ON state of the ITO/**TPF27OPI**/Al device.

in detail using theoretical models. The I-V curves of TPF27OPI in the OFF state under a low positive voltage (0-1.6 V), as shown in Fig. 10(a), follow the Schottky emission model,¹⁸ described by the equation: $J = AT^2 \exp \left| -q \left(\phi_{\rm B} - \sqrt{qV/4\pi\varepsilon_{\rm i}d} \right) / kT \right|$. This suggests that a Schottky barrier is formed at the ITO interface due to the work function differences between the ITO electrode (-4.80 eV) and the HOMO (-5.90 eV) of TPF270PI. When the applied electric field reaches the threshold voltage, electric field-induced charge transfer occurs. Electrons transit from the HOMO to the LUMO of TPF27OPI, leaving holes that spread over the imide moieties. These holes give rise to an open channel for charge carrier migration. Therefore, an abrupt increase of the current in the device could be observed at the threshold voltage, indicating the formation of a high conductivity state (the ON state). During the subsequent positive sweeps of the ON state, as shown in Fig. 10(b), the I-V curve of TPF27OPI follows the Ohmic conduction model¹⁹ described by the equation: $J = qn\mu V/d$. The relationship between current density (J) and voltage (V) is a linear correlation, which is similar to the conductive mechanism of metal. The change from OFF state to ON state indicates that the switching behavior of the device dependent on the current through the TPF27OPI layer is switched on. Both the Schottky emission model and the Ohmic conduction model are suitable for the OFF state and the ON state of TPF99OPI, as shown in Fig. S16 (ESI[†]).

Combining the calculated frontier molecular orbitals and the oscillator strengths from S_0 to S_i transitions of the simulation models, the possible electronic transition processes occurring in the **TPF27OPI** and the **TPF990PI** systems are described, as shown in Fig. 11. For the **TPF270PI** system, the HOMO and the



Fig. 11 The plausible electronic transition processes occurring in **TPF27OPI** and **TPF990PI**.

LUMO+2, LUMO+3, and LUMO+4 orbitals tend to mainly locate on the TPF27DA unit (donor, D), while the LUMO and the LUMO+1 orbitals tend to distribute completely on the ODPA unit (acceptor, A). The electronic transition corresponds to promotion of the electrons from the ground state to the excited state. This suggests¹⁻³ that some electrons at the HOMO gain enough energy and transit to the LUMO+2 orbital to give rise to an excited state (combining the oscillator strength and their contribution), as the applied bias reaches the threshold voltage. However, the excited state which is highly energetic and unstable tends to relax to the lowest excited state (the LUMO) with internal conversion. Thus charge transfer can occur to form conductive charge-transfer (CT) complexes. The electronic transition occurring in the TPF99OPI system is similar to the higher LUMO+4 orbital through the intermediate LUMO+3, LUMO+2, and LUMO+1 orbitals, and then to the LUMO to form charge-transfer (CT) complexes. Once the charge-transfer (CT) state is formed under the applied voltage, an abrupt increase in current is observed and the device is transited to the conductivity state (ON state).

Conclusions

In summary, we have successfully synthesized two novel tetraphenyl fluorene-based functional polyimides, **TPF27OPI** and **TPF99OPI**. Both of the polyimides show excellent thermal properties and obvious photoluminescence properties. **TPF99OPI** shows a strong fluorescence with a blue shift compared to **TPF27OPI**. The PI-based memory device, ITO/**TPF27OPI**/Al shows nonvolatile WORM type switching behavior, while the ITO/**TPF99OPI**/Al one shows volatile SRAM type switching behavior. These results are related to the fluorene structure located in the polymer main chain and side chain, which affects the conjugation of polyimides. In addition, molecular simulations, and the optical and electronic chemical properties were used to clarify the CT processes and explain the resistive switching mechanisms. These results suggest that the memory switching behaviors of the PI-based devices can be affected and adjusted by the chain structure and spatial structural design of the polyimides.

Experimental

Materials

4,4'-Oxydiphthalic dianhydride (ODPA), tetrabutylammonium perchlorate (TBAP), hydrazine hydrate and ferrocene were purchased from Aladdin. 2,7-Dibromo-9,9-diphenylfluororene, 2,7-dibromofluorene and 4-fluoronitrobenzene were purchased from TCI. Palladium on activated carbon (10% Pd (Pd/C)) and tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) were purchased from Alfa Aesar. Phenylboronic acid and 4-aminophenylboronic acid were purchased from Soochiral Chemical Science & Technology Co., Ltd. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), and methanol were obtained from Guangzhou Chemical Works. All other reagents were of analytical grade and used as received from commercial sources, unless otherwise mentioned.

Instrumentation

Cyclic voltammetry (CV) measurements were obtained using a Bio-Logic VMP-300 multi-channel electro-chemical workstation using a three-electrode cell at a rate of 50 mV s⁻¹ in CH₃CN solution (TBAP, 0.1 mol mL⁻¹). A PI thin film coated onto an ITO glass substrate was used as the working electrode, Ag/AgCl and KCl (sat.) as the reference electrode and a platinum disk as the auxiliary electrode. The current-voltage (I-V) measurements of the memory device were obtained using a Keithley 4200-SCS semiconductor with a Keithley 4205-PG2 pulse generator. Wideangle X-ray diffraction (WAXD) measurements were performed on a SmartLab X-ray diffractometer with a sweeping rate of 10° min⁻¹. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Infrared spectra (IR) were recorded using a Bruker spectrometer. Mass spectra (MS) were recorded on a Thermo EI mass spectrometer. Thermal gravimetric analysis (TGA) was performed on a TA Q50 and differential scanning calorimetry (DSC) was carried out with a NETZSCH DSC 204 at a rate of 20 $^{\circ}$ C min⁻¹ under nitrogen. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Hitachi U-3900. Fluorescence spectra were recorded using a Shimadzu RF-5301PC spectrometer with a slit width of 5 nm for polyimides and 3 nm for monomers, respectively. The thickness of the vacuum evaporated Al electrodes and the spin-coated PI thin films was measured using a Kosaka Surfcorder ET150 and a Hitachi S-4800 field emission scanning electron microscope (SEM).

Synthesis of the monomers

Synthesis of 4,4'-(9,9-diphenyl-9*H*-fluorene-2,7-diyl)dianiline (TPF27DA). 4-Aminophenyl-boronic acid (2.74 g, 0.02 mol) and 2,7-dibromo-9,9-diphenylfluororene (1) (4.76 g, 0.01 mol) were dissolved in 200 mL of THF. Then 2 mol mL⁻¹ K₂CO₃ solution

and a few drops of Aliquat336 were added. Then a few drops of the $Pd(PPh_3)_4$ catalyst were added and the reaction mixture was stirred at 80 °C for 24 h under N₂. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography using dichloromethane/*n*-hexane (v/v = 2/1). The yield of the product is about 86% as a yellow powder.

¹H NMR (400 MHz, DMSO- d_6) δ 7.90 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.51 (s, 2H), 7.27 (dt, J = 26.0, 8.1 Hz, 14H), 6.62 (d, J = 8.2 Hz, 4H), 5.24 (s, 4H). ¹³C NMR (101 MHz, DMSO- d_6) δ 153.22, 150.14, 147.66, 141.90, 139.04, 130.24, 129.62, 129.22, 129.01, 128.43, 126.90, 124.41, 122.44, 116.14, 66.93. FT-IR (KBr, cm⁻¹): 3462, 3371 (N–H, stretching), 1278 (C–N, stretching). MS (m/z): [M]⁺ calc. for C₃₇H₂₈N₂, 500.63. Found, 500.23.

Synthesis of 2,7-dibromo-9,9-bis(4-nitrophenyl)-9*H*-fluorene (WuBrDN). The intermediate WuBrDN (3) was synthesized according to a previously reported procedure.²⁰ 2,7-Dibromofluorene (2) (16.21 g, 0.05 mol), 4-fluoronitrobenzene (14.14 g, 0.10 mol) and potassium tertbutoxide (5.61 g, 0.01 mol) were dissolved in DMF (100 mL) and stirred for 48 h under N₂ at 120 °C. After reaction, the product (3) was purified by silica gel column chromatography using dichloromethane/*n*-hexane (v/v = 1/2). The yield of the product was about 80% as a white powder.

¹H NMR (400 MHz, DMSO- d_6) δ 8.19 (d, J = 8.6 Hz, 4H), 8.04 (d, J = 8.1 Hz, 2H), 7.73 (s, 4H), 7.45 (d, J = 8.7 Hz, 4H).

Synthesis of 9,9-bis(4-nitrophenyl)-2,7-diphenyl-9*H*-fluorene (TPF99DN). Phenylboronic acid (6.10 g, 0.05 mol) and intermediate compound (3) (11.12 g, 0.02 mol) were dissolved in 200 mL of THF. Then 2 mol mL⁻¹ aqueous K_2CO_3 solution and a few drops of Aliquat336 were added. Then a few drops of the Pd(PPh₃)₄ catalyst were added and the reaction mixture was stirred at 80 °C for 24 h under N₂. After cooling to room temperature, the product (4) was concentrated and purified by silica gel column chromatography using dichloromethane/*n*-hexane (v/v = 1/4). The yield of the product is about 72% as a light white powder.

¹H NMR (400 MHz, DMSO- d_6) δ 8.20 (d, J = 8.5 Hz, 4H), 8.16 (d, J = 7.9 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.80 (s, 2H), 7.68 (d, J = 7.6 Hz, 4H), 7.57 (d, J = 8.6 Hz, 4H), 7.47 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.4 Hz, 2H).

Synthesis of 4,4'-(2,7-diphenyl-9*H***-fluorene-9,9-diyl)dianiline (TPF99DA).** A mixture of intermediate compound (4) (5.61 g, 0.01 mol), the 10% Pd/C catalyst (0.5 g), hydrazine monohydrate (16 mL), and ethanol (200 mL) was placed in a three-necked flask and heated at 80 °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. The yield of the product is about 88% as a white powder.

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 4H), 7.58 (s, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 4H), 6.45 (d, *J* = 8.1 Hz, 4H), 4.94 (s, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 155.36, 148.96, 142.10, 141.32, 140.17, 134.51, 130.81, 130.13, 129.18, 128.46, 127.74, 125.71, 122.71, 115.57, 65.73. FT-IR (KBr, cm⁻¹): 3422, 3341 (N–H, stretching), 1285 (C–N, stretching). MS (*m*/*z*): [M]⁺ calc. for C₃₇H₂₈N₂, 500.63. Found, 500.23.

Preparation of the polyimides

The synthesis of **TPF27OPI** was used as an example to illustrate the general synthetic procedure, as shown in Scheme 2. To a solution of **TPF27DA** (0.5006 g, 1 mmol) in 4 mL of freshly distilled anhydrous DMF, the dianhydride ODPA (0.3102 g, 1 mmol) was added in one portion. The mixture was stirred at 20 °C under argon for 24 h to form poly(amic acid) (PAA) solution. The PAA solution was subsequently coated on a clean dry glass plate, followed by thermal imidization at 80 °C/1 h, 160 °C/1 h, 240 °C/1 h and 350 °C/1 h in a vacuum. After cooling, it was peeled with hot water. Due to the insolubility of the PI, the degree of polymerization of the PAA was estimated by inherent viscosity (η_{inh}). The η_{inh} value measured using an Ostwald viscometer was 0.87 dL g⁻¹. FT-IR (air, cm⁻¹): 1780 (asym, C=O), 1720 (sym, C=O), 1367 (C–N) and 740 (imide ring).

TPF99OPI was prepared by a similar method to that used for **TPF27OPI**. And the Ostwald viscosity of **TPF990PAA** was 0.51 dL g⁻¹. FT-IR (air, cm⁻¹): 1782 (asym, C=O), 1724 (sym, C=O), 1371 (C-N) and 742 (imide ring).

Fabrication and characterization of the memory devices

ITO glass substrates were cleaned by ultrasonication with water, acetone, and ethanol each for 10 min, and then cleaned by plasma for 10 min. Homogenous PAA solutions were prepared in DMF and filtered. The PAA films were prepared by spin-coating onto the ITO glass substrate at a speed rate of 2500 rpm for 60 s. Then the PAA film was heated to 350 °C at a rate of about 10 °C min⁻¹ under N₂. The thickness of the smooth PI thin films was 60 nm. Finally, an aluminum (Al) top electrode with a thickness of 100 nm was deposited onto the polyimide film surface through a shadow mask (each electrode at 0.5 × 0.5 mm²) by thermal evaporation under vacuum. The sandwich memory devices were eventually prepared with the ITO/PI/Al configuration.

Molecular simulations

The molecular simulations, molecular geometry, molecular orbitals and the BUs of polyimide were calculated and optimized in the Gaussian 09 program package by means of density functional theory (DFT) using Becke's three-parameter hybrid density functional method with Lee–Yang–Parr's correction functional (B3LYP) method, and the 6-31G(d) basis set. Time-dependent DFT (TD-DFT) was additionally applied in oscillator strength calculations and transition contributions.²¹

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