

High Performance Volatile Polymeric Memory Devices Based on Novel Triphenylamine-based Polyimides Containing Mono- or Dual-Mediated Phenoxy Linkages

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ABSTRACT: Two novel functional polyimides (PIs), PI(AAPT-TPA) and PI(APT-TPA), consisting of electron-donating 4-amino-4'-(p-aminophenoxy)-triphenylamine (AAPT) or 4,4'-bis(p-aminophenoxy)-triphenylamine (APT) and electron-accepting phthalimide moieties, were prepared for the memory device applications. The TPA moieties as electron donor are expected to enhance the electron donating and charge transport ability with phthalimide moieties (electron acceptor). The monophenoxy linkage PI(AAPT-TPA) had a higher T_g and a lower band gap than the dual-phenoxy linkage PI(APT-TPA). It suggested the more rigid backbone of the former and led to different memory characteristics. The memory devices with the configuration of ITO/PI/Al exhibited two conductivity states and could be swept positively or negatively with a high ON/OFF current ratio of $10^8 - 10^9$. The PI(AAPT-6FDA) device relaxed from the ON state to the OFF state quickly after the applied voltages was removed, whereas the ON state of the PI(APT-6FDA) device could remain for around 4 min after the power was turned off. It suggested that dynamic random access memory (DRAM) was exhibited for the PI(AAPT-6FDA) device and that static random access memory (SRAM) was for the PI(APT-6FDA) device. The volatile memory characteristics were probably attributed to the unstable charge transfer (CT) complex based on the weak theoretical dipole moments of the studied PIs. The dual-mediated phenoxy linkage of PI(APT-6FDA) led to the more twisted conformation compared to the monosubstituted PI(AAPT-6FDA) based on the theoretical analysis by the density functional theory (DFT) method. It thus produced a potential barrier for delaying the back CT process by the electric field and explained the SRAM characteristic. The present study suggested the importance of the TPA structure for the memory characteristics. The fast switching and high ON/OFF characteristics also indicated the new TPA based polyimides for advanced memory technology.

Introduction

Resistive switching behavior has been primarily studied in amorphous silicon-based materials for the last 30 years. It was found that the digital data could be stored by applying or discharging electrical charges through a simple device configuration consisting of two electrode layers sandwiching the storage medium. As compared to the traditional inorganic semiconductorbased memories, polymeric memory devices are extensively attractive nowadays because of the advantages of rich structure flexibility, low-cost, solution processability, and three-dimensional stacking capability.^{1–3} The recently studied polymer systems exhibit memory switching characteristics, including conjugated polymers,^{4–7} functional polyimides (PIs),^{8–16} polymers with specific pendent chromophores^{17–20}, and polymer nanocomposites (metal nanoparticle^{21–23} and fullerene^{24–26} embedded). The widely reported electrical switching phenomena in polymers and the corresponding polymer electronic memories as an emerging area in organic electronics have been reviewed by Kang and co-workers recently.^{2,3}

Among all the studied polymer systems, PIs are promising candidates for memory device applications because of their

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excellent physical and chemical properties besides the electrical switching behavior.^{8–16} Functional PIs containing both electron donor and acceptor moieties within a repeating unit contribute to electronic transition between the ground and excited states, which could be manipulated by the induced charge transfer (CT) from donor (D) to acceptor (A) under applied electric fields.⁸⁻¹¹ Among the studied functional PIs, the triphenylamine (TPA)-based PIs attract significant attention.^{8,9,14-16} For example, the memory device of a TPA-functionalized polyimide PI(TP6F) exhibited dynamic random access memory (DRAM) behavior while a device based on PI(PYTPA) (containing combined donor effects from both TPA and diphenylpyridine) showed the improved DRAM performance as reported by Kang and coworkers.^{8,9} Meanwhile, Ree and co-workers also propose a series of TPA-based PIs for memory characteristics.^{14–16} They found that PI(6F-2TPA) (two connected TPA rings) showed stable digital nonvolatile write-once-read-many-times (WORM) and volatile DRAM memory characteristics depending on film thickness.¹⁴ Besides, a flash-type memory of PI(6F-HAB-TPAIE) bearing two pendent TPA groups and a unipolar WORM memory of PI(6F-HTPA) having an attached hydroxyl group on TPA were also reported recently.^{15,16} However, Kang and co-workers also found that the conformational changes induced by the incorporated mediators on polymer backbone would result in

Scheme 1. Syntheses of PI(AAPT-6FDA) and PI(APT-6FDA)



PI(AAPT-6FDA)

increased torsional displacement between the two monomer moieties and then produce a potential barrier for the back electron transfer.¹¹ However, the relationship between the polymer structure and memory device characteristics requires further exploration.

In this study, we report the syntheses and memory device characteristics of two new TPA-based PIs, such as PI(AAPT-6FDA) derived from 4-amino-4'-(p-aminophenoxy)triphenylamine (AAPT) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and PI(APT-6FDA) from 4,4'-bis(p-aminophenoxy)triphenylamine (APT) and 6FDA (Scheme 1). The TPA moieties as electron donor are expected to enhance the electron donating and charge transport ability with phthalimide moieties (electron acceptor) via phenoxy linkage (L) for device applications. The thermal, optical, and electrochemical properties of PI(AAPT-6FDA) and PI(APT-6FDA) were also characterized. These PIs could be well dissolved in common organic solvents and easily processed into a smooth thin film layer. The memory behavior was conducted by a simple sandwich device configuration consisting of polymer films between indium-tin oxide (ITO) bottom electrode and Al top electrode. The mono- or dualmediated phenoxy linkages between the TPA and phthalimide moieties, represented as (D-L-A)_n (PI(AAPT-6FDA)) or (L-D- $L-A)_n$ (PI(APT-6FDA)), was found to significantly affect the volatile memory behaviors. PI(AAPT-6FDA) exhibited DRAM performance, while PI(APT-6FDA) showed the static random access memory (SRAM) behavior. In order to clarify the switching mechanism of the memory devices, theoretical calculations under the density functional theory (DFT) method at the B3LYP level with the 6-31G(d) basic set was applied to analyze the geometry and electronic transitions of the studied polymers. The obtained electrical characteristics not only suggested that PI-(AAPT-6FDA) and PI(APT-6FDA) were excellent candidates for a volatile type memory but also presented an understanding of the TPA structural effects on the memory device performance.

Experimental Section

Materials. p-Iodophenol, p-fluoronitrobenzene, aniline, tritbutylphosphine (96+%), copper powder (99.5+%), 18-crown-6-ether (98+%), palladium-activated carbon (Pd 10 wt %), DMAc, and toluene were purchased from Wako, Japan and dimethyl sulfoxide (DMSO) was purchased from Aldrich. Tris-(dibenzylideneacetone)dipalladium (0) $(Pd_2(dba)_3)$ (>75%) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from TCI and were used as received. The detailed syntheses and characterization of 4-iodo-4'-nitrodiphenyl ether (INE), N-(4-nitrophenyl)aniline, 4-nitro-4'-(p-nitrophenoxy)triphenylamine (NNPT), and 4,4'-bis(p-nitrophenoxy)triphenylamine (NPT) are described in the Supporting Information.

Synthesis of 4-Amino-4'-(*p*-aminophenoxy)triphenylamine (AAPT). Hydrazine monohydrate (10 mL) was added dropwise to a solution of NNPT (2.14 g, 5.00 mmol) and palladiumactivated carbon (0.0224 g) in ethanol (15 mL), and the mixture was refluxed for 24 h. The reaction solution was filtered through Celite to remove palladium-activated carbon and washed with THF. The filtrate was concentrated and poured into water. The precipitate was collected by filtration and purified by recrystallization from chloroform and hexane to yield 1.26 g (69% in yield) of white crystals. IR (KBr), ν (cm⁻¹): 3460, 3379 (N–H stretching). ¹H NMR (300 MHz, δ , ppm): 7.13 (t, J = 8.0 Hz, ArH, 2H), 6.94 (d, J = 9.0 Hz, ArH, 2H), 6.80-6.73 (m, ArH, 9H), 6.59-6.55 (m, ArH, 4H), 4.92 (s, N-H, 2H), 4.82 (s, N-H, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆, δ, ppm): 154.83, 149.49, 147.13, 146.67, 145.86, 142.86, 136.42, 129.63, 128.43, 125.81, 121.16, 120.44, 120.06, 118.43, 115.79, 115.69. Anal. Calcd for C₂₄H₂₁N₃: C, 78.5; H, 5.76; N, 11.4; found, C, 78.4; H, 5.90; N, 11.2

Synthesis of 4,4'-Bis(*p*-aminophenoxy)triphenylamine (APT). APT was prepared by a similar procedure according to the synthesis of AAPT, starting from NPT. APT was obtained as white crystals in 90% yield. IR (KBr), ν (cm⁻¹): 3460, 3375 (N–H stretching). ¹H NMR (300 MHz,CDCl₃, *δ*): 7.19 (t, J = 7.8 Hz, ArH, 2H), 7.03–6.98 (m, ArH, 6H), 6.89–6.81 (m, ArH, 9H), 6.73 (d, J = 8.1 Hz, ArH, 4H), 3.53 (s, N–H, 4H); ¹³C NMR (75 MHz, CDCl₃, *δ*, ppm): 154.87, 149.46, 148.80, 142.90, 142.83, 129.46, 126.37, 122.37, 121.74, 121.19, 118.64, 116.67. Anal. Calcd for C₃₀H₂₅N₃: C, 78.4; H, 5.48; N, 9.14; found, C, 78.3; H, 5.67; N, 8.96.

Synthesis of Poly[4-amino-4'-(p-aminophenoxy)triphenylamine-hexafluoroisopropyl-idenediphthalimide] (PI(AAPT-6FDA)). 6FDA (0.444 g, 1.00 mmol) was added into a solution of AAPT (0.367 g, 1.00 mmol) in dehydrated DMAc (solid contents 15 wt %) under nitrogen. The reaction mixture was stirred at room temperature for 24 h to give a poly(amic acid) (PAA) solution. A reaction mixture of acetic anhydride (0.1479 g, 1.49 mmol) and pyridine (0.1146 g, 1.49 mmol) was added to the above PAA solution. The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 24 h. The resulting solution was poured into methanol, and the precipitate was collected by filtration and washed with methanol. The final product was dried at 200 °C under vacuum for 10 h, and the polymer yield was 92%. The number average molecular weight (M_n) and weight average molecular weight (M_w) values estimated from GPC were 4.49×10^4 and 7.90×10^4 , respectively, with the polydispersity index (PDI = M_w/M_n) at 1.76. IR (KBr), ν (cm⁻¹): 1786, 1724 (C=O stretching), 1381 (C-N stretching). ¹H NMR (DMSO- d_6 , δ , ppm): 8.20–8.00 (m, ArH, 4H), 7.80 (s, ArH, 2H), 7.49 (d, J = 8.7 Hz, ArH, 2H), 7.36 (d, J = 8.4 Hz, ArH, 4H), 7.22-7.09 (m, ArH, 11H). Anal. Calcd for C₄₃H₂₃N₃: C, 66.6; H, 2.99; N, 5.42; found, C, 66.2; H, 3.30; N. 5.17.

Synthesis of Poly[4,4'-bis(*p*-aminophenoxy)triphenylaminehexafluoroisopropyl-idenediphthalimide] (PI(APT-6FDA)). Using APT as a diamine, PI(APT-6FDA) was synthesized by a procedure similar to that use for PI(AAPT-6FDA). The yield of PI(APPA-6FDA) was 93%. M_n , M_w , and PDI values of PI-(AAPT-6FDA) were 3.17×10^4 , 6.27×10^4 , and 1.98, respectively. IR (KBr), ν (cm⁻¹): 1786, 1728 (C=O stretching), 1377 (C-N stretching). ¹H NMR (DMSO- d_6 , δ , ppm): 8.12 (d, J =8.1 Hz, ArH, 2H), 7.93 (d, J = 8.7 Hz, ArH, 2H), 7.76 (s, N-H, 1H), 7.43 (d, J = 8.7 Hz, ArH, 4H), 7.27 (t, J = 7.8 Hz, ArH, 2H), 7.15–6.96 (m, ArH, 15H). Anal. Calcd for C₄₉H₂₇N₃: C, 68.2; H, 3.70; N, 4.68; found, C, 67.3; H, 3.35; N, 4.69.

Characterization. NMR spectra were recorded on a BRU-KER DPX-300S spectrometer at resonant frequencies of 300 MHz for 1 H and 75 MHz for 13 C nuclei using CDCl₃ or DMSO- d_6 as the solvent and tetramethylsilane as the reference. FT-IR spectra were measured by a Horiba FT-120 Fourier transform spectrophotometer. Number- and weight-average molecular weights $(M_n \text{ and } M_w)$ were evaluated by GPC on a JASCO PU-2080 Plus with two polystyrene gel columns (TSK GELS GMH_{HR}-M). DMF containing 0.01 M LiBr was used as a solvent at a flow rate of 1.0 mL \cdot min⁻¹ calibrated by polystyrene standard samples. The UV-visible optical absorption spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. The absorbance of polymer solutions was evaluated in the wavelength range of 280-800 nm. Elemental analyses were performed on a Yanaco MT-6 CHN recorder elemental analysis instrument. Thermal properties were estimated from a Seiko TG/DTA 6300 thermal analysis system (TGA) and a TA Instruments DSC-Q100 differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 and 6 °C/min, respectively. Cyclic voltammogram was performed at room temperature using a working electrode (ITO, polymer film area of about $10 \times 30 \text{ mm}^2$), a homemade reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 0.1 V/s (CHI 611B electrochemical analyzer). A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile was used as an electrolyte. The thickness of the polymer film was measured with a Microfigure Measuring Instrument (Surfcorder ET3000, Kosaka Laboratory Ltd.).

Fabrication and Measurement of the Memory Device. The memory device was fabricated on the indium-tin oxide (ITO)coated glass, with the configuration of ITO/polyimides/Al. Before the fabrication of the polymer layer, the ITO glass was precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. A 25 mg/mL of well-dissolved PI(AAPT-6FDA) or PI(APT-6FDA) polymer solution in DMAc was first filtered through 0.45 μ m pore size of PTFE membrane syringe filter. Then, the filtered solution was spin-coated onto the ITO glass at a speed rate of 1000 rpm for 60 s and annealed at 150 °C for 30 min under nitrogen. The thickness of the thin film was determined to be around 40-50 nm. Finally, a 300-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of $0.5 \times 0.5 \text{ mm}^2$ 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 (maintained as common), and Al was set as the anode during the voltage sweep. The probe tip used 10 μ m diameter tungsten wire attached to a tinned copper shaft with a point radius $< 0.1 \ \mu m$ (GGB Industries, Inc.). All of the electronic measurements were performed in a glovebox.

Computational Methodology. Molecular calculations studied in this work have been performed with the Gaussian 03 program package.²⁷ Equilibrium ground state geometry and electronic properties of basic unit of PI(AAPT-6FDA) and PI(APT-6FDA) were optimized by means of the density functional theory (DFT) method at the B3LYP level of theory (Beckesstyle three-parameter density functional theory using the Lee– Yang–Parr correlation functional) with the 6-31G(d) basic set.

Results and Discussion

Syntheses and Characterization of Monomers and Polymers. The monomer synthesis of AAPT was described in the Experimental Section and also shown in the Scheme S1(a) of the Supporting Information. First, the precursory N-(4nitrophenyl)aniline and 4-iodo-4'-nitrodiphenyl ether (INE) were prepared from 4-fluoronitrobenzene and aniline, and from 4-fluoronitrobenzene and 4-iodophenol, respectively. Then, the Ullman reaction of N-(4-nitrophenyl)aniline and INE produced 4-nitro-4'-(p-nitrophenoxy)triphenylamine (NNPT), which was further hydrogenated to AAPT. Similar to AAPT, APT was prepared in three steps as shown in Scheme S1(b) (Supporting Information). The palladiumcatalyzed N-arylation reaction of aniline with two equivalents of INE produced 4,4'-bis(p-nitrophenoxy)triphenylamine (NPT), which could be converted to APT with the catalytic reduction. The characteristic nitro absorption peaks of all nitro compounds at around 1580 and 1340 cm⁻¹ in the FT-IR spectra disappeared, and the new absorption peaks at around 3450 and 3370 cm⁻¹ appeared after the reduction of NNPT and NPT, which were properly assigned to amino groups. The ¹H NMR spectra of these two diamine compounds are presented in Figure 1 with the assignments of all peaks. The signals at 4.92 and 4.82 ppm were assigned to the asymmetric amino groups of AAPT, while those at 3.53 ppm were assigned to the amino groups of APT. In addition, the ¹³C NMR and elemental analysis clearly supported the formation of all monomers. The above results suggest the successful preparation of the AAPT and APT monomers.

The polymers, PI(AAPT-6FDA) and PI(APT-6FDA), were prepared by the polycondensation of diamines (AAPT and APT) with a dianhydride (6FDA) in two steps, as shown in Scheme 1. First, diamine and 6FDA were mixed in N,N-dimethylacetamide (DMAc) (solid content 15 wt %)



Figure 1. ¹H NMR spectra of monomer (a) AAPT and (b) APT in CDCl₃.



Figure 2. FTIR absorption spectra of PI(AAPT-6FDA) and PI(APT-6FDA).

under nitrogen to yield a viscous PAA solution. Then, chemical imidization was carried out by adding acetic anhydride and pyridine into the PAA solution to produce the polyimide. The desired structures of the polyimides were confirmed by FT-IR spectra, which showed the characteristic absorption peaks of the imide group at 1780 cm⁻¹ (asymmetrical stretching of carbonyl) and 1720 cm⁻¹ (symmetrical stretching of carbonyl), and the C–N bond at around 1370 cm⁻¹, as presented in Figure 2. Moreover, the desired formations of all polymers were confirmed by ¹H NMR, shown in Figure 3, and elemental analysis. The M_n values of PI(AAPT-6FDA) and PI(APT-6FDA) were 44900 and 31700 as determined by Gel Permeation Chromatography (GPC). Both polymers were readily soluble in common organic solvents such as tetrahydrofuran (THF), *N*,*N*-di-

methylformamide (DMF), DMAc, N-methylpyrrolidone (NMP), and chloroform. The high solubility may be attributed to the introduction of flexible ether linkages and hexafluoroisopropyl units in the polymer structure. The thermal stability of these two polyimides was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere (Figure S1, Supporting Information). The 1% weight-loss temperatures $(T_{d1\%})$ of PI(AAPT-6FDA) and PI(APT-6FDA) were determined to be around 517 and 514 °C, respectively. These PIs not only showed excellent thermal stability but also possessed high glass transition temperatures (Tg) of 276 and 252 °C for PI(AAPT-6FDA) and PI(APT-6FDA), respectively (see Figure S2, Supporting Information). The lower T_g of PI(APT-6FDA) than that of PI(AAPT-6FDA) also indicated the more twisted polymer backbone of the former. The excellent thermal stability of PIs is expected to meet the requirement of heat resistance in the electronics industry.

Optical and Electrochemical Properties. Figure 4 shows the UV-vis absorption spectra of the studied polyimides in THF solution and thin film state. PI(AAPT-6FDA) exhibits absorption peak maxima (λ_{max}) around 300 and 308 nm in solution and thin film states, respectively, while those of PI(APT-6FDA) are around 301 and 303 nm, respectively. The above absorption peaks are attributed to the π - π * transition delocalized along the π -electronic system. Besides, PI(AAPT-6FDA) apparently exhibits more intense absorption intensity in the wavelength above 350 nm as compared to PI(APT-6FDA) in thin film state. It indicates that the monomediated phenoxy linkage could have a better coplanarity than the dual-mediated one, in which the charges are transferred from the APT/AAPT to 6FDA via the linkage(s), when both polymer structures are alike.¹¹ As a result, the



Figure 3. ¹H NMR spectra of (a) PI(APT-6FDA) and (b) PI(AAPT-6FDA) in DMSO-d₆.



(Y) $E_{onset}^{OX} \sim 0.96 V$ $E_{onset}^{OX} \sim 0.90 V$ 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 Potential (V)

Figure 4. Optical absorption spectra of PI(AAPT-6FDA) and PI-(APT-6FDA) in THF solution and as thin films.

optical band gap (E_g^{opt}) of PI(AAPT-6FDA) and PI(APT-6FDA), estimated from the onset optical absorbance, are 3.15 and 3.55 eV, respectively. Therefore, the larger E_g^{opt} of PI(APT-6FDA) than that of PI(AAPT-6FDA) probably resulted from the more twisted conformation by introducing

Figure 5. Cyclic voltammograms of PI(AAPT-6FDA) and PI(APT-6FDA) on an ITO electrode in 0.1 M TBAP/acetonitrile solution with Ag/AgCl as reference electrode and Pt wire as counter electrode.

one more phenoxy linkage, which will be further discussed in the theoretical analysis section.

Figure 5 shows the cyclic voltammagram (CV) of PI-(AAPT-6FDA) and PI(APT-6FDA) films on ITO glass

using a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile. Both PI(AAPT-6FDA) and PI(APT-6FDA) exhibit reversible p-doping behavior during the anodic scan. The onset oxidation (E_{onset}^{ox}) of PI(AAPT-6FDA) and PI(APT-6FDA) is around 0.96 and 0.90 V vs Ag/Ag⁺, respectively, and thus, the highest occupied molecular orbital (HOMO) level is -5.32Note that the $E_{\text{ferrocene}}^{1/2}$ is 0.90 V vs Ag/Ag⁺, respectively, and thus, the estimated and -5.26 eV, respectively. Note that the $E_{\text{ferrocene}}$ 0.44 V from the CV measurement without any polymer film coated on ITO glass. Besides, the lowest occupied molecular orbital (LUMO) energy levels of PI(AAPT-6FDA) and PI(APT-6FDA) estimated from the difference between the optical band gap and HOMO energy are -2.17 and -1.71 eV, respectively. The result suggests that the frontier orbitals of PI(AAPT-6FDA) are more stabilized as compared to PI(APT-6FDA), and the additional twisted phenoxy linkages increased the LUMO energy level significantly, probably due to the nonlinear or twisted conformation of the polymer backbone.

Memory Device Characteristics of the Polymers. The memory effects of PI(APT-6FDA) and PI(AAPT-6FDA) are demonstrated by the current-voltage (I-V) characteristics of an ITO/polymer/Al sandwich device. The polymeric memory devices store data based on the high- (ON) and lowconductivity (OFF) response to the external applied voltages.¹ Figure 6 exhibits the typical I–V curves of the memory devices fabricated with PI(APT-6FDA) and PI-(AAPT-6FDA). For the case of PI(APT-6FDA) (see Figure 6a), the device is initially in the OFF state ("0" signal in data storage) with a current in the range of 10^{-12} – 10^{-14} A as the voltage swept from 0 to -3.5 V. When the voltage increases further, it induces an abrupt increase in current at a threshold voltage of about -3.5 V, as indicated by the transition from the OFF state to ON state ("1" signal in data storage). The ON/OFF current ratio of the studied memory device is as high as 10^9 , which leads 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 0 to -6 V (second sweep). The third sweep is conducted after turning off the power for about 4 min. The device can be reprogrammed, starting from the OFF state, to the ON state again with an accurate threshold voltage of -3.6 V and 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. Similar positive switching phenomena as in the negative sweep are also observed. After remaining in the ON state during the repeated negative sweep (the fourth sweep), the memory cannot reset to the OFF state by the continuous applied positive bias from 0 to 6 V (fifth sweep) and thus shows nonerasable switching behavior. However, after turning off the power for 4 min, the device can be reprogrammed to the ON state repeatedly with a threshold voltage of 3.8 V and similarly retain the ON state (the sixth and seventh sweeps). Hence, it could be concluded that the memory device possessed a "remnant", yet volatile, nature of the ON state because the stored data are finally lost.¹¹ This unstable ON state of the volatile memory device can be maintained by a refreshing voltage pulse of -1 V of 1 ms duration every 5 s (named the rf trace). The switching behavior indicates that the device is rewritable (over 20 sweeps) with small variations on threshold voltage and also can be written symmetrically and bidirectionally. The I-V curves exhibiting the volatile property can be measured in at least 10 devices with reproduced data. The stability of



Figure 6. Current-volatge (I-V) characteristics of (a) PI(APT-6FDA) and (b) PI(AAPT-6FDA) memory device.



Figure 7. Retention times on the ON and OFF states of the ITO/ PI(APT-6FDA)/Al device under a continuous readout voltage.

the memory effect was also evaluated under the same conditions.

Figure 7 shows the retention times and stress tests of both the ON and OFF states of PI(APT-6FDA). Initially, the memory device starts to turn ON or OFF to a high or low conductivity state. Under a constant stress of -1 V, no obvious degradation in current is observed for both ON and OFF states for at least 10^4 s during the readout test. The stimulus effect of read pulses on the ON and OFF state was also investigated for the long time test (Figure 8). The pulse period and width are 3 and 2 μ s, respectively, as shown in the inset of Figure 8. The PI(APT-6FDA) memory device is stable for at least 10^8 continuous read pulses of -1 V. Therefore, the switching behavior on remnant stored data and the volatile nature of memory device can explain the functionality of a SRAM.¹¹

Meanwhile, the electrical behavior of the PI(AAPT-6FDA) (only one phenoxy linkage between the TPA and 6FDA moieties) device was also studied as shown in Figure 6b. The I–V curve observed during the positive and negative sweep still keeps the volatile characteristics. As compared to the PI(APT-6FDA) device (two phenoxy linkages between the TPA and 6FDA moieties), the main difference is the short period of time for the retained ON state of the PI(AAPT-6FDA) device. Initially, the device is in the OFF state with quite a low current level of $10^{-11}-10^{-14}$ A. The transition from the OFF state to the ON state was observed with a bidirectional abrupt current



Figure 8. Stimulus effect of read pulses on the ON and OFF states of the ITO/PI(APT-6FDA)/Al device. The insert shows the pulse shapes in the measurement.

increase (the first or third and fifth sweep). Besides, the turn ON threshold voltage and ON/OFF current magnitudes in both electrical sweeps are also comparable. The third sweep is performed after turning the power for off for usually less than 30 s. The OFF state can be further recovered to a stored state again when the switching voltage was reapplied indicating that the memory device is rewritable. The short retention ability of the ON state determines the DRAM type of PI(AAPT-6FDA). This field-induced electronic transition is similar to the previous device based on the PI(TP6F).⁸ The volatile process can be repeated many times for 10 different cells with a reproducible switching as well. Different from the memory characteristics of PI(TP6F), PI(AAPT-6FDA) with a bidirectional writing property could not relax to the OFF state by a reverse bias. It suggests the effect of the conformational change induced by the phenoxy linkage on the memory characteristic. However, one phenoxy linkage between the TPA and 6FDA moieties cannot efficiently stabilize the CT complexes and thus exhibit the DRAM type memory behavior. In order to clarify the detailed converting mechanism, theoretical analysis was applied and discussed in the following section.

Proposed Switching Mechanism by Theoretical Analysis. Molecular simulation on the basic unit of PI(AAPT-6FDA) and PI(APT-6FDA) was carried out by DFT/B3LYP/6-31G(d) with the Gaussian 03 program.²⁷ The sketch map of the structures for the basic unit (BU) of PI(AAPT-6FDA) and PI(APT-6FDA) and optimized structures is plotted to the left of Figure 9. The trifluoromethyl groups of PIs are not included in the BU since these fragments do not have significant differences in electronic properties.^{8–11} The PI-(APT-6FDA) (represented as (L-D-L-A)_n) shows the more twisted conformation relative to the PI(AAPT-6FDA) (represented as (D-L-A)_n) due to the incorporation of the additional mediated noncoplanar geometry of phenoxy linkage. It also contributes to the blue-shifted absorbance of PI(APT-6FDA) than PI(AAPT-6FDA), as discussed above.



Figure 9. Electronic density contours of molecular orbitals and electrostatic potential surface (ESP) of the basic units: PI(AAPT-6FDA) and PI(APT-6FDA) memory devices.

The right part of Figure 9 shows the charge density isosurfaces of the basic unit of PI(AAPT-6FDA) and PI-(APT-6FDA) with the most energetically favorable geometry. The relative ordering of the occupied and virtual molecular orbitals gives a reasonable indication of the excited properties and charge transport ability. Both the HOMO and LUMO+2 isosurfaces tend to locate on triphenylamine (D), while the LUMO and LUMO+1 located on phthalimide (A). Besides, the HOMO and higher excited state (LUMO+1 and LUMO+2) are slightly distributed on the phenoxy linkages on PI(AAPT-6FDA) or PI(APT-6FDA). The electronic transition corresponds to promoting an electron from the ground state to the excited state. As the applied bias at threshold voltage, electrons at the HOMO with sufficient energy transit to LUMO+2 within TPA unit to give rise to excited state. CT can be observed to form the conductive complex through processes such as indirectly from the LUMO+2 to the LUMO+1 and then to the LUMO and also directly from the HOMO to LUMO. This indicates that the electron transfer subsequent to the excitation of the AAPT or APT moiety leads to the intra- or intermolecular CT state. Besides, the device switching to the ON state with a symmetrically comparable threshold voltage of either polarity also supports the switching mechanism of electric-field induced CT.^{9,11} As compared to the previous PI(BBPO) memory device¹¹ (oxadiazole moieties as relative donor and phthalimide as relative acceptor with two phenoxy linkages, (L-D-L-A)_n type and PI(APT-6FDA)) (replacement of the oxadiazole moieties by TPA) this also shows a similar SRAM performance. The slight difference is the threshold voltage since the overlapping of the HOMO with LUMO+1 and LUMO+2 at the oxadiazole units contributes more possibilities to be excited except for the CT from HOMO to the highest energy of LUMO+2. In the two distinct heterocyclic ring units, the action of the perpendicular electric field on the dihedral angle is shown to increase because of the inclusion of suitable functional groups.²⁸ CT is sensitive to the dihedral angle that creates a potential barrier along the molecules as the geometry varies to the more twisted one. Therefore, the CT occurs in the PI(APT-6FDA) device from TPA (D) to phthalimide(A) through the phenoxy linkages (L) followed by the modulation of conformation with an increased dihedral angle between the D and A units. The enhanced dihedral angle between the ground and excited states was also verified by theoretical calculation,¹¹ which agrees with the increase in torsional angle based on the action of a static electric field perpendicular to the ring-ring bond.²⁸ The phenoxy linkages are considered to be the suitable moiety on the whole systems as a mediator for the CT process with conformation changes of the molecules, which can increase the back CT energy barrier and possibly prevent the recombination of segregated charges. This electrical switching under the applied negative and positive threshold voltage is suggested to form a stable environment temporarily and store the transferred charges. It can prevent the charge from going back to the initial state even after the application of reverse bias.^{28,29} Finally, the PI(APT-6FDA) still relaxes to the initial conformation after the removal of the applied electric field for a short period of time. The dihedral angles between the ring moieties reduce to the original state, and also, the potential barriers of back CT disappear. Hence, the back CT occurs from the phthalimide to TPA (reset to the OFF state) and confirms the volatile switching behavior.

However, the PI(AAPT-6FDA) device provides only monomediated phenoxy linkage (L) between the D and A units indicating a more rigid and also less twisted structure relative to PI(APT-6FDA). The only one-mediated phenoxy linkage on PI(AAPT-6FDA) cannot induce enough potential barriers for the back CT since the other side can still contribute to the charge recombination through the D-A connection. Therefore, the unstable CT states lead to the DRAM behavior, which is the same as that of the memory device based on PI(TP6F)⁸ and PI(PYTPA).⁹ The positive and negative charges are segregated from the CT process and localized in the donor and acceptor under the electric bias. When the power is turned off, the unstable CT states rapidly return to the original OFF state. Combined with the remarkable difference in thin film state UV absorption, it suggests that the dual-mediated phenoxy linkages PI(APT-6FDA), similar to that reported for PI(BPPO), would more possibly form temporary electric field induced CT due to the larger inter- and intrachain twisting effects, while the phenoxy linkage of PI(AAPT-6FDA) with a less twisted conformation still makes it behave as PI(TP6F).⁸ Moreover, PI(APT-6FDA) and PI(AAPT-6FDA) show close theoretical dipole moments of 2.87 and 2.65 D, respectively. The smaller dipole moment compared to those of the sulfur containing PIs (around 6.00 D) probably leads to the unstable conductive complex. Both contributions make PI(APT-6FDA) a less volatile (but still with a volatile nature) memory device than PI(AAPT-6FDA). As a result, the memory devices based on PI(APT-6FDA) and PI(AAPT-6FDA) show SRAM and DRAM behaviors, respectively, and the CT mechanism can also be supported by our theoretical calculation.

Conclusions

We have successfully synthesized two new TPA-based polyimides, PI(AAPT-6FDA) and PI(APT-6FDA), for memory device application. The memory devices with the configuration of ITO/PI(APT-6FDA) or PI(AAPT-6FDA)/Al exhibited distinct volatile memory characteristics of SRAM and DRAM, respectively. Moreover, each memory device shows a high ON/OFF current ratio of 10⁹, a long retention time of 10⁴ s, and device-to-device switching uniformity. The theoretical analysis suggests that the CT mechanism could be used to explain the memory characteristics of the polyimides studied here. The weak dipole moment of the PI(AAPT-6FDA) and PI(APT-6FDA) provide an unstable CT complex for the volatile memory device. The dual-mediated phenoxy linkges of PI(APT-6FDA) led to the more twisted conformation compared to the monosubstituted PI(AAPT-6FDA) on the basis of theoretical analysis. It thus produced a potential barrier for delaying the back charge transfer (CT) process by the electric field and explained the SRAM characteristic. However, the PI(AAPT-6FDA) device makes a more volatile ON state because of the possible lack of the back CT barriers. Thus, the result provides the strategies for the design of functional PIs for advanced memory device applications.

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Supporting Information Available: Detailed syntheses and characterization of 4-iodo-4'-nitrodiphenyl ether (INE), *N*-(4-nitrophenyl)aniline, 4-nitro-4'-(*p*-nitrophenoxy)triphenylamine (NNPT), and 4,4'-bis(*p*-nitrophenoxy)triphenylamine (NPT), and TGA and DSC curves of PI(AAPT-6FDA) and PI(APT-6FDA) under nitrogen atmosphere. This material is free of charge via the Internet at http://pubs.acs.org.

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