Programmable digital nonvolatile memory behaviors of donor–acceptor polyimides bearing triphenylamine derivatives: effects of substituents

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Two aromatic polyimides bearing triphenylamine (TPA) derivatives with reasonably high molecular weights were synthesized: poly(4,4′,6-trimethyl-2,4,6-trimethylphenyl)-N,N-4,4′-diphenylene hexafluoroisopropylidenediphthalimide) (6F-TPA-Me3 PI) and poly(4-(dimethylaminophenyl)-N,N-4,4′-diphenylene hexafluoroisopropylidenediphthalimide) (6F-TPA-NMe2 PI). These polymers were thermally and dimensionally very stable, providing high-quality nanoscale thin films using a conventional solution coating process. The film densities, optical properties, and electrochemical properties were determined. The polymers displayed a different nonvolatile memory behavior that depended on the substituents of the TPA unit. The 6F-TPA-Me3 PI film showed a unipolar write-once-read-many-times (WORM) memory behavior, whereas the 6F-TPA-NMe2 PI film revealed unipolar and bipolar switching memory behavior. All PI films displayed excellent retention in both the OFF- and ON-states, even under ambient conditions. The ON/OFF current ratio was high, up to 108–109. All memory behaviors were governed by a mechanism that involved trap-limited space charge limited conduction and local filament formation. The memory characteristics may originate from the electron-donating TPA and substituents and from the electron-accepting hexafluoroisopropylidinyl and imide units in the polymer backbone, which acted as effective charge-trapping sites. The film density was found to significantly influence the memory behavior. This study demonstrated that the thermally and dimensionally stable 6F-TPA-Me3 and 6F-TPA-NMe2 PIs are suitable active materials for the low-cost mass production of high-performance programmable memory devices that can be operated with very low power consumption. Moreover, the memory mode and its polarity may be tuned by changing the substituent on the TPA unit.

Introduction

The world market for nonvolatile memory devices has grown rapidly as the demand for mobile devices has increased.3 Higher density nonvolatile memory devices are in high demand for the storage of multimedia data, such as videos. Polymer materials generally exhibit easy processability, good flexibility, high mechanical strength, and good scalability. Their properties can be easily tailored through chemical synthesis. Moreover, polymers can be processed at low costs and are easily incorporated into the multi-stack layer structures fabricated for high-density memory devices. Significant research efforts have been applied toward the development of advanced materials with properties and processability that meet the production requirements for nonvolatile memory devices.5–6 The high-performance polymers based on aromatic polyimides (PIs) under development yield several advantages, including excellent mechanical properties, high thermal stability, high dimensional stability, good planarization, good adhesion, high hydrolytic stability, high chemical resistance, and long-term stability.7–10 Several PIs have been introduced as the active materials in nonvolatile memory devices.11–14 For example, poly(4,4′-aminotriphenylene hexafluoroisopropylidenediphthalimide) (6F-TPA PI) displays electrically bistable ON and OFF switching behavior in a volatile memory mode (i.e., dynamic random access memory (DRAM)) rather than in a nonvolatile memory mode.11 In contrast, poly(4,4′-amino(4-hydroxyphenyl) diphenylene hexafluoroisopropylidenediphthalimide) (6F-TPA-OH PI) (the backbone of which is identical to that of 6F-TPA PI except for the presence of an additional hydroxyl substituent per chemical repeat unit) exhibited permanent nonvolatile memory...
behavior (i.e., write-once-read-many-times (WORM) memory) rather than volatile DRAM behavior.\textsuperscript{12} These results suggested that the electrically bistable memory characteristics of a polymer depend heavily on its chemical components. An understanding of the chemical components and their role in the memory characteristics is, therefore, essential for the development of advanced polymers for high performance nonvolatile memory devices. Bistable memory characteristics have not, however, been extensively investigated.

Here, we report the effects of substituents on the electrical memory characteristics of 6F-TPA PI analogs prepared from two different triphenylamine (TPA) derivatives: poly(N-(2,4, 6-trimethylphenyl)-N,N-4,4'-diphenylene hexafluorosopropylidenediphtalimide) (6F-TPA-Me\textsubscript{3} PI) and poly(N-(4-dimethylaminophenyl)-N,N-4,4'-diphenylene hexafluoroisopropylidenediphtalimide) (6F-TPA-NMe\textsubscript{2} PI) (Fig. 1a). These PIs exhibited various types of memory behavior, namely, unipolar WORM and ON/OFF switching-type memory and bipolar ON/OFF switching type memory, depending on the incorporated substituents. The underlying switching mechanism was investigated, and the interfaces between the PI films and the metal electrodes in devices were examined.

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**Results and discussion**

6F-TPA-Me\textsubscript{3} PI in thin films showed the longest absorption maximum peak around 342 nm (=\(\lambda_{\text{max}}\)) in the UV-vis spectrum (Fig. 2a). Similar absorption peak was observed for 6F-TPA-NMe\textsubscript{2} PI (Fig. 2b). From the measured UV-vis spectra, the band gap (which is the difference between the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level) was estimated to be 3.15 eV for 6F-TPA-Me\textsubscript{3} PI and 3.07 eV for 6F-TPA-NMe\textsubscript{2} PI.

6F-TPA-Me\textsubscript{3} PI was found to have an oxidation halfwave potential (E\textsubscript{1/2}) of 0.38 V vs. Ag/AgCl (Fig. 2A). For 6F-TPA-NMe\textsubscript{2} PI, the E\textsubscript{1/2} was measured to be 0.32 V vs. Ag/AgCl (Fig. 2B). The external ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) redox standard potential E\textsubscript{1/2} was measured to be 0.43 V vs. Ag/AgCl in acetonitrile. Assuming that the HOMO level for the Fc/Fc\textsuperscript{+} standard is -4.80 eV with respect to the zero vacuum level, from the measured E\textsubscript{1/2} and band gap data the HOMO and LUMO levels were calculated to be -4.75 and -1.60 eV for 6F-TPA-Me\textsubscript{3} PI, and -4.68 and -1.61 eV for 6F-TPA-NMe\textsubscript{2} PI respectively.

The PI films in contact with metal electrodes and silicon substrates (Fig. 1c) were studied by synchrotron XR analysis. Representative XR profiles of the PI films are shown in Fig. 3. All XR data were satisfactorily fit using Parratt’s fitting algorithm.\textsuperscript{15,16} The analysis results are summarized in Table 1. PI films deposited on the silicon substrates revealed a surface roughness of only 0.5 nm, indicating that both PI polymers provided high-quality thin films via conventional solution coating and a subsequent drying process. The electron density \(\rho_e\) was measured to be 390.1 nm\textsuperscript{3} for 6F-TPA-Me\textsubscript{3} PI and 400.7 nm\textsuperscript{3} for 6F-TPA-NMe\textsubscript{2} PI. These results indicated that the 6F-TPA-Me\textsubscript{3} PI film electron density was slightly lower than that of the 6F-TPA-NMe\textsubscript{2} PI. These \(\rho_e\) values agreed with those measured for the PI films deposited on Al bottom electrodes. These results collectively indicated that no aluminium atoms or ions diffused into the PI film layers during the PI film deposition.

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**Fig. 1** (a) Chemical structures of aromatic polyimides bearing two triphenylamine derivatives: 6F-TPA-Me\textsubscript{3} PI and 6F-TPA-NMe\textsubscript{2} PI. (b) A schematic diagram of the memory devices fabricated with nanoscale thin films of the PIs and aluminium (Al) top and bottom electrodes. (c) Schematic diagrams of three types of samples for X-ray reflectivity measurements.

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**Fig. 2** UV-vis spectra and CV responses of the PI films which were coated on quartz substrates and fabricated with Au electrodes supported by silicon substrates respectively: (a,A) 6F-TPA-Me\textsubscript{3} PI and (b,B) 6F-TPA-NMe\textsubscript{2} PI. The CV measurements were carried out in aqueous 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile using an electrochemical workstation (IM6ex impedance analyzer) with a platinum gauze counter electrode and an Ag/AgCl (3.8 M KCl) reference electrode. A scan rate of 100 mV s\textsuperscript{-1} was used.
6F-TPA-Me₃ PI and (b) 6F-TPA-NMe₂ PI. The symbols are the measured data and the solid line represents the fit curve assuming a homogeneous electron density distribution within the film. The inset shows a magnification of the region around the two critical angles: a and c, are the critical angles of the film and the substrate (silicon or Al electrode, respectively).

In light of the above results, devices in a simple Al/PI (30 nm thick)/Al sandwich structure were fabricated using the PI polymers, and the current–voltage (I–V) characteristics were investigated. The measured I–V profiles are shown in Fig. 4. The measured value was found to be 841.8 ± 0.3 nm/C₀, larger than that of aluminium. These results collectively indicated that a thin aluminium oxide layer formed on top of the PI films coated on the silicon substrates. The roughness of the layer in contact with air, lower or upper layer, was 0.7 nm. Its roughness value was found to be comparable to the surface roughness values of the PI films coated on top of the Al bottom electrodes during deposition of the PI films onto the Al top electrodes. Finally, the XR analysis data for the Al mixed layer (which is due to the roughness of interface) for PI/Al systems, respectively indicated that a thin aluminium oxide layer formed on top of the Al bottom electrodes during deposition of the PI films onto the Al top electrodes. The Al top electrodes deposited on the PI films also revealed the presence of an interlayer. The thickness of the Al top electrodes under vacuum. Furthermore, the results suggested that such a thin interfacial layer arose from the mechanical mixing between the PI film with a surface roughness and the aluminium or oxide. These results indicated that aluminium oxide did not form at the interface between the PI films and the Al bottom electrodes (which is due to the roughness of interface) for PI/Al systems, respectively indicated that a thin aluminium oxide layer formed on top of the Al bottom electrodes during deposition of the PI films onto the Al top electrodes. 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as-fabricated 6F-TPA-Me3 PI film initially exhibited a high resistance (OFF-state). However, this PI polymer revealed an abrupt increase in the current at −2.2 V (which corresponded to the critical voltage $V_{c,ON}$ for switching on the device) upon application of a negative voltage with a current compliance of 0.01 A (Fig. 5a). This OFF-to-ON transition in a memory device corresponds to a writing process. The ON-state was preserved, even after the power was turned off or during reverse and forward voltage sweeping with a current compliance of 0.01 A or lower or higher (Fig. 5a). A similar OFF-to-ON transition was observed upon application of a positive voltage to the polymer film (Fig. 5A). These results collectively indicated that 6F-TPA-Me3 PI exhibited unipolar WORM memory behavior. The ON/OFF current ratio was measured to be $10^{7}$–$10^{8}$, depending on the compliance current and the reading voltage.

The as-fabricated 6F-TPA-NMe2 PI film was also initially in an OFF-state. Application of a negative voltage of less than −4.0 V, along with a current compliance of 0.01 A to switch the device on, produced an abrupt increase in the device current at −3.2 V ($= V_{c,ON}$) (Fig. 5b). Once the PI polymer had reached an ON-state, it remained in that state even after the power had been turned off or during sequential forward voltage sweeps under a current compliance of 0.01 A. We note, however, that in the ON-state, the device could be switched off by applying a negative voltage with a current compliance of 0.1 A (which was higher than that chosen for the switching-ON process). Subsequent application of a negative voltage with a current compliance of 0.1 A produced an abrupt decrease in the device current near −0.8 V, indicating that the device underwent a sharp electrical transition from the ON-state to the OFF-state. Similar ON and OFF switching behavior was observed for the device during positive voltage sweeps under variable compliance current (Fig. 5B). These results informed that 6F-TPA-NMe2 PI exhibited unipolar switching memory behavior, which differed significantly from the WORM memory behavior observed for the 6F-TPA-Me3 PI. The ON/OFF current ratio was $10^{5}$–$10^{9}$, depending on the turn-on compliance current and the reading voltage.

The 6F-TPA-NMe2 PI films further revealed bipolar ON–OFF switching behavior. Application of a negative voltage between 0 V and −4.0 V with a current compliance of 0.01 A switched on the PI polymer at −3.1 V (Fig. 5c). The ON-state remained present even after the power had been turned off. Moreover, the ON-state persisted during the second voltage sweep from 0 V to −4.0 V with the same compliance current. The PI polymer did return to the OFF-state at +0.8 V during the reverse voltage sweep with a compliance current of 0.1 A. Similar bipolar switching behavior was also observed for the positive voltage sweeps and the subsequent negative voltage sweeps (Fig. 5C).

The stabilities of the ON- and OFF-states in the devices were examined at room temperature under ambient conditions using a reading voltage of +1.0 V. Once the 6F-TPA-Me3 PI film had been switched to the ON-state by applying a voltage of +3.0 V with a compliance current of 0.01 A, the ON-state persisted without degradation for a test period of $10^{4}$ s (Fig. 6a). The OFF-state also persisted without degradation for the duration of the test period (Fig. 6a). A similar ON-state stability was observed for the 6F-TPA-NMe2 PI film (Fig. 6b). Switching of the 6F-TPA-NMe2 PI film ON-state back to the OFF-state upon application of a voltage of −1.5 V with a compliance current of 0.1 A also yielded a stable persistent OFF-state without degradation for the duration of the test period (Fig. 6b).
devices functioned properly after storage under ambient conditions for 2 years. Overall, the devices exhibited excellent reliability, even under ambient conditions.

The electrical switching characteristics and the current conduction mechanisms of the PI films in the devices were investigated by further analyzing the measured $I$–$V$ data using various conduction models. This data analysis showed that the $I$–$V$ data for the OFF-states of both PI polymers could be satisfactorily fit using the trap-limited space charge limited conduction (SCLC) model (Fig. 7a and A), and the $I$–$V$ data for the ON-states could be satisfactorily fit using the ohmic conduction model (Fig. 7b and B). Furthermore, the current levels of the devices in the ON-state were independent of the device cell size, indicative of heterogeneous local filament formation. These results suggest that the excellent nonvolatile memory behavior of the 6F-TPA-Me3 and 6F-TPA-NMe2 PI films was governed by trap-limited SCLC and local filament formation.

The influence of the turn-on compliance current on the turn-off current was investigated by testing the 6F-TPA-NMe2 PI devices as a function of the turn-on compliance current. This analysis found that as the turn-on compliance current increased, the current required to switch off the device increased (Fig. 8). In addition, the resistance of the ON-state decreased as the turn-on compliance current increased. The turn-ON and turn-OFF voltages did not vary significantly with the turn-on compliance current. These results could be explained under the following considerations. As the turn-on compliance current was increased, additional carriers became trapped in the active PI film layer in the device before the transition from the OFF-state to the ON-state. This trapping of carriers increased the number of conducting pathways, which increased the turn-off current. Thus, a fixed turn-on compliance current should yield a constant turn-off current. To test this, the reliabilities of the ON- and OFF-voltages and the turn-off current at a fixed turn-on compliance current (0.01 A) were tested by repeating the switching process. Under a positive bias, the ON- and OFF-voltages as well as the turn-off current did not vary significantly for a constant turn-on compliance current. Similar switching behavior was observed in the negative voltage sweeps (data not shown). These results indicate that the current-controlled electrical switching behavior observed in the 6F-TPA-NMe2 PI could be described in terms of the local filament formation theory.

The charge trapping sites in the active PI film layers may depend on the chemical composition of the polymer. The two PIs studied here had identical backbones. Along the polymer backbone, the TPAs units, imide carbonyl oxygens, and hexafluoroisopropylidenyl fluorines can act as electron donors and, thus, as nucleophilic sites. In contrast, the imide carbonyl carbons and hexafluoroisopropylidenyl carbon can act as electron acceptors and, thus, as electrophilic sites. 6F-TPA-Me3 PI additionally includes three methyl substituents per TPA unit as electron donors with a moderate power. The methyl substituents could potentially strengthen the nucleophilicity of the TPA unit rather than act as nucleophilic sites. 6F-TPA-NMe2 PI included

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**Fig. 6** Retention times of the ON- and OFF-state of the Al/PI (30 nm thick)/Al devices, as probed with a reading voltage of +1.0 V: (a) 6F-TPA-Me3 PI and (b) 6F-TPA-NMe2 PI.

**Fig. 7** Experimental (symbols) and fitted (solid lines) $I$–$V$ curves for the Al/PI (30 nm thick)/Al devices: (a,A) OFF-state with the ohmic (below 0.8 V) and the trap-limited SCLC (above 0.8 V) model and (b,B) ON-state with the ohmic current model.

**Fig. 8** On-state resistance and the turn-off current of the devices fabricated with 6F-TPA-NMe2 PI as a function of the turn-on compliance current. The current needed to turn off the device increases, whereas the resistance of the ON-state decreases with increases in the turn-on compliance current. In these measurements, a current compliance of 0.1 A was set for switching the device off.
an additional dimethylamine substituent per TPA unit. Such dimethylamine substituents are relatively good electron donors. Furthermore, they can act as charge delocalization sites (i.e., resonance sites) in conjunction with the linked aromatic ring, thereby acting as nucleophilic sites. These nucleophilic and electrophilic groups may act as charge-trapping sites in the PI film layers. Filaments form from these charge-trapping sites in polymer films under an electrical field (i.e., application of a voltage), and their response to the current flow is mainly due to charge hopping between the charge-trapped sites localized in the intra- and intermolecular PI chains in the conduction paths (i.e., filaments).

The energy barrier for hole injection from the Al electrode (with a work function $\Phi$ of $-4.28$ eV) to the active PI film layer (HOMO level) was estimated to be 0.47 eV for 6F-TPA-Me$_3$ PI and 0.40 eV for 6F-TPA-NMe$_2$ PI. The energy barrier for electron injection from the electrode to the active PI film layer (LUMO level) was estimated to be 2.68 eV for the 6F-TPA-Me$_3$ PI and 2.67 eV for 6F-TPA-NMe$_2$ PI. Overall, the PI films showed a lower energy barrier for hole injection than that for electron injection. These results suggested that the conduction processes in the devices were dominated by hole injection.

In comparison, the energy barrier for hole injection was slightly higher for 6F-TPA-Me$_3$ PI than for 6F-TPA-NMe$_2$ PI. Thus, one could expect that in the device, the 6F-TPA-Me$_3$ PI film required a higher $V_{c,ON}$ than the 6F-TPA-NMe$_2$ PI film. Contrary to expectations, the measured $V_{c,ON}$ was lower for the 6F-TPA-Me$_3$ PI film than for the 6F-TPA-NMe$_2$ PI film (Fig. 5). A similar situation was reported for the 6F-TPA and 6F-TPA-OH PIs in devices fabricated with Al top and indium-titanium oxide (ITO) bottom electrodes.$^{11,12}$ The 6F-TPA PI (50 nm thick) with a lower energy barrier of 0.33 eV revealed a $V_{c,ON} = +3.2$ V whereas the 6F-TPA-OH PI (54 nm thick) with the energy barrier of 0.46 eV yielded $V_{c,ON} = +2.7$ V. These results collectively suggested that differences in the energy barriers of the active polymer layers on the electrode could not solely reflect differences in the critical switching-ON voltages.

Interestingly, the PIs of our study demonstrated different memory behavior, depending on the electron-donating substituents of the TPA unit even though they had identical polymer backbones. 6F-TPA-Me$_3$ PI exhibited unipolar WORM memory behavior, as discussed above. The unipolar WORM memory behavior was similar to that observed for 6F-TPA-OH PI$^{14}$ but quite different from the DRAM characteristics observed for 6F-TPA PI.$^{11}$ These results collectively suggest that the three electron-donating methyl substituents played a similar role as the electron-donating hydroxyl substituent, that is, significantly changing the memory behavior of 6F-TPA PI. Such electron-donating substituents may increase the nucleophilicity of the TPA unit. The TPA units with enhanced nucleophilicity may provide more effective charge-trapping sites, thereby improving the instabilities in the memory behavior of 6F-TPA PI.

On the other hand, the 6F-TPA-NMe$_2$ PI showed unipolar and bipolar switching memory behavior that differed significantly from the WORM memory behavior observed for 6F-TPA-Me$_3$ PI and 6F-TPA-OH PI and from the DRAM behavior of 6F-TPA PI. The dimethylamine substituent included one nitrogen atom with a lone electron pair and two methyl groups, which strengthened the electron-donating capacity relative to the methyl group. Thus, this substituent significantly increased the nucleophilicity of the TPA unit. Moreover, the nitrogen atom contributed to the aromatic resonance in the substituted phenyl ring of the TPA unit. These two factors cooperated to yield a strong charge-trapping site at the dimethylamine substituent, thereby increasing the charge-trapping sites in the PI film. The 6F-TPA-NMe$_2$ PI film also presented a slightly larger electron density (400.7 nm$^{-2}$) than that (390.1 nm$^{-2}$) of the 6F-TPA-Me$_3$ PI film. These results confirmed that the 6F-TPA-NMe$_2$ PI film had a higher concentration of charge-trapping sites compared to the 6F-TPA-Me$_3$ PI film. Such a high concentration of charge-trapping sites shortened the interdistance between the charge-trapping sites, thereby providing better conduction paths upon application of an electric field to the PI film. These properties of the dimethylamine substituent significantly ameliorated the instabilities associated with the memory behavior of the 6F-TPA PI as well as the permanent nonvolatile memory behavior of the 6F-TPA-Me$_3$ and 6F-TPA-OH PIs.

Conclusions

We synthesized two aromatic PIs bearing TPA derivatives with reasonably high molecular weights: 6F-TPA-Me$_3$ and 6F-TPA-NMe$_2$ PIs. These polymers showed high thermal and dimensional stabilities compared to conventional aromatic PIs. The polymers produced high-quality nanoscale thin films with smooth surfaces via conventional solution coating processes. The film densities (i.e., electron densities), as well as the HOMO and LUMO levels, were determined.

The Al/PI/Al devices initially exhibited a high resistance (OFF-state). During positive and negative voltage sweeps, the PIs exhibited different nonvolatile memory behaviors depending on the substituents of the TPA unit. The 6F-TPA-Me$_3$ PI film showed unipolar WORM memory behavior, whereas the 6F-TPA-NMe$_2$ PI revealed unipolar and bipolar switching memory behavior. All PI films revealed excellent retention of both the OFF- and ON-states, even under ambient conditions. The films also exhibited high ON/OFF current ratios up to $10^6$–$10^9$.

The memory behavior was found to be governed by a mechanism involving trap-limited SCLC and local filament formation. The unipolar WORM memory characteristics of the 6F-TPA-Me$_3$ PI originated from the electron-donating power of the triphenylamine unit enhanced by three methyl substituents in addition to the hexafluoroisopropylidene and imide units in the polymer backbone, which acted as effective charge-trapping sites. In comparison, the unipolar and bipolar switching memory characteristics of the 6F-TPA-NMe$_2$ PI may be attributed to the dimethylamine substituents to act as charge-trapping sites and to enhance the electron-donating power of the TPA unit in addition to the charge-trapping hexafluoroisopropylidene and imide units in the polymer backbone. This study additionally found that the film density significantly affected the observed memory behavior. Larger film density yielded a higher concentration of charge-trapping sites. Such highly concentrated charge-trapping sites shorten the interdistance of the charge-trapping sites, providing better conduction paths under application of an electric field to the active polymer film.
Furthermore, the substituents influenced the HOMO and LUMO levels of the 6F-TPA PI. Thus, the energy barrier for charge injection in the PI depended on the substituents. A lower energy barrier requires a higher critical switching-ON voltage however, which suggests that the critical switching-ON voltages of the active PI films depended on other factors in addition to the energy barriers in the electrode.

Overall, this study demonstrated that the thermally dimensionally stable 6F-TPA-Me3 and 6F-TPA-NMe2 PIs are suitable active materials for the low-cost mass production of high-performance programmable memory devices with or without polarity that can be operated with very low power consumption, a high ON/OFF current ratio, and a high thermal and dimensional stability. Moreover, the memory mode could be tuned by changing the substituents on the TPA unit.

**Experimental section**

6F-TPA-Me3 PI was prepared from hexafluoroisopropyldenediphthalic anhydride (6F) and 4,4'-diamino-2',4',6'-tri(methyltriphenylamine (TPA-Me3) as described in the literature. In a similar manner, 6F-TPA-NMe2 PI was synthesized from the polymerization of 6F' with 4,4'-diamino-4'(dimethylamino)triphenylamine (TPA-NMe2). For the obtained PIs, the inherent viscosities were determined at 0.5 g dL⁻¹ concentration using a Tammson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (one column, MIXED-D from Polymer Laboratories) connected with a refractive index detector from Schambeck SFD Gmbh, which was calibrated with polystyrene standards. The GPC analysis was performed at a flow rate of 1 mL min⁻¹ at 70 °C using N,N-dimethylformamide (DMF) as the eluent. The inherent viscosities were determined to be 0.48 g dL⁻¹ for 6F-TPA-Me3 PI and 0.53 g dL⁻¹ for 6F-TPA-NMe2 PI. The 6F-TPA-Me3 PI was determined to have a weight-average molecular weight (Mw) of 121 000 and a polydispersity index (PDI) of 1.69 by GPC analysis. Thermal properties were measured at a heating rate of 20 °C min⁻¹ in nitrogen atmosphere using a thermogravimetric analyzer (Perkin-Elmer Pyris 1 TGA), a differential scanning calorimeter (Perkin-Elmer Pyris Diamond DSC), and a thermo-mechanical analyzer (Perkin-Elmer TMA 7). The 6F-TPA-Me3 PI was found to reveal a glass transition temperature Tg of 338 °C and a 10 wt% weight loss at 550 °C (=Td,10 degradation temperature). The 6F-TPA-NMe2 PI was found to reveal 336 °C Tg and 595 °C Td,10.

Optical properties were measured using an ultraviolet-visible (UV-vis) spectrometer (Scinco model S-3100). Cyclic voltammetry (CV) was carried out in 0.1 M tetrabutylammonium tetrakisfluoroborate in CH3CN (acetoniitrile) by using an electrochemical workstation (IM6ex impedance analyzer) with a platinum gauze counter electrode and an Ag/AgCl (saturated KCl) reference electrode, and the polymer was coated on the gold (Au) electrode deposited on the silicon substrate. A scan rate of 100 mV s⁻¹ was used.

For fabricating memory devices, homogeneous solutions of each PI were prepared by dissolving the polymer (1 wt%) in cyclopentanone. The resulting solutions were filtered through PTFE-membrane micro filters with a pore size of 1.0 μm. Thin PI films of about 30 nm thickness were prepared from the filtered solutions by spin-coating onto bottom electrodes at 2000 rpm for 60 s, followed by drying on a hot plate at 80 °C in vacuum for 1 day. The resulting film thickness was determined by using a spectroscopic ellipsometer (model M2000, Woollam). Aluminium (Al) bottom electrodes with a thickness of 300 nm were prepared on glass substrates by electron-gun sputtering while Al top electrodes with a thickness of 300 nm were deposited onto the polymer films through a shadow mask by thermal evaporation, with a size of 2.0 × 2.0 to 0.5 × 0.5 mm² (Fig. 1b). Current–voltage (I–V) measurements were carried out using a Keithley 4200-SCS semiconductor analyzer and a probe station equipped with a heating stage. In all cases, bias voltage was applied with respect to the bottom electrode. All electrical experiments were conducted without any device encapsulation either in ambient condition or in nitrogen atmosphere.

For X-ray reflectivity (XR) experiments, three kinds of samples were prepared for each polymer: (a) 30 nm thick PI films on silicon (Si) substrates with native oxide layer; (b) 30 nm thick PI films on the 10 nm thick Al or Au electrodes which were deposited on Si substrates by electron-beam sputtering and (c) thermally evaporated 10 nm thick Al electrodes on the 30 nm thick PI films coated onto Si substrates (Fig. 1c). XR data were measured at the 3C2 beamline of the Pohang Light Source. Samples were mounted on a Huber four-circle goniometer, and a scintillation counter with an enhanced dynamic range (Bede Scientific, EDR) was used as a detector. The measured reflected intensities were normalized to the intensity of the incident beam, which was monitored using an ionization chamber.

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