

Thermally stable and high ON/OFF ratio non-volatile memory devices based on poly(triphenylamine) with pendent PCBM†

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High ON/OFF ratio electrically bistable non-volatile WORM memory devices were prepared based on poly(triphenylamine) with different amounts of pendent PCBM. With the introduction of 10 wt% PCBM into P-TPA via covalent bonding, a memory device with low switching-ON voltage (0.9 V) and high ON/OFF ratio (10^9) could be obtained. The device performance remained satisfactory under the heating condition up to 100 °C which is beneficial to maintain device stability for computer application when other components produce heat.

Nowadays, organic polymers are attracting much interest in the development of optoelectronic devices such as light-emitting diodes, transistors, solar cells, electrochromic (EC) devices, and memory devices due to their advantages of low cost, lightweight, solution processability, and availability of structural varieties.¹ Among the several kinds of polymer-based electronics, polymeric nonvolatile switching memory devices have emerged as a promising next generation memory device.² Compared with conventional inorganic memory materials, polymeric memory materials store information in the form of high (ON) and low (OFF) current state instead of storing the amount of charges in a cell of silicon devices. In addition, polymeric memory materials offer higher data storage density, ease of miniaturization, longer data retention time, faster speed, and lower power consumption for practical use.³ Thus, polymeric materials with electrical bistability resulting from conductivity difference in response to the applied electric field begin to stand out conspicuously because they are able to overcome the problems and challenges in scaling down from micro-scale to nano-scale.

Although there are numerous kinds of polymers used in memory devices, they are generally classified into four categories: conjugated polymers,⁴ polymers with pendent electroactive chromophores,⁵ functional polyimides,⁶ and hybrid composites.⁷ Among these

categories, hybrid composites were widely used in memory device applications owing to their excellent mechanical properties and interesting memory behaviors. In the beginning, polymers were just used as matrix materials for small molecules.⁸ Supplementary components such as organic molecules or metal particles in the polymer matrix were utilized as electron donors or electron acceptors to produce charge transfer complex formation.⁹ Afterwards, the electro-active molecules such as carbon nanotubes (CNTs)¹⁰ and graphene oxide¹¹ were blended into the “donor-containing polymer” matrix to investigate the resulting memory behavior. Recently, PCBM containing hybrid films were widely used as the active layer in memory applications.¹² At this stage, the design of polymer chemical structure plays a very significant role. Furthermore, the domain size of the supplementary material in the polymer matrix is also key to nano-scale memory devices.

Triphenylamine (TPA) and its derivatives are well-known candidates for hole transport materials in organic photo-electronic devices due to their stable radical cations and good hole-mobility.¹³ Besides, TPA-based polymers with good thermal stability are not only used as the hole-transport layer in electroluminescent devices but also widely investigated in the fields of electrochromic¹⁴ and memory applications.¹⁵ In our previous study, memory devices were fabricated by blending PCBM, as the acceptor, with donor-containing poly-4-methoxytriphenylamine (P-TPA).^{12a} The memory devices with the configuration of ITO/PCBM:P-TPA/Al exhibited both dynamic random access memory (DRAM) and write-once-read-many-times (WORM) properties controlled by the concentration of PCBM. The strong interaction between PCBM and TPA could be a result of well-dispersed PCBM clusters within PCBM:P-TPA hybrid films. The obtained hybrid films revealed bistable WORM behavior at higher concentration up to 10 wt% PCBM. However, when compared with the high ON/OFF ratio of 5 wt% PCBM:P-TPA, the memory device using 10 wt% PCBM:P-TPA showed much lower ON/OFF ratio.

In this article, we introduced PCBM into donor-containing P-TPA via covalent bonding to further enhance uniform dispersion of PCBM with a high weight fraction as shown in Fig. 1. Poly-(triphenylamine) with pendent PCBM was expected to have different

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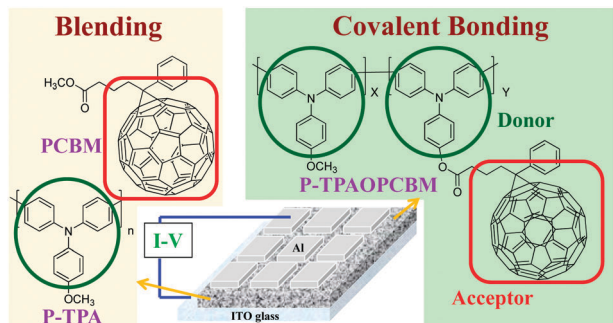


Fig. 1 Chemical structures of active layers and schematic diagram of the memory device.

memory properties compared to blending hybrid composites, such as switching-on voltage and operation stability, under thermal treatment. The starting materials, 4-hydroxy-triphenylamine (OHTPA) and phenyl-C61-butyric acid (PCBA), were prepared according to previous literature.¹⁶ A novel monomer TPAOPCBM was synthesized by esterification of PCBA with OHTPA in the presence of 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC) and 4-dimethylaminopyridine (DMAP) as shown in Fig. 2. Addition of DMAP could accelerate the EDC-activated esterification of carboxylic acids and eliminate side reactions even for sensitive acids.¹⁷ The new compound TPAOPCBM was further utilized to synthesize polymers **P-TPAOPCBM5** and **P-TPAOPCBM10** with different amounts of 4-methoxy-TPA *via* oxidative coupling reaction. For detailed synthetic procedures and characterization of TPAOPCBM and polymer **P-TPAOPCBM**, please refer to the ESI.†

The resulting memory characteristics of **P-TPAOPCBM5** and **P-TPAOPCBM10** hybrid films were investigated using the current-voltage (*I*-*V*) characteristics of an ITO/hybrid film/Al sandwich device and compared with those of 5 wt% and 10 wt% **PCBM:P-TPA** blending composites, respectively, as shown in Fig. 3. Within the sandwich device, the polymer film was used as an active layer between Al and ITO as the top and bottom electrodes as shown in Fig. 1. To avoid the thickness of the polymer film affecting memory properties, a standard thickness (50 nm) was defined. Fig. 3(a) demonstrates the *I*-*V* result of **P-TPAOPCBM5** which was measured in steps of 0.1 V with 0.01 A compliance current. During the first negative sweep from 0 V to -6 V, the device stayed in the low-conductivity (OFF) state with a current range

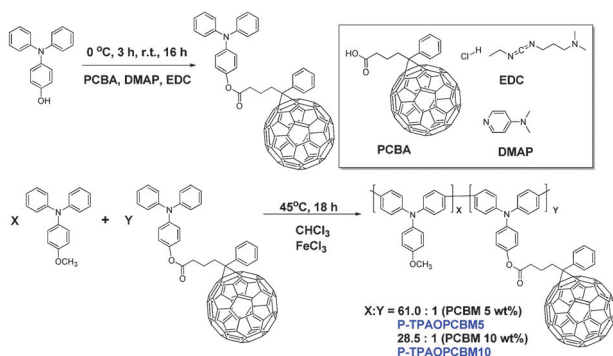


Fig. 2 Synthesis procedures.

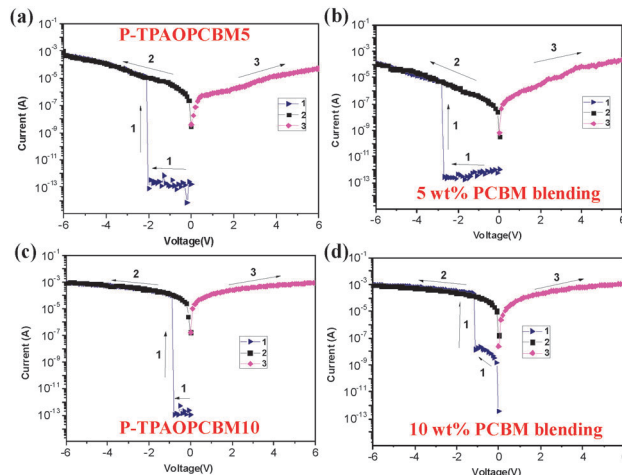


Fig. 3 Current-voltage (*I*-*V*) characteristics of memory devices with the active layers (a) **P-TPAOPCBM5**, (b) 5 wt% **PCBM:P-TPA** blending, (c) **P-TPAOPCBM10** and (d) 10 wt% **PCBM:P-TPA** blending.

10^{-12} – 10^{-13} A initially, and then the current increased abruptly from 10^{-13} to 10^{-5} A (high-conductivity state) at the threshold voltage of -2.0 V, indicating the transition from the OFF state to the high-conductivity (ON) state. In a memory device, this OFF-to-ON transition can be defined as a “writing” process. The device remained at the ON state during the subsequent negative scan (the second sweep) and then positive scan (the third sweep). Once the memory device reached the ON state, it remained there even after power was turned off for 1 hour or longer. These results indicate that the device derived from the **P-TPAOPCBM5** film exhibits non-volatile WORM memory behavior. Fig. 3(b) depicts the *I*-*V* results of 5 wt% **PCBM:P-TPA**, which exhibits the same WORM property. Compared to introduction of **PCBM** into **P-TPA** *via* covalent bonding, 5 wt% **PCBM:P-TPA** prepared by the blending method revealed slightly higher switching-on voltage (-2.8 V).

The electrical characteristics of **P-TPAOPCBM10** and the 10 wt% **PCBM:P-TPA** blending composite are shown in Fig. 3(c) and (d), respectively. **P-TPAOPCBM10** has lower switching-on voltage (0.9 V), and exhibits much higher ON/OFF ratio (10^9) than the 10 wt% blending composite (10^4). Therefore, the memory device of **P-TPAOPCBM** possesses low power consumption and misreading can be easily avoided in practical applications. In order to further investigate the stability of the WORM memory characteristic of hybrid composites, **P-TPAOPCBM10** and the 10 wt% **PCBM:P-TPA** blending composite were chosen for heat treatment at 100 °C after switching to ON state and the results are depicted in Fig. 4. Fig. 4(a) demonstrates that the ON state of the 10 wt% **PCBM:P-TPA** blending composite recovered to the original OFF state after treatment at 100 °C due to back charge transfer. However, the memory device of **P-TPAOPCBM** remained in the high conductivity state even after thermal treatment as shown in Fig. 4(b) which is beneficial to maintain device stability for computer application when other components produce heat.

To gain more insight into the switching mechanism, molecular simulation on the basic unit was carried out by

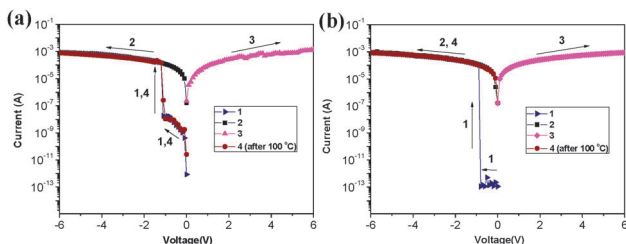


Fig. 4 Current–voltage (I – V) characteristics of (a) 10 wt% PCBM:P-TPA blending and (b) P-TPAOPCBM10 memory devices under thermal treatment.

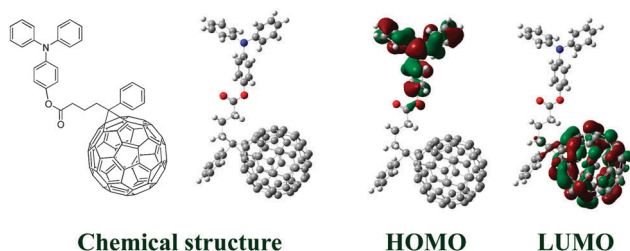


Fig. 5 Gaussian 09 simulation results.

DFT/B3LYP/6-31G(d) with the Gaussian 09 program. The charge density isosurfaces of the basic unit and the most energetically favorable geometry are summarized in Fig. 5. For the TPAOPCBM system, the HOMO energy level was located mainly at the electron-donating TPA moieties, while the LUMO energy levels were located at the electron-withdrawing PCBM units. According to the charge transfer mechanism,^{6a,15d} the high external applied electric potential may facilitate electron transfer from the HOMO of the donor TPA moiety to the LUMO of acceptor PCBM. Hence, the partially filled LUMO and HOMO of PCBM and the TPA moiety resulted in negative and positive charges, respectively. Therefore, carriers could be generated within the polymer hybrid for bringing out a tremendous decrease in electric resistance and an abrupt increase in conductivity after charge transfer.

In summary, high ON/OFF ratio electrically bistable non-volatile memory devices were prepared based on poly(triphenylamine) with different amounts of pendent PCBM. By introducing 10 wt% PCBM into P-TPA via covalent bonding, a WORM memory device with lower switching-ON voltage (0.9 V) and much higher ON/OFF ratio (10^9) than that of blending composites could be obtained. Besides, the device performance remained satisfactory under the heating condition up to 100 °C. This is crucial for maintaining device stability in computer applications when other components produce heat.

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