

# Electrically bistable memory devices based on poly(triphenylamine)–PCBM hybrids†

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**Due to the strong interaction between PCBM and triphenylamine, PCBM could be well distributed into poly-4-methoxytriphenylamine (P-TPA). The resulting hybrid films exhibited DRAM behavior at low PCBM concentrations, while they revealed WORM property at higher, 5 wt% and even up to 10 wt%, PCBM concentrations.**

Conventional memory devices, which depend on semiconductor-based integrated circuits, play an important role in the development of today's information technology.<sup>1</sup> However, with the rapid growth of the information industry, there is a growing demand for the establishment of next generation memory devices characterized by higher data storage density, longer data retention time, high speed, low power consumption, and low cost.<sup>2</sup> Thus, polymeric materials containing electrical bistability resulting from conductivity difference in response to the applied electric field begin to stand out conspicuously and have predominance in facing the problems and challenges in scaling down from the micro-scale to the nano-scale.

There have been a number of demonstrations for the application of polymers in memory devices, such as conjugated polymers,<sup>3</sup> functional polyimides,<sup>4</sup> and polymers with pendent electroactive chromophores.<sup>5</sup> Besides, the hybrid composites were extensively prepared for memory device applications and exhibited interesting memory behavior. In the beginning, polymers were used as a matrix material for small molecules.<sup>6</sup> The 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.<sup>7</sup> Afterward, the electro-active molecules such as carbon nanotubes (CNT)<sup>8</sup> and graphene oxide<sup>9</sup> were blended into the “donor-containing polymer” matrix to investigate the resulting memory behavior. In particular, PCBM containing hybrid films were most widely used as the active layer in the memory application.<sup>10</sup> At this stage, the design of polymer chemical structure takes an important position and the domain size of the

supplementary material in the polymer matrix is also the key issue for the nano-scale memory device.

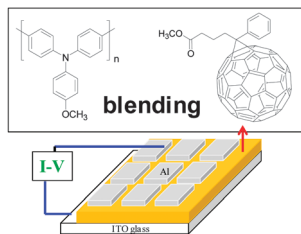
Triphenylamine (TPA) and its derivatives are well-known candidates for hole transport materials in organic photo-electronic devices due to their resulting stable radical cations and good hole-mobility.<sup>11</sup> Besides, TPA-based polymers with good thermal stability are not only used as the hole-transport layer in electroluminescent devices but also widely investigated in the fields of electrochromic<sup>12</sup> and memory applications.<sup>13</sup> However, the application of wholly TPA containing polymers in hybrid memory devices has not yet been discussed to date. Compared to conjugate polymers,<sup>10b,d</sup> non-conjugate TPA-based polymers are not only advantageous in decreasing the OFF current and thus increasing the ON/OFF ratio but are also expected to have strong interaction with PCBM as shown in Fig. S3 (ESI†) and favor the well dispersion of PCBM into the wholly TPA-containing polymers that could result in keeping the memory behavior of the hybrid film at higher PCBM content. Furthermore, TPA with an electron-donating methoxy substituent at the *para*-position exhibited good electrochemical stability,<sup>13d</sup> and thus could be expected to have excellent rewriting ability in memory devices.

In this communication, we therefore fabricate the memory devices by blending the PCBM as the acceptor with the donor-containing poly-4-methoxytriphenylamine (**P-TPA**) as shown in Fig. 1. Monomer 4-methoxytriphenylamine was prepared according to the literature, and polymer **P-TPA** was also synthesized *via* oxidative coupling reaction.<sup>14</sup> The detailed synthetic procedure and basic properties are described in the ESI.† The electrochemical behavior of the studied material was investigated using cyclic voltammetry (CV) conducted by the cast film on an indium–tin oxide (ITO)-coated glass slide as a working electrode in anhydrous acetonitrile, using 0.1 M of TBAP as a supporting electrolyte, and the results are summarized in Table S3 (ESI†). The typical CV diagram of **P-TPA** is depicted in Fig. S2 (ESI†) and  $E_{\text{onset}}$  was utilized to calculate HOMO. There is one reversible oxidation redox couple and the low oxidation potential of **P-TPA** could be attributed to the *para*-position substituted electron-donating methoxyl group. The LUMO energy level (2.34 eV) was calculated from HOMO (5.17 eV) and energy gap (2.83 eV) reported before.<sup>14</sup>

The resulting memory characteristics of these hybrid films were investigated by the current–voltage ( $I$ – $V$ ) characteristics of

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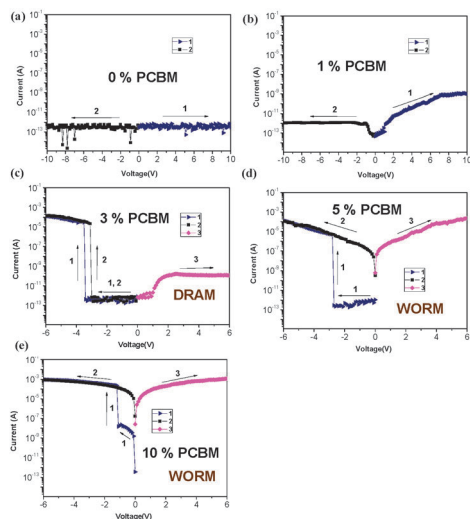
† Electronic supplementary information (ESI) available: Experimental section. Table: inherent viscosity, molecular weights, solubility behavior, thermal, and electrochemical properties. Figure: TGA, CV, device diagram of polymers. See DOI: 10.1039/c3cc40693h



**Fig. 1** Chemical structures of hybrid materials and schematic diagram of the memory device.

an ITO/hybrid film/Al sandwich device as shown in Fig. 1. Fig. 2(a) and (b) demonstrate the  $I$ - $V$  results of pristine **P-TPA** and 1 wt% **PCBM:P-TPA**, which were conducted in the steps of 0.1 V with 0.01 A compliance current. Both the memory devices of pristine **P-TPA** and 1 wt% **PCBM:P-TPA** were kept at a low-conductivity (OFF) state during the positive and negative scans. Although 1 wt% **PCBM:P-TPA** exhibited a slightly higher OFF current due to the superadded PCBM, there was no electrical switching capability indicating the insulator characteristic.

Fig. 2(c) and (d) depict the  $I$ - $V$  results of 3 wt% **PCBM:P-TPA** and 5 wt% **PCBM:P-TPA**, respectively. During the first sweep from 0 V to  $-6$  V, the devices remained at the OFF state with a current range of  $10^{-12}$ – $10^{-13}$  A in the beginning but increased abruptly to the ON state with the current of  $10^{-5}$  A (high-conductivity state) at threshold voltages of  $-3.4$  V (3 wt% **PCBM:P-TPA**) and  $-2.8$  V (5 wt% **PCBM:P-TPA**), implying the writing process. In the case of 3 wt% **PCBM:P-TPA**, the ON state was instantly recovered to the OFF state after removing the applied bias and could be switched to the ON state again at the switch-on voltage of  $-3.0$  V (line 2). The positive scan from 0 V to 6 V (line 3) shows no switching phenomenon by positive bias. The short retention time of this device is indicated as dynamic random access memory (DRAM) behavior. The DRAM behavior of 3 wt% **PCBM:P-TPA** is rewritable and the result of the rewritability test is shown in Fig. S5 (ESI<sup>†</sup>). In contrast, the device fabricated with 5 wt% **PCBM:P-TPA** remained at the ON state during the subsequent negative scan (line 2) and then positive scan (line 3).

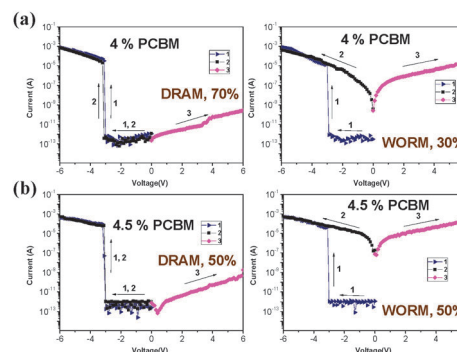


**Fig. 2** Current-voltage ( $I$ - $V$ ) characteristics of the ITO/PCBM:**P-TPA**/Al memory device with (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, and (e) 10 wt% PCBM weight fractions.

Besides, the ON state could be kept even after turning off the power for 30 minutes or a longer time since it has been switched on. Thus, this  $I$ - $V$  characteristic indicates that the memory device based on the 5 wt% **PCBM:P-TPA** hybrid film revealed non-volatile WORM memory property. Furthermore, the higher PCBM containing hybrid film such as the 10 wt% **PCBM:P-TPA** device still preserved the WORM property, while increasing PCBM concentration could enhance both ON and OFF current the switch-on voltage decreased from  $-2.8$  V to  $-1.3$  V as depicted in Fig. 2(e).

In order to explore the transition from DRAM to WORM by increasing the PCBM content from 3 wt% to 5 wt%, the intermediate 3.5 wt%, 4 wt%, 4.5 wt% **PCBM:P-TPA** hybrid films were prepared to fabricate the sandwich device for investigating the electrical characteristics. 3.5 wt% **PCBM:P-TPA** exhibited DRAM behaviour, while DRAM and WORM properties were both present in the device based on 4 wt% and 4.5 wt% **PCBM:P-TPA** as shown in Fig. 3. Using 4 wt% **PCBM:P-TPA** as an example, the current suddenly increased from  $10^{-12}$ – $10^{-13}$  A to  $10^{-4}$  A at the switch-on voltage of  $-3.0$  V during the negative sweep (line 1). In some cases, the ON state returned to the OFF state as soon as turning off the power and could be again turned to the ON state at the same switch-on voltage (line 2). The subsequent sweep (line 3) implied that this device could not be switched by positive bias, corresponding to negative-active DRAM which is similar to the device fabricated by 3 wt% **PCBM:P-TPA**. In other cases, the ON state could be read by the subsequent ambipolar sweep (lines 2 and 3), and the ON state could be maintained even after 30 minutes without any electrical impulse, indicating the WORM behavior which is similar to the device based on 5 wt% **PCBM:P-TPA**. 4 wt% **PCBM:P-TPA** shows 70% DRAM and 30% WORM behavior while 4.5 wt% **PCBM:P-TPA** shows 50% DRAM and 50% WORM behavior implying that 3.5–4.5 wt% **PCBM:P-TPA** should be the critical concentration of the DRAM–WORM transition state of the memory device.

The memory characteristics of these polymer hybrids include insulator, DRAM, and WORM types as the PCBM weight fraction changes from 0 wt% to 10 wt% in the **P-TPA** matrix. According to the charge transfer mechanism,<sup>4a</sup> the high externally applied electric potential may facilitate electron transfer from the HOMO of donor **P-TPA** to the LUMO of acceptor PCBM. Hence, the partially filled LUMO and HOMO of PCBM and **P-TPA** resulted in negative and positive charges, respectively. Therefore, carriers could be generated within the polymer hybrid for bringing out a tremendous decrease in the



**Fig. 3** Current-voltage ( $I$ - $V$ ) characteristics of the ITO/PCBM:**P-TPA**/Al memory device with (a) 4 wt% and (b) 4.5 wt% PCBM weight fractions.

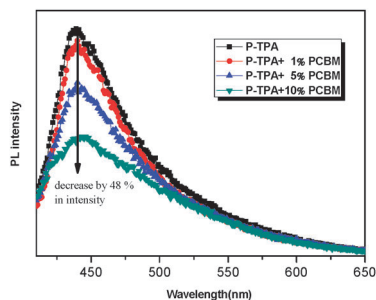


Fig. 4 Photoluminescence spectra of PCBM:P-TPA hybrid thin films.

electric resistance and an abrupt increase in the conductivity after charge transfer.

The solid state photoluminescence (PL) spectra of the **P-TPA** and **PCBM:P-TPA** excited at the absorption  $\lambda_{\max}$  (380 nm) are presented in Fig. 4. In comparison to pristine **P-TPA**, the fluorescence of **PCBM:P-TPA** was quenched obviously decreasing PL intensity by 48 wt% as the PCBM fraction increased to 10 wt%, indicating the charge transfer from the electron-donating TPA within the **P-TPA** to the dispersed electron-accepting PCBM. Thus, the charge transfer phenomenon could occur once the applied voltage overcomes the energy barrier, then the generated carriers and charged moieties consequently induce a sharp increase in the current.

The morphology of the **PCBM:P-TPA** hybrid films was further analyzed by TEM measurement, and the TEM images of these **PCBM:P-TPA** spin-coating thin films are shown in Fig. 5. The dark regions indicate the formation of PCBM clusters, which were well dispersed in the matrix **P-TPA**, and the diameter slightly increased with enhancing the weight fraction of PCBM (1–3 nm at 1–5 wt%). The higher amount of PCBM clusters with the small domain size within the matrix **P-TPA** could stabilize the charge separation state, hindering from back recombination even under the reverse bias. Thus, the high conductance state can be retained for a much longer time, changing the devices from DRAM to WORM type memory characteristic. Compared to previous work,<sup>15</sup> PCBM with 10 wt% concentration in **P-TPA** still exhibited WORM memory behavior, which might be attributed to the strong interaction between TPA and PCBM, resulting in small domain size of PCBM (less than 3 nm with some aggregation size of 5–10 nm).

In summary, the high ON/OFF current ratio polymer hybrid memory materials based on the thermally stable **P-TPA** with incorporating the electron acceptor PCBM *via* blending have

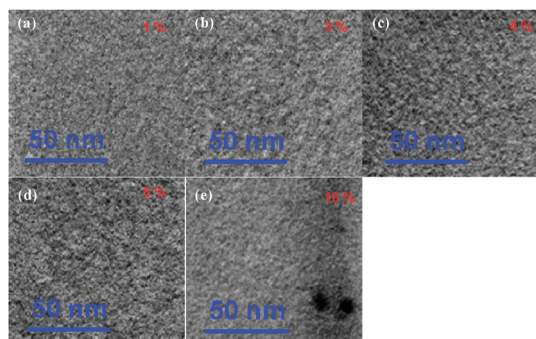


Fig. 5 The TEM images of (a) 1 wt%, (b) 3 wt%, (c) 4 wt%, (d) 5 wt%, and (e) 10 wt% PCBM:P-TPA spin-coating films.

been successfully prepared and investigated systematically. The memory devices with the configuration of ITO/PCBM:**P-TPA**/Al exhibited both DRAM and WORM properties controlled by the concentration of PCBM. The strong interaction between PCBM and TPA resulting in well-dispersed PCBM clusters within **PCBM:P-TPA** hybrid films revealed bistable WORM behavior even at higher, up to 10 wt%, PCBM concentrations.

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