

Novel solution-processable fluorene-based polyimide/
TiO₂ hybrids with tunable memory properties†

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Chia-Liang Tsai,‡ Chih-Jung Chen,‡ Pei-Hsuan Wang, Jiang-Jen Lin
and Guey-Sheng Liou*

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A new hydroxyl-containing fluorene-based polyimide FOH-6FPI hybrid with different TiO₂ contents was prepared and used for memory device applications. The resulting films exhibited tunable memory properties from DRAM, SRAM, to WROM at different TiO₂ concentrations from 0 wt% to 50 wt% with a high ON/OFF current ratio (10⁸).

The use of polymeric materials in electronic devices, such as light-emitting devices,¹ transistors,² and solar cells³ has attracted significant attention due to the advantages of rich structural flexibility, low-cost, solution processability, and three-dimensional stacking capability.⁴ Besides this, polymeric memory devices have been investigated as a promising alternative to the conventional semiconductor-based memory devices. As compared to the traditional inorganic memory materials, polymeric memory materials store information in the form of high (ON) and low (OFF) current state and have the superior properties of higher data storage density, longer data retention time, faster speed, and lower power consumption.⁵ Thus, polymeric materials with electrical bistability resulting from the conductivity difference in response to the applied electric field begin to stand out conspicuously and are predominant materials for facing the problems and challenges of scaling down from micro-scale to nano-scale.

For resistive type memory materials, electron donor-acceptor polymers are considered as suitable materials because charge transfer (CT) between the donor and acceptor moieties can give rise to a highly conductive state. There have been a number of demonstrations of the application of donor-acceptor polymers in memory devices, such as conjugated polymers,⁶

polymers with pendent electroactive chromophores,⁷ functional polyimides,⁸ and hybrid composites.⁹ Among all the studied donor-acceptor systems, aromatic polyimides are promising candidates for memory device applications due to the excellent thermal dimensional stability, chemical resistance, mechanical strength, and high ON/OFF current ratio, resulting from the low conductivity in the OFF state. According to previous studies, triphenylamine-based polyimides could overcome the solution processability problems of aromatic polyimides and revealed diverse memory properties.¹⁰ However, there was no reference for organosoluble fluorene-based carbo polyimides, which also have excellent thermal stability, for memory applications.

Furthermore, CT complex formation could be enhanced by introduction of supplementary components such as organic molecules or metallic particles into the polymer hybrid as electron donors or electron acceptors.¹¹ As compared with the polymer memory devices with organic molecules or metallic particles, relatively few studies have been conducted on the polymer memory devices containing semiconducting particles.¹² Because of the low LUMO energy level (4.2 eV),¹³ TiO₂ could be used as an electron acceptor in hybrid system to facilitate and stabilize CT complex formation for increasing retention time of memory characteristics in device application. Furthermore, compared with conducting supplementary components such as PCBM, CNT, graphene, and metallic particles,¹⁴ the introduction of TiO₂ could prevent the detriment of decreasing the ON/OFF ratio at high TiO₂ content, resulting from the low conductivity in the OFF state. In this study, we therefore fabricate memory devices derived from the new hydroxy-containing fluorene-based polyimide FOH-6FPI hybrid materials with tunable TiO₂ contents. The hydroxyl groups could react with titanium butoxide (Ti(OBu)₄), providing organic-inorganic bonding at each repeating unit. The detailed synthetic procedure and basic properties are described in the ESI.†

The electrochemical behaviour of FOH-6FPI was investigated by cyclic voltammetry (CV) conducted by the cast film on an indium-tin oxide (ITO)-coated glass slide as working electrode

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, 4th Sec., Taipei 10617, Taiwan. E-mail: gsliau@ntu.edu.tw; Fax: +886-2-33665237; Tel: +886-2-33665070

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‡ These authors contributed equally to this work.

in anhydrous acetonitrile, using 0.1 M of TBAP as a supporting electrolyte, and the results are summarized in Table S4.† A typical CV diagram of **FOH-6FPI** is shown in Fig. S6,† and E_{onset} of the oxidation redox couple was utilized to calculate HOMO. The UV-vis absorption spectrum of **FOH-6FPI** is shown in Fig. S7,† and the onset wavelength of optical absorption was utilized to obtain the optical energy band gap (E_g). The LUMO energy level (2.82 eV) was calculated from HOMO (6.02 eV) and energy gap (3.20 eV).

The resulting memory characteristics of these hybrid films were investigated by the current–voltage (I - V) characteristics of an ITO/hybrid film/Al sandwich device as shown in Fig. 1. Fig. 2(a) demonstrates the I - V results of pristine **FOH-6FPI** conducted in the steps of 0.1 V with 0.01 A compliance current. During the first positive sweep from 0 V to 6 V, the device stayed at the OFF state with a current range of 10^{-12} to 10^{-13} A, meaning that the positive applied voltage could not switch the memory device on. In contrast, during the second negative sweep from 0 V to -6 V, the current increased abruptly from 10^{-12} to 10^{-13} to 10^{-5} A at the threshold voltage of -5.0 V, indicating the transition from the OFF state to 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 third sweep) and then positive scan (the fourth sweep). The ON state was instantly recovered to OFF state after removing the applied bias for 15 seconds and could be switched to the ON state again at the switch-on voltage of -4.9 V (the fifth sweep). The sixth sweep was conducted to make sure the device could open to the ON state again. The short retention time of this device is indicated as dynamic random access memory (DRAM) behaviour.

The I - V results of 7 wt% TiO_2 :**FOH-6FPI** (**FTP-7**) are depicted in Fig. 2(b). A sharp increase of the current could be observed at -4.5 V during the second negative sweep. The device of **FTP-7** maintained in the ON state after turning off the power for a longer period of time than **FOH-6FPI**. The fifth sweep was conducted after turning off the power for about 5 minutes and the device could be switched to the ON state again at the threshold voltage of -4.3 V. The longer retention time at the ON state yet volatility, as well as the randomly accessible ON and OFF states is similar to the data remanence behavior of static random access memory (SRAM). Fig. 2(c) and (d), and S11† summarize the memory results for **FTP-10** and **FTP-30**, respectively. Comparing to volatile DRAM and SRAM properties, the

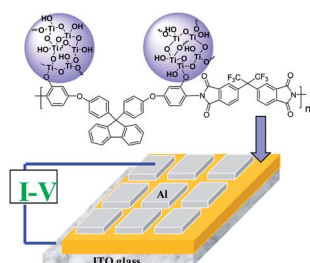


Fig. 1 Chemical structures of hybrid materials and schematic diagram of the memory device.

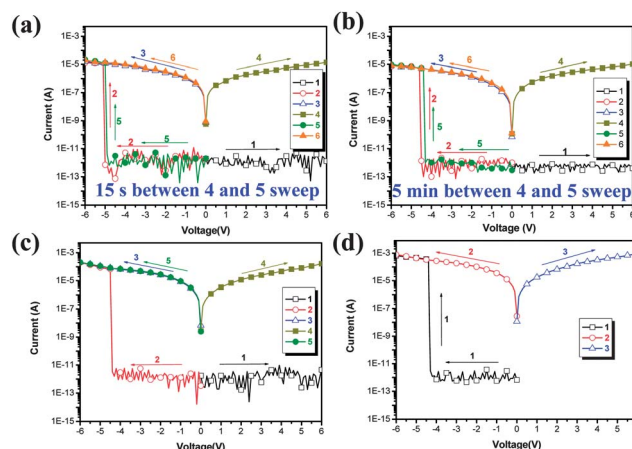


Fig. 2 Current–voltage (I - V) characteristics of the ITO/hybrid materials/Al memory device (a) **FOH-6FPI**, (b) **FTP-7**, (c) **FTP-10**, (d) **FTP-30**.

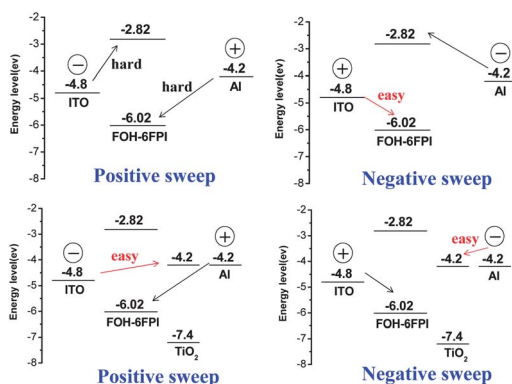
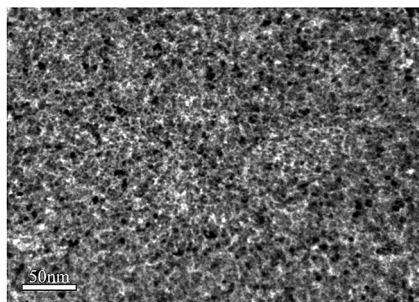
ON state of **FTP-10** and **FTP-30** could be retained even after turning off the power for 30 minutes or longer time since it has been switched on. Thus, this I - V characteristic indicates that the memory devices based on **FTP-10** and **FTP-30** hybrid films revealed non-volatile write-once-read-many-times (WORM) memory properties. Furthermore, the higher TiO_2 containing hybrid film **FTP-30** could be switched to ON state by the positive voltage at 2.9 V as shown in Fig. S11.†

In order to explore the transition from DRAM to SRAM (5 minutes) by introducing 7 wt% TiO_2 into **FOH-6FPI**, the intermediate **FTP-5** hybrid films was prepared to fabricate the sandwich device for investigating the electrical characteristics. DRAM and SRAM properties were both present in the device of **FTP-5** as shown in Fig. S8.† The probability of the resulting DRAM and SRAM behaviours of **FTP-5** was 70% for DRAM and 30% for SRAM, respectively, while the SRAM behaviour of **FTP-5** only possessed a 1 minute retention time. The memory properties of **FTP-8**, **FTP-9** and **FTP-50** were also investigated and the results are available in the ESI.† The memory properties of **FOH-6FPI** hybrid materials with different TiO_2 contents from 0 wt% to 50 wt% are summarized in Table 1. Generally, with the introduction of TiO_2 amount increased, the memory device revealed a longer retention time and could be switched to the ON state by applying both positive and negative voltages.

To understand the memory behaviour of polyimide **FOH-6FPI** clearly, molecular simulation on the basic unit was carried out using DFT/B3LYP/6-31G(d) with the Gaussian 09 program as shown in Fig. S13.† The HOMO of **FOH-6FPI** is located mainly at the electron-donating fluorene moiety, while LUMOs are distributed around the electron-withdrawing phthalimide units, adjacent phenyl ring, and hexafluoroisopropylidene group. According to previous literature,^{10a} when the applied electric field reach the switching-on voltage, some electrons in the HOMO accumulate energy and transition to the LUMO to form a charge transfer complex (ON state) by different ways. When the intra- or intermolecular CT occurred by the applied electric field, the generating holes can be delocalized to the fluorene moieties forming an open

Table 1 Memory properties of **FOH-6FPI** hybrid materials

PI + TiO ₂ hybrid	0 wt%	5 wt%	7 wt%	8 wt%
Memory properties	DRAM	DRAM/SRAM (1 min)	SRAM (5 min)	SRAM (9 min)
PI + TiO ₂ hybrid	9 wt%	10 wt%	30 wt%	50 wt%
Memory properties	WORM	WORM	WORM (biswitch)	WORM (biswitch)

**Fig. 3** HOMO and LUMO energy levels of **FOH-6FPI** along with the work function of the electrodes.**Fig. 4** TEM image of the hybrid material **FTP-50**.

channel in the HOMO of the polyimides for the charge carriers (holes) to migrate through.

Based on this proposed mechanism, when the negative sweep was conducted, the hole injected from the bottom electrode ITO to the HOMO of polymer due to the lower band gap between ITO (-4.8 eV) and HOMO as shown in Fig. 3. In contrast, during the positive sweep, it is difficult to inject the hole from the top electrode Al into the HOMO of the polymer because of larger energy gap between the work function of Al (-4.2 eV) and HOMO of the polymer, thus the memory device could not be switched to the ON state. However, with the introduction of TiO₂ into **FOH-6FPI**, the hybrid materials have a low LUMO energy level and could be switched to the ON state at positive sweep. This phenomenon could be attributed to the smaller band gap between LUMO of TiO₂ (-4.2 V) and work function of ITO (-4.8 V).

TEM was also used to characterize the morphology of the prepared hybrid films as shown in Fig. 4. The dark regions indicate the formation of TiO₂ clusters with domain size around 5 nm which were well dispersed in the matrix **FOH-6FPI** even at 50 wt% TiO₂ content. Comparing to previous literature,¹⁵ hybrid films with much enhanced distribution of TiO₂ in this study could afford excellent film quality and avoid filament formation. Because of the low LUMO of TiO₂, the obtained PI hybrids with a higher amount of TiO₂ and small domain size within the matrix **FOH-6FPI** could facilitate and stabilize the charge separation state, hindered by back recombination even under the reverse bias. Thus, the high conductance state can be retained for a much longer time, tuning the devices from DRAM to SRAM, and even WORM type memory characteristics. Furthermore, high ON/OFF ratio of these hybrid materials could be maintained even at high TiO₂ content due to the insulator behavior of TiO₂, resulting in low conductivity in the OFF state.

Conclusions

In summary, novel polymer hybrid memory materials exhibiting a high ON/OFF current ratio (10^8) based on the new polyimide **FOH-6FPI** with incorporating the electron acceptor TiO₂ *via* covalent bonding have been successfully prepared and investigated systematically. The resulting hybrid films revealed a very small domain size of TiO₂ around 5 nm and tunable memory properties from DRAM, SRAM, to WORM at different TiO₂ concentrations from 0 wt% to 50 wt%.

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