A conjugated copolymer of 9,9-dihexylfluorene and Eu-complexed benzoate (PF6Eu) for write-once read-many-times (WORM) memory application was demonstrated in a sandwich structure of Al/PF6Eu/ITO. The device exhibited: a high ON/OFF current ratio up to 10^7, stable ON and OFF states with read cycles up to 10^8 at a read voltage of 1 V, and projected stability up to 10 years at a constant stress of 1 V.

**Experimental**

PF6Eu, containing both the electron-donor (9,9'-dihexylfluorene) and electron-acceptor (europium complex) groups, was synthesized via the Suzuki coupling copolymerization, hydrolysis of the benzoate units, and post-chelation. The number-average molecular weight of PF6Eu was around 41100, with a polydispersity index of about 2.54 and a Eu weight content of 3.24 wt %. The molecular weight of PF6Eu was around 41100, with a polydispersity index of about 2.54 and a Eu weight content of 3.24 wt %. The number-average molecular weight of PF6Eu was around 41100, with a polydispersity index of about 2.54 and a Eu weight content of 3.24 wt %. The number-average molecular weight of PF6Eu was around 41100, with a polydispersity index of about 2.54 and a Eu weight content of 3.24 wt %.

Figure 1. (a) Molecular structure of the conjugated copolymer PF6Eu with the composition of x/y = 0.92/0.08. (b) Schematic diagram of the memory device consisting of a thin film (~50 nm) of PF6Eu sandwiched between an ITO substrate and an aluminum top electrode (~0.5 µm). (c) Typical J-V characteristics of the Al/PF6Eu/ITO device in the ON and OFF states and the J-V curves of the Al/PF6Eu/ITO device based on conjugated poly(9,9-dihexylfluorene) (PF6) without the europium complex moiety.
visible spectra were obtained on a Shimadzu UV-NIR 3100 spectrophotometer. The absorption spectra of the memory device in the ON and OFF states were measured in reflectance mode, using an integrating sphere (ISR-260).

The memory device had the simple structure of a PF6Eu film (50 nm in thickness) sandwiched between an indium-tin oxide (ITO) bottom electrode and an aluminum top electrode (0.5 μm in thickness) (Fig. 1b). For the fabrication of the memory device, the ITO/glass substrate was precleaned with water, acetone, and isopropanol, in that order, in an ultrasonic bath for 15 min. A toluene solution of PF6Eu (10 mg/mL) was spin-coated onto ITO, followed by solvent removal in a vacuum chamber at 10−2 Torr and 50°C for 12 h. The thickness of the polymer layer was about 50 nm. Aluminum top electrodes (for needle contacts) of 0.4 × 0.4, 0.2 × 0.2, 0.15 × 0.15 mm, and 0.5 μm in thickness were thermally evaporated onto the polymer surface at about −10−2 Torr through a shadow mask. The devices were characterized, under ambient conditions, using a Hewlett-Packard 4156A semiconductor parameter analyzer equipped with an Agilent 16440A SMU/pulse generator.

Results and Discussion

The memory effect of PF6Eu is shown in the current density-voltage (J-V) characteristics of Fig. 1c. Initially, the as-fabricated device was at its low conductivity state (OFF-state). The current density in the low voltage range on the first sweep was quite low (in the orders of 10−10 to 10−8 A/cm2). When a switching threshold voltage of about 3 V was applied, an abrupt increase in J from 10−8 to 10−2 A/cm2 was observed, indicating the device transition from a low conductivity state to a high conductivity state (ON-state, the first sweep). This electrical transition from the OFF-state to the ON-state serves as the “writing” process for the memory device. The device exhibited good stability in this high-conductivity state during the subsequent forward and reverse voltage scans (Fig. 1c). It remained in the ON-state even after turning off the power (the second sweep) and did not return to the low conductivity state upon applying a negative bias (the third sweep). Thus, this device exhibits the WORM-type memory effect.

For comparison, a similar device based on the conjugated poly(9,9-dihexylfluorene) (PF6) homopolymer, was also fabricated. The J-V characteristics of the Al/PF6Eu/ITO and Al/PF6/iTO devices are compared in Fig. 1c. As a conjugated polymer, delocalized charge carriers can migrate through the π-conjugated backbone of the fluorene group. Thus, PF6 is semiconducting. The J of the device based on PF6 increased steadily (from ~10−7 to 10−2 A/cm2) with increasing bias (V) in either positive or negative sweep without any abrupt increase in current density. Thus, PF6 does not exhibit electronic bistability and memory effect. Although PF6Eu is also a conjugated polymer, the current density of the device based on PF6Eu was much lower than that of PF6 in the low voltage range during the first sweep. PF6Eu has a 9,9-dihexylfluorene to Eu-complexed benzene molar ratio of about 0.92:0.08. The europium complexes along the conjugated backbone in the copolymer probably served as temporary barriers to block the charge carriers. Lanthanide ions have a [Xe]4f55s25p6 electronic configuration, in which electrons in the 4f level are shielded by the filled 5s2 and 5p6 orbitals, resulting in a weak crystal field and directional effect.23 The lanthanide complexes distinguish themselves from the transition metal complexes by a high (up to 12, due to larger ionic radii) and variable coordination number (3-12, due to weaker crystal fields).24 The coordination number of the europium complex in PF6Eu is 8. Thus, it is an electron-deficient complex and can act as an electron acceptor to block the charge carriers (holes). The molar ratio of the europium complex to fluorene group in conjugated PF6Eu is much higher than that of the europium complex to carbazole group in nonconjugated PKEu. The latter exhibits flash-type memory behavior.20 There were not many free charge carriers in PF6Eu and the device based on PF6Eu was at its low conductivity state in the low voltage range during the first sweep. When a switching threshold voltage of about 3 V was applied, charge carriers were induced at a high electric field. The charge carriers can now migrate freely through the π-conjugated backbone and the device is switched from the low conductivity state to the high conductivity state. For PF6Eu, the fluorene groups can only assume a “shoulder-to-shoulder” conformation due to the rigid nature of the π-bond and steric hindrance. It is difficult for the fluorene groups to form CT complexes with the europium complexes. Charge separation in polyfluorene composites with internal donor/acceptor heterojunction is well-known.25 PF6Eu can thus retain its doped state. As a result, the device based on PF6Eu remains at the high conductivity state once it has been switched ON. The presence of both the long alky side chains in fluorene and the bulky Eu complex substituent in the present copolymer reduces interchain interactions, and thus interchain carrier hopping.

For PF6Eu, the highest occupied molecular orbital (HOMO), associated with the fluorene moiety, and the lowest unoccupied molecular orbital (LUMO), associated with the europium complex, are −5.66 and −3.50 eV, respectively, as determined from the onset redox potentials in Fig. 2a.26 The band gaps (Eg) of the fluorene moiety and europium complex are 2.98 and 3.05 eV, respectively, determined from the UV-visible absorption edges27 of the PF6 moiety and Eu complex21 (Fig. 2b). Thus, the HOMO and LUMO of the fluorene moiety and europium complex in PF6Eu are −5.66 and −2.68 eV, respectively. Due to the low molar ratio of the Eu complex to fluorene (0.08:0.92) in the present copolymer, the LUMO and HOMO energy levels of the fluorene moieties probably were not affected to a large extent. The CyV of PF6Eu also reveals that the oxidation peak of the fluorene moieties and the reduction peak of the Eu complex are well separated and fall in opposite potential regions. The HOMO of the fluorene moiety is higher than that of the hole-transporting PVK (~5.80 eV),28 indicat-
ing that PF6Eu is a p-type material with the holes as the dominant charge carriers. Hole transport properties of fluorene-containing polymers have been widely studied. However, under a low bias voltage (0–3 V), hole mobility in PF6Eu is blocked by the europium complex with a very low HOMO energy level (OFF state). With the configuration of the present device (Al/PF6Eu/ITO), the barrier height of the Al/fluorene (HOMO level) contact (1.38 eV) is similar to that of the ITO/Eu complex (LUMO level) contact (1.34 eV) when PF6Eu is at its ground state (OFF state). When the electric field exceeds the barrier (~1.3 eV), electrons are injected into the LUMO of the Eu complexes and holes are injected into the HOMO of the fluorene moieties. The charged LUMO (radical anion) of the Eu complex and the charged HOMO (radical cation) of the fluorene moiety form a channel for charge carriers through nonradiative intersystem transition. The polymer becomes p-doped under the induction of the electric field and switches to the high conductive state (ON state). Due to the high electron affinity (EA) of the Eu complex (4.0 eV, as calculated from CyV results), the radical anions can coexist with the surrounding radical cations of the fluorene moieties.

The stability constant (K) of the radical anions can be estimated from the onset potentials of the first and second reduction peaks in the CyV curve of Fig. 2a:

\[ \lg K = \frac{E_{Re}^2 - E_{Re} - E_{Re}^D}{0.059} = 13.6 \]  

indicating that the radical anions are quite stable. The fluorene radical cations are less stable with an \( \lg K \) of only 3.2. However, a sufficient degree of spin delocalization of the conjugated fluorene segments in PF6Eu will stabilize the radical cations. Thus, the doped state of PF6Eu is stable and the high conductive state can be maintained. The UV-visible absorption spectrum of PF6Eu shows a decrease in intensity and a broadening in line width at the turn-on voltage, in comparison to that of the OFF state (Fig. 2b). With the further increase in intensity of the absorption peak at around 390 nm (associated with the fluorene moieties) upon further increase in voltage stress (at 7.6 V), a new absorption band in the short wavelength range has also appeared. The result indicates that, in addition to UV-visible light, the fluorene moieties were also excited by the electric field in the ON state. Under the high field stress, the fluorene moieties are charged to the radical anion state, accounting for the appearance of the new absorption band. The obvious advantage of this copolymer system over other physically doped systems lies in the fact the dopants in PF6Eu are covalently bonded to the polymer chain. Thus, the phenomena of ionic aggregation and phase separation can be avoided when the memory device is under long term operation.

To further understand the present PF6Eu device transition from the OFF-state to the ON-state in WORM-type memory behavior, the J-V curves in both states were analyzed in terms of theoretical models. For the OFF-state, the J-V curve can be fitted with the Schottky emission model:

\[ J \approx T^2 \exp \left( \frac{\alpha V}{T} - \frac{\phi_d}{kT} \right) \]  

wherein \( T \) is room temperature (298 K), \( \alpha = \sqrt[4]{\frac{q}{4\pi e d}} \), \( \phi_d \) is the barrier height, \( e_d \) is the dynamic permittivity of the insulator, and \( d \) is the film thickness (Fig. 3a). The result suggests that the current before the device transformation from the OFF-state to the ON-state was controlled by charge injection from the electrode. For the ON-state, the J-V curve can be simulated by a combination of the space-charge-limited model and the Ohmic model as follows:

\[ J \approx \frac{9e_i \mu V^2}{8d^3} + V \exp \left( -c/T \right) \]  

wherein \( \mu \) is the mobility of carriers and \( c \) is a positive constant independent of \( V \) or \( T \). The J-V characteristics were dominated by the space-charge-limited model. This result (Fig. 3b) suggests that after the electrical transition, the current through the device changes from a charge injection current to a space-charge-limited current. This change from a charge injection current in the OFF-state to a space-charge-limited current in the ON-state also accounts for the symmetric J-V characteristic of PF6Eu in the ON-state (Fig. 1c).

The performance of the WORM device based on PF6Eu was evaluated under ambient conditions. Inset (i) in Fig. 4a shows the ratio of the ON-to-OFF-state current as a function of applied voltage for the same sweep. An ON/OFF current ratio as high as 10^7 has been achieved for the memory device. This feature promises a low misreading rate through the precise control over the ON- and OFF-states. In addition to a low misreading rate, the stability is always an important issue in memory device performance. The effect of continuous read pulses of 1 V [inset (ii)] on the ON- and OFF-states was investigated. As shown in Fig. 4a, no resistance degradation was observed for the ON- and OFF-states after more than one hundred million (10^8) read cycles, indicating that both states are insensitive to read cycles. The stability of the device under a constant stress of 1 V is shown in Fig. 4b. Though a slight degradation in current density for the ON- and OFF-states was observed, an ON/OFF current ratio of ~10^3 could be maintained when projected to 10 years. The performance of the present polymer memory device compares favorably with that of the known single-layer molecular (nonpolymeric) memory devices. Electrical transitions in some polymer films have been attributed to the formation of conductive filaments between the two metal electrodes under a high electric field. The good reproducibility and stability of the memory phenomena in the present device ruled out such filament or polymer degradation effects. The current density for the three different area devices (0.4 × 0.4, 0.2 × 0.2, and 0.15 × 0.15 mm) was independent of the device area, further indicating the absence of such effects. The polymer WORM device offers the distinct advantage for high density data storage, over other existing memory technologies, through its capability for 3D stacking. Traditional three-terminal memory cells occupy an area of \( 9F^2 \), where \( F \) is the minimum feature size, while the cell area for a WORM device is only \( 4F^2 \).
Figure 4. (a) Effect of read cycles on the ON and OFF states. Inset (i) shows the ON/OFF current ratio as a function of applied voltage for the same sweep. Inset (ii) shows the pulses used for this measurement. (b) Stability of the Al/PF6Eu/ITO device in either ON or OFF state under a constant stress (1 V).

Conclusions

In summary, a nonvolatile polymer memory device, based on the conjugated copolymer of 9,9-dihexylfluorene and Eu-complexed benzoate (PF6Eu), is demonstrated in a sandwich structure of Al/ PF6Eu/ITO. It exhibited a transition from a Schottky emission-controlled current to a space-charge-limited current upon induction by a threshold field. After the device was transformed to the high conductivity state, it remained in the ON-state even after the power was turned off or swept negatively. The device can be used as a write-once read-many-times (WORM) electronic memory, with a high ON/OFF current ratio up to $10^7$, stable ON- and OFF-states up to $10^8$ read cycles at a read voltage of 1 V, and projected stability up to 10 years at a constant voltage stress of 1 V. The polymer WORM memory is expected to meet the demand for high capacity and inexpensive data storage in increasingly sophisticated handheld applications and disposable electronics.