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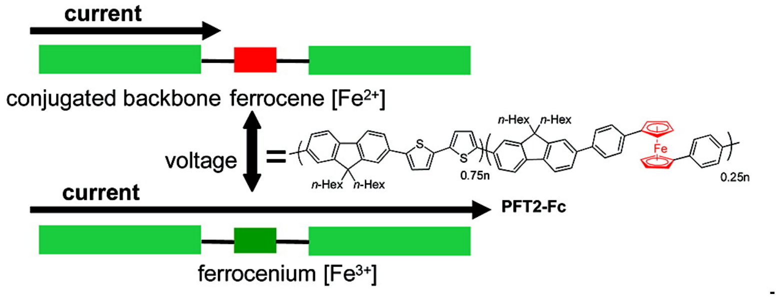

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Synthesis and Nonvolatile Memory Behavior of Redox-Active Conjugated Polymer-Containing Ferrocene

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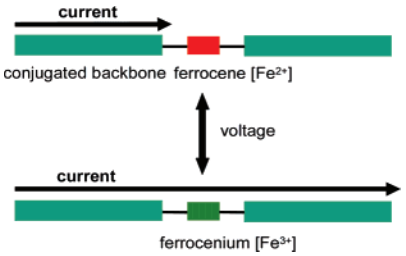
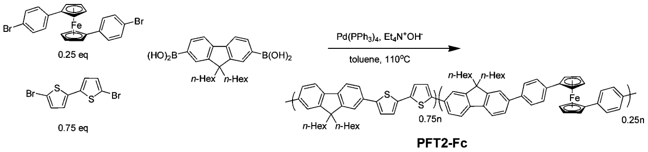
During the past decade, organic electronics have attracted a great amount of attention after their applications on light emitting diodes,[1] transistors,[2] and photovoltaic cells were demonstrated.[3] This attention is due to their high potentials and advantages in flexible and low-cost devices arising from solution processes such as spin-casting and ink-jetting.[4] Among the several research fields on organic electronics, one of the newly emerging areas is the organic memory application[5] where information is stored in organic materials that are sandwiched by two electrodes. In addition to the common advantages for organic electronics listed above, the organic memory advantages also include good scalability and 3D stacking to achieve low-cost but high-density memory. Recently, many research groups have reported nonvolatile organic memory devices based on charge transfer,[6] redox,[7] metal filament growth,[8] conformational change,[9] and a charge-trapping mechanism.[10] Also demonstrated is write-once/read-many-times (WORM)-type memory using irreversible change in the organic material.[11] Many of the reported devices are fabricated by vacuum deposition of the active organic materials or spin-coating from the blend solution of multiple components. However, only few reports are precedent using the single polymer system with solution process.[7,12] Herein, we demonstrate the synthesis of a new conjugated polymer with redox active functionality, ferrocene, in the polymer main chain and its nonvolatile memory behavior when fabricated into the memory devices.

In organic memory devices, the data are stored as “0” and “1” based on a change in the resistance of the organic layer. This change from one state to another state with different resistance must be reversible, and the new state should be stable enough to retain its information to meet the requirement for the nonvolatile memory. Our initial study on nonvolatile organic memory began with focusing onto ferrocene as the active component since its redox was very well-studied and ferrocenium (Fe^{3+}), its oxidized form, is also stable which gives the possibility for nonvolatility. In addition, relatively simple methods for the syntheses of ferrocene-containing polymers are precedent,[13] but not much of their applications were explored. Of particular interest are the reports showing increases in the conductivity of film containing ferrocene by photo-oxidation[14] or by introduction of chemical oxidants.[15] On the basis of these observations, we reasoned that if ferrocene was linked to a conjugated polymer, the change in current by redox process would be enhanced, and this can be utilized as a resistance memory (Scheme 1).

Scheme 1. Postulated Mechanism for Memory Behavior



Scheme 2. Synthesis of Ferrocene Containing Polymer, PFT2-Fc



With these considerations, we designed a conjugated polymer containing ferrocene based on the well-known backbone, PFT2, previously used in organic thin-film transistor (OTFT) devices.[16] This backbone was chosen for two reasons: high carrier mobility and the easy synthesis. For organic memory purposes, the new polymer PFT2-Fc was prepared by the similar route as the synthesis of PFT2[16] except for the random insertion of a ferrocene unit into the polymer backbone: 0.75 equiv 2,5′-dibromo-bithiophene and 0.25 equiv 1,1′-bis(*p*-bromophenyl)-ferrocene[17] was copolymerized with 9.9-dihexylflourene-2,7-diboronic acid via Suzuki polycondensation (Scheme 2). The resulting polymer with orange color was obtained in 89% isolated yield and was soluble in common organic solvents, such as THF, toluene, and chloroform. Integration of NMR spectra showed an expected ratio for ferrocene moiety and bithiophene unit to be about 3:1 which is equal to the monomer feed ratio. (Fc content of 9 wt %) The resulting polymer had a number-average molecular weight (M_n) of 13 000 g/mol (relative to narrow dispersed polystyrene standards) obtained by size exclusion chromatography (SEC) and a PDI of 2.2, an expected value for the step-growth polymerization.

To get more insights into the electrochemical properties of PFT2-Fc, the highest occupied molecular orbital (HOMO) energy level of the polymer was measured by photoelectron spectroscopy and found to be 5.3 eV. From UV−vis absorption spectra, the optical band gap of 2.4 eV was obtained from the onset of the low-energy optical absorption peak edge at 520 nm (See Figure 1 in Supporting Information (SI)). These values suggested that PFT2-Fc was a semiconducting polymer, not much different from the parent polymers, PFT2.[16] However, a different behavior was noticed from cyclic voltametry showing two reversible redox peaks rather than one. (SI, Figure 2) The peaks at 0.58 and 0.97 V were assigned to the oxidation potential for ferrocene and that of the conjugated backbone in the polymer, respectively.

With the chemical and physical information in hand, the memory device was fabricated by spin-coating 0.9 wt % solution of PFT2-

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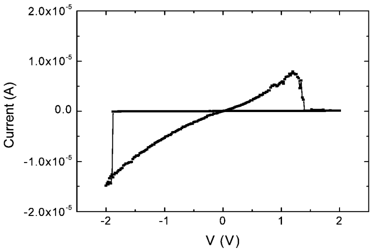

Figure 1. I−V characteristics of PFT2-Fc device.

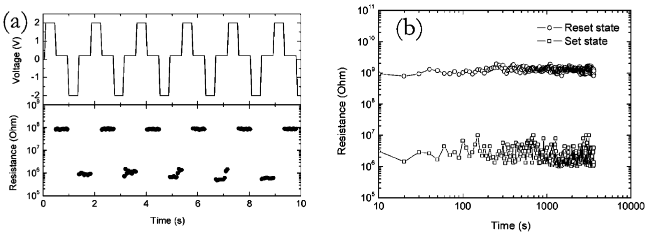

Figure 2. (a) Current responses during the write−read−erase−read voltage cycle, (b) retention time of the on- and off-state data.

Fc in chlorobenzene onto the ITO patterned glass to give a film thickness in the range of 50−60 nm. Then a 5 nm thick lithium fluoride (LiF) layer was deposited by vacuum deposition followed by the deposition of 80 nm thick aluminum (Al) as the top electrode. Devices with 5 nm thick LiF layer gave the optimal performance while thinner layers gave poor performance. The role of LiF layer is not clear at this moment, but it seems the high built-in field formation due to its large dielectric constant ($\epsilon \approx 9.1$) is responsible for better charge injection, thus, better memory performance.[18]

At first, a device fabricated with PFT2 showed no memory behavior. However, memory behavior was observed for PFT2-Fc devices by sweep-mode current−voltage (I−V) characteristics (Figure 1). Bias was applied to the ITO electrode with respect to the top Al electrode. Initially the device was at the low-conducting state (off-state). Then the current abruptly increased at −1.9 V implying a transition from the off-state to a high-conducting state (on-state) presumably because of the oxidation of ferrocene groups. This observation can be viewed as ferrocene acting like a voltage-dependent in-situ dopant resulting in the enhancement of the conductivity of the polymer film. This on-state persisted until the device was switched back to off-state at the positive bias of 1.4 V. These observations strongly support that the presence of the ferrocene unit is crucial for the memory behavior.

The endurance of our memory device was measured in nitrogen atmosphere and examined by write−read−erase−read cycles (−2 V/0.2 V/2 V/0.2 V, respectively) in pulse mode (Figure 2a). More than 100 cycles with on/off ratio up to 10^3 were observed. It is worthwhile to emphasize that the threshold voltages (V_{th}) for both on and off states are low at ±2 V for the device of 60 nm in thickness. The low operating voltage is desirable for low-power memory devices. We speculate that the low V_{th} of the device arises from the low-redox potential of the ferrocene functionality in PFT2-Fc backbone.

Last, the retention time for PFT2-Fc device was measured to demonstrate the nonvolatility of the organic memory device, and it was found that the device stably retained the on/off states for more than 7 h (Figure 2b). The origin of the retention time of the polymer device is believed to be due to the unique property of ferrocene's stable redox where ferrocenium can maintain its oxidized state. This observation is vividly demonstrated from a previous study by Higgins and co-workers who showed that only ferrocenium was detected by XPS even after the oxidized film of ferrocene-containing polythiophene was reduced at 0 V and held at that potential for 5 min.[19] They found that the polymer film was reduced back to ferrocene moiety only when a sufficiently large over-potential was applied.

In conclusion, we demonstrated a nonvolatile organic memory device using a ferrocene containing conjugated polymer, PFT2-Fc, as an active material. The device operated at low driving voltages with high on/off ratio. Although the retention time and the switching cycle are still far from satisfactory when compared to the current Si technology, the research on organic memory is still in its infant stage, and its device performance is expected to increase as the methods of the fabrication process improve.

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Supporting Information Available: Details of experimental procedures, UV−vis, electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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