Ferrocene-cored-conjugated dendrimer with electrical bistability

Chae Kyu Kim\textsuperscript{a}, Won-Jae Joo\textsuperscript{b}, Eun Seok Song\textsuperscript{a}, Hyung Joo Kim\textsuperscript{a}, Jina Kim\textsuperscript{a}, Chiyoung Park\textsuperscript{a}, Hoing Lae Lee\textsuperscript{a}, Chulhee Kim\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Inha University, Department of Polymer Science and Engineering, Hyperstructured Organic Materials Research Center, Incheon 402-751, Republic of Korea
\textsuperscript{b} Materials Laboratory, Samsung Advanced Institute of Technology, Republic of Korea

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Abstract

In this study, we report synthesis of a ferrocene-cored-conjugated dendrimer and its electrical property. The ferrocene-cored-conjugated dendrimer is covalently linked by a redox active ferrocene moiety and $\pi$-conjugated dendrons. Photophysical properties showed a remarkable fluorescence quenching of the dendrimers possibly due to electron transfer from the ferrocene moiety to the half-occupied HOMO level of the conjugated dendrons. The $I$–$V$–$R$ (current–voltage–resistance) characteristics of the single layer device, ITO/dendrimer/LiF/Al, exhibited clear electrical bistability for organic memory application, i.e. the low-conductivity state (OFF state) and the high-conductivity state (ON state). The result would provide a new class of materials with further opportunities for organic electronics.

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1. Introduction

Recently, conjugated polymers with various functional units have been extensively investigated to modulate photoelectronic properties for potential applications such as photodetector, data storage, biosensor, and catalyst [1–4]. In particular, incorporation of redox-active transition metal centers into the backbone of conjugated polymers can provide unique properties due to electronic interaction between metal center and conjugated moiety. There is a strong orbital coupling between polymer backbone and metal center, which provide an efficient charge transfer mechanism in those materials [5–8]. Due to the interesting characters, metal-containing conjugated polymers and molecules are expected to provide further opportunities for important applications in organic electronics. However, in spite of the established synthetic methods and unique properties of those materials, their applications still have remained in an early stage.

Organic memory devices with electrical bistability have been recognized as the envisioned applications in organic electronics due to their potential advantages of low-cost, easy processing, flexibility, and large area fabrication [9–12]. The electrical bistability represents two stable electrical states, i.e. the low-resistance state (ON state) and the high-resistance state (OFF state). Various types of electrically bistable systems have been reported and the mechanisms have been proposed to explain the existence of electrical bistability [13–18]. Recently, electrically bistable organic–inorganic hybrid memory devices have been reported using organic donor molecules and acceptor such as gold nanoparticles, fullerene, and Eu complex [19–24]. The proposed mechanism of the systems is an electric field induced charge transfer between donors and acceptors. In addition, polyimides with donor and acceptor moieties were demonstrated as a new class of materials for memory device application [25,26]. Therefore, we reasoned that conjugated dendrimers with transition metal in the core would be a unique system as memory material with electrical bistability due to efficient charge transfer between metal and conjugated moiety of dendrimer. Here, we report on the synthesis of ferrocene-containing $\pi$-conjugated dendrimer and their electrical characteristics for organic memory application.

We designed new conjugated dendrimer in which redox active ferrocene moiety as a donor and conjugated dendrons as...
an acceptor are covalently linked, so that the electrical bistability would be achieved via electron transfer between ferrocene and conjugated dendron moiety. Several research groups reported on the dendrimers with redox-active subunit like ferrocene in the interior or at the surface of dendrimers [27–32]. The works usually described molecular recognition for ionic compounds via electrochemical study, inclusion complexation by host molecules, or synthesis and their electrochemical properties itself. However, there has never been an example of \( \pi \)-conjugated dendrimers with the redox-active ferrocene unit or their application for organic electronics.

In this work, we report the synthesis of ferrocene-cored-conjugated dendrimer. In addition, we fabricated two-terminal devices for investigating the characteristics of electrical bistability for organic memory application.

2. Experimental

2.1. Materials and instruments

Anhydrous methylene chloride and other chemicals from Aldrich were used as received. Stb-GD-OH and ferrocene-1,1\textsuperscript{'}-diacid fluoride were synthesized by following a literature procedure [33,34]. \(^1\)H and \(^13\)C NMR spectra were recorded on a Varian UNITY INOVA 400 at 400 and 100 MHz, respectively. FT-IR spectra were obtained using Perkin-Elmer System 2000 FT-IR spectrophotometer. MALDI-TOF spectra were obtained using Voyager Biospectrometry time of flight mass spectrometer (Perspective Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive ionization. Dithranol was used as the matrix. Elemental analysis data were obtained using CE Instrument EA 1110. UV–vis spectra were recorded on Hewlett-Packard 8452A spectrophotometer. Photoluminescence spectra were measured using Shimadzu RF-5301PC spectrofluorophotometer.

2.2. Device fabrication and test

ITO-coated glass plates were cleaned with sonication in acetone and isopropyl alcohol prior to use as a substrate. On the top of the substrate, a chlorobenzene solution of the conjugated dendrimer (1 wt%) was spin-coated at speed in the range of 1800–2000 rpm for 60 s and dried at 110 \( ^\circ \)C for 30 min. The film thickness was 50 nm. A 2 nm-thick LiF alloy was vacuum-deposited on the organic layer as a blocking layer. Finally, top Al electrode was then vacuum-deposited on the layer at \( 5 \times 10^{-6} \) Torr. The device has a cross point array with a cell size of 0.3 mm \( \times \) 0.3 mm. The electrical characteristics of the device were measured by using a current/voltage source measurement unit (Keithly 2400).

3. Synthesis

3.1. Synthesis of Stb-1G-FcD

Stb-1GD-OH (0.6 g, 0.6 mmol) and 4-dimethylamino-pyridine (DMAP, 0.13 g, 1.04 mmol) were added to a methylene chloride solution of ferrocene-1,1\textsuperscript{'}-diacid fluoride (0.07 g, 0.26 mmol), and then stirred at room temperature for 3 h under nitrogen. The product mixture was washed with water and extracted with methylene chloride. The product mixture extracted in the organic layer was purified by column chromatography on silica gel using hexane/CH\(_2\)Cl\(_2\) (5:1, v/v) as an eluent. Further purification was performed by precipitation into CH\(_2\)Cl\(_2\)/methanol (1:20, v/v) to yield Stb-1G-FcD as a purple solid. (Yield 0.37 g, 68%), mp 296 \( ^\circ \)C.

\(^1\)H NMR (400 MHz, CDCl\(_3\): \( \delta \) 1.32 (s, 72H, tBu), 4.48 (t, \( J \) = 1.8 Hz, 4H, \( \text{cp} \)), 4.95 (t, \( J \) = 1.8 Hz, 4H, \( \text{cp} \)), 5.32 (s, 4H, \( \text{–Ph–C} = \text{H–C} \text{H–Ph–C} \text{H–ester–} \)), 6.98 (d, \( J \) = 16.1 Hz, 4H, \( \text{–CH=CH–Ph–rBu} \)), 7.06 (s, 8H, \( \text{–Ph–C} \text{H=CH–Ph–C} \text{H–Ph–C} \text{H–ester–} \)), 7.08 (d, \( J \) = 16.1 Hz, 4H, \( \text{–CH=CH–Ph–rBu} \)), 7.36 (d, \( J \) = 8.4 Hz, 16H, \( \text{–Ph–rBu} \)), 7.38 (s, 4H, \( \text{–Ph–C} \text{H–Ph–C} \text{H–ester–} \)), 7.40 (s, 12H, \( \text{–CH=CH–Ph–C} \text{H–ester–} \)), 7.44 (d, \( J \) = 8.4 Hz, 16H, \( \text{–Ph–rBu} \)), 7.52 (s, 2H, \( \text{–Ph–C} \text{H–ester–} \)); \(^{13}\)C NMR (100.64 MHz, CDCl\(_3\): \( \delta \) 31.33, 34.66, 72.04, 72.68, 73.17, 123.76, 124.22, 124.55, 125.51, 125.64, 126.43, 127.70, 128.32, 128.98, 129.13, 134.55, 137.12, 137.66, 138.04, 138.18, 150.87, 170.36; IR (KBr): \( \nu \) = 3026, 2962, 2902, 2868, 1719, 1594, 1509, 1459, 1363, 1271, 1133, 1021, 961, 894, 847; MS (MALDI-TOF): Calcd for C\(_{154}\)H\(_{158}\)FeO\(_4\) 2128.74, found 2128.74.

4. Results and discussion

4.1. Synthesis and photophysical properties

The synthetic route to the ferrocene-cored-conjugated dendrimer, Stb-1G-FcD is described in Scheme 1. We have synthesized Stb-1G-FcD by coupling the focal hydroxyl unit of the conjugated dendron, Stb-1GD-OH, with ferrocene-1,1'-diacid fluoride. The dendrimers were characterized by using $^1$H and $^{13}$C NMR, FT-IR spectra, elemental analysis, and MALDI-TOF mass spectrometry. The dendrimer was soluble in methylene chloride, chloroform, and THF. The absorption spectrum of Stb-1G-FcD in methylene chloride ($10^{-6} \text{M}$) in Fig. 1 shows an absorption maximum at 320 nm due to the stilbene unit [35]. The PL spectra of the free dendron units, Stb-1GD-OH ($\lambda_{\text{ex}} = 320 \text{ nm}$) in methylene chloride ($10^{-5} \text{ M}$), exhibited the emission maximum at 430 nm. The PL spectra of Stb-1G-FcD in methylene chloride ($10^{-5} \text{ M}$) excited at 430 nm showed a remarkable quenching of the emission from the conjugated dendron moiety as shown in Fig. 1, possibly due to electron transfer from the ferrocene moiety to the half-occupied HOMO level of the conjugated dendrons [36]. A quenching mechanism due to Förster-type energy transfer from the dendron wedge to the ferrocene core may be ruled out considering that the ferrocene moiety has a larger HOMO-LUMO gap than the conjugated dendron unit as shown from the absorption spectra in Fig. 1 [35,37].

4.2. $I-V-R$ characteristics of the devices
(ITO/dendrimer/LiF/Al)

The electrical bistability of Stb-1G-FcD was investigated by using a two terminal single layer device (ITO/dendrimer/LiF/Al) fabricated through the following procedure. On the top of a clean 80 nm-thick ITO-coated glass, a 1,2-dichloroethane solution of the dendrimer (1 wt%) was spin-coated at a speed of 1800 rpm. The film thickness was 50 nm. A 2 nm-thick LiF layer was vacuum-deposited onto the organic layer as a blocking layer, and then Al was deposited with a thickness of 80 nm as a top electrode. The LiF layer blocks the diffusion of Al atoms into the organic layer during thermal vapor deposition of Al electrode. The device has a cross point array with a cell size of 0.09 mm$^2$. The current–voltage–resistance ($I-V-R$) data of the ITO/Stb-1G-FcD/LiF/Al is shown in Fig. 2.

In the first scan from 0 to $-2.8 \text{ V}$, a high resistance and low current state was maintained. Then a sudden increase of current from 0 to $-7.5 \times 10^{-5} \text{ A}$ occurred at around $-2.8 \text{ V}$. This result indicates that a transition of the device took place from a state of low conductivity (OFF state) to high conductivity (ON state), which corresponds to “writing” process in memory devices. The resistance of the device in the ON state was about three orders of magnitude lower than that in the OFF state at the low voltage region. After the transition, the device in the ON state was maintained as the bias was applied from $-2.8$ to $+2.8 \text{ V}$. The ON state with high conductivity was abruptly changed back to a low conductivity state at around $+2.8 \text{ V}$, which could be used as an “erasing” process in a memory device. The $I-V-R$ property of the device provides an opportunity for an application as a non-volatile memory device. We suggest that the charge transfer from the ferrocene to the conjugated dendron moiety would induce a bistability in conductivity of the ferrocene-cored-conjugated dendrimers.

5. Conclusion

In this article, we report the synthesis of ferrocene-cored-conjugated dendrimer in which a redox active ferrocene moiety is covalently linked with π-conjugated dendrons. In addition, their $I-V-R$ characteristics exhibited electrical bistability which can be utilized for application of a non-volatile organic memory device. This result would provide a new class of materials with further opportunities for organic electronics.

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References