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Soluble dendrimers europium(III) β-diketonate complex for organic memory devices

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Abstract

We report the synthesis of a soluble dendrimers europium(III) complex, tris(dibenzoylmethanato)(1,3,5-tris[2-(2′-pyridyl)benzimidazoly]methylbenzene)–europium(III), and its application in organic electrical bistable memory device. Excellent stability that ensured more than 10^6 write–read–erase–reread cycles has been performed in ambient conditions without current-induced degradation. High-density, low-cost memory, good film-firming property, fascinating thermal and morphological stability allow the application of the dendrimers europium(III) complex as an active medium in non-volatile memory devices.

Keywords: Memory devices; Dendrimers molecules; Europium complex; Organic electrically bistable memory device

1. Introduction

During the past two decades several types of electronic and optoelectronic devices based on organic materials have been intensively studied, including light-emitting diodes [1], photovoltaic cells [2], field-effect transistors [3], optical pumped lasers [4] and switches [5]. Some of these devices have achieved commercial viability due to their advantages in terms of low cost, large area, flexible and lightweight. Recently, another important electronic device, organic electrically bistable memory device (OBMD), has become one important subject [6–14] due to its applications in microelectronics technology. A memory device features a bistable behavior of having two states associated with strongly different conductivities at the same applied voltage. The OBMD has a nanosecond writing time and exhibits the non-volatile memory effect, which makes it ideal for applications in flash memory. High performance OBMD with a structure of organic/metal/organic was reported by Yang's group in 2002 [6]. Since then, a variety of organic materials have been used for OBMD [9–11], and various techniques for device fabrication have been proposed [12–14]. Despite these encouraging achievements, development of OBMD are still in the exploratory stage, further improvement in performance is desired.

It is generally accepted that a morphologically stable amorphous organic layer will lead to a long lasting electronic device. Crystallization or melting of amorphous organic materials is considered to be responsible for device degradation [15]. Dendrimers organic molecules show excellent film-firming property, fascinating thermal and morphological stability as active medium in organic optoelectronic devices, and are widely used in organic light-emitting diodes [16–20]. Amongst dendrimers molecules studied, organic system have been extensively studied [16]. Little attention has been devoted to metal complexes [17–20]. In this communication, we report a dendrimers europium(III) complex, tris(dibenzoylmethanato)(1,3,5-tris[2-(2′-pyridyl)benzimidazoly]methylbenzene)–europium(III), $Eu_3(DBM)_9(TMMB)$. DBM is usually chosen as the

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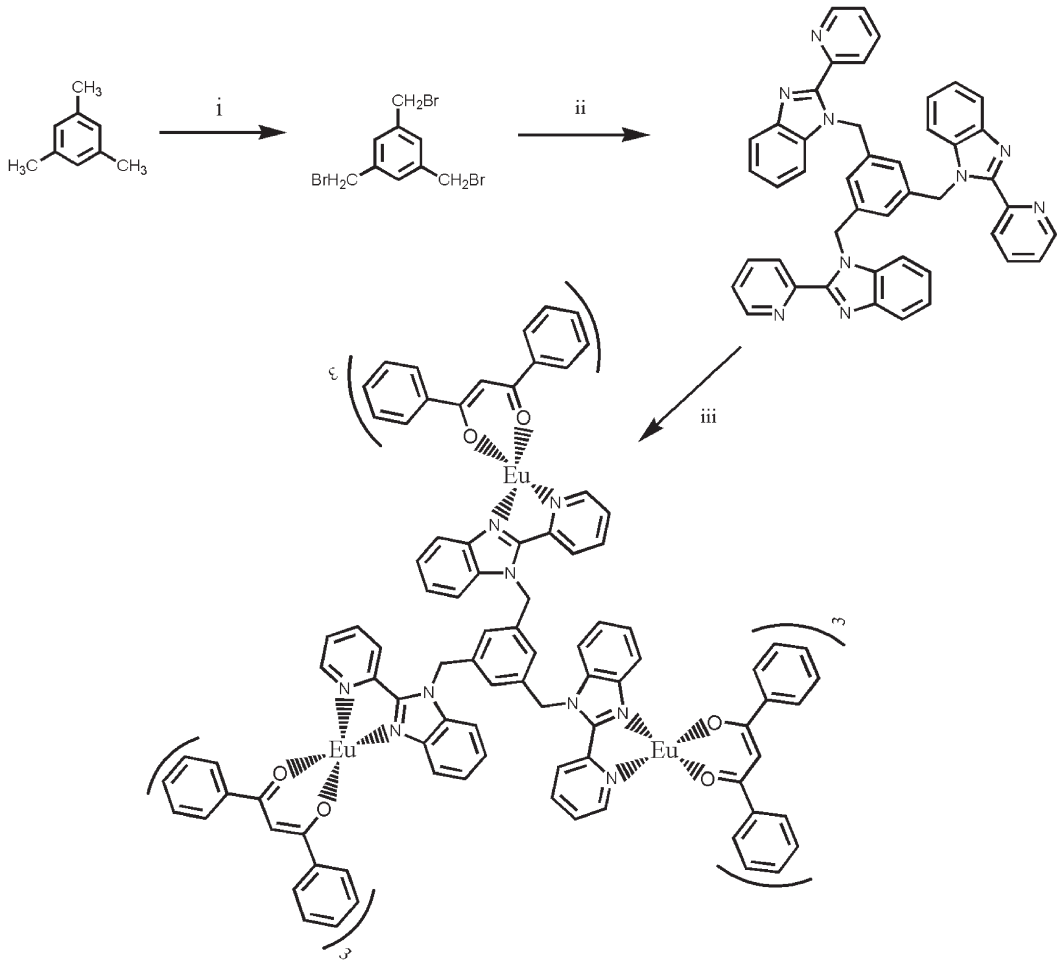

Scheme 1. Synthetic route to TMMB and $Eu_3(DBM)_9(TMMB)$. *Reagents:* i, *N*-bromosuccinimide; ii, 2-(2-pyridyl)-benzimidazole; iii, dibenzoylmethanato, $EuCl_3{\cdot}(H_2O)_6$.

ligand of europium(III) complexes and play a role as an electron-acceptor [10], and 2-(2-Pyridyl)-benzimidazole (PyBM) is also an electron-acceptor [21]. To enhance the electron-accepting ability and the solubility of the resulting material, here PyBM and DBM are combined into one dendrimers europium(III) complex. The OBMD based on $Eu_3(DBM)_9(TMMB)$ doped poly(*N*-vinylcarbazole) (PVK) as an active medium were fabricated. As we know, PVK is good hole-transporting polymer and also as an electron-donor [22]. When doping electron-accepting $Eu_3(DBM)_9(TMMB)$ into PVK, the formation of charge transfer between $Eu_3(DBM)_9(TMMB)$ and PVK leads to the bistable effects [23].

2. Experimental details

2.1. Preparation and characterization of $Eu_3(DBM)_9(TMMB)$

The synthesis route of $Eu_3(DBM)_9(TMMB)$ is depicted in Scheme 1.

A mixture of mesitylene (2.8 ml, 0.02 mol), *N*-bromosuccinimide (10.62 g, 0.06 mol), and benzoyl peroxide (0.11 g) in CCl_4 (30 ml) was stirred and heated under N_2 for 14 h at 90 °C. After filtering, the filtrate was washed with water and dried with anhydrous Mg_2SO_4. Upon concentration of the CCl_4 solution, a colourless needle crystal was precipitated. Recrystallization in a 1:1 mixture of ethanol/hexance afforded 6.56 g product (yield, 92%). ^{1}H NMR (CD_3OD):δ 4.55 (s, 6H), 7.42 (s, 3H).

A mixture of 1,3,5-tris(bromomethyl) benzene (0.357 g, 1 mmol), PyBM (0.600 g, 3 mmol), sodium hydroxide (0.12 g, 3 mmol) and DMF (30 ml) was stirred and heated under N_2 for 15 h at 120 °C. It was subsequently poured into ice water (100 ml), after extraction with dichloromethane (3 × 30 ml). The organic layer was washed with water and dried over anhydrous Mg_2SO_4. The solvent was then evaporated, the resulting residue was purified by silica gel column chromatography to give 0.11 g product (yield, 16%). ^{1}H NMR (500 MHz, $CDCl_3$): δ5.89 (s, 6H), 6.90 (s, 3H), 7.05–7.08 (t, 3H), 7.14–7.19 (t, 6H), 7.28–7.32 (d, 3H), 7.69–7.73 (t, 3H), 7.83–7.85 (d, 3H), 8.19–8.26 (d, 6H). EI-MS: *m*/*z*: 700 (M^+).

A solution of DBM (0.20 g, 0.9 mmol) and TMMB (75 mg, 0.1 mmol) was dissolved in a mixture of hot ethanol/chloroform under stirring. The solution turned yellow immediately after sodium hydroxide (36 mg, 0.9 mmol) was added. Then $EuCl_3{\cdot}(H_2O)_6$ (36.6 mg, 0.1 mmol) in 2 ml of ethanol was added dropwise to the stirred solution. The mixture was stirred for 1 h at 60 °C. The red product was collected by filtration and

recrystallized from ethanol, resulting in 75% yield. Elemental analysis for $C_{180}H_{132}N_9O_{18}Eu_3$. Calcd: C, 68.11; H, 4.69; N, 4.20. Found: C, 68.31; H, 4.16; N, 3.97. Fourier-transform IR spectroscopy (KBr pellet): [cm^{-1}] 3058, 3025, 2966, 2928, 1549, 1518, 1458 (C═O, chelated to Eu^{3+}), 618, 508, 413 (O–Eu–O), 3425 (N–H), 1595 (C═N), 1550, 1478 (imidazole ring).

2.2. Fabrication and characterization of the memory device

The device structure used in this study is indium–tin–oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (50 nm)/PVK:$Eu_3(DBM)_9$(TMMB) (100 nm)/LiF (0.5 nm)/Ca (20 nm)/Ag (200 nm). A 50 nm thick layer of PEDOT:PSS was spin-coated on the ITO coated glass substrate with a speed of 2000 rpm (rpm: revolutions per minute) for 1 min. After the thin film was dried at 120 °C in an oven for 15 min, then an 100 nm-thick $Eu_3(DBM)_9$(TMMB) doped PVK (Aldrich, MW = 9×10^4) layer was prepared by spin-coating the chloroform solution with PVK concentration of 10 mg/ml, and $Eu_3(DBM)_9$(TMMB) of 1 mg/ml at 1200 rpm for 1 min. Finally, 0.5 nm thick LiF, 20 nm Ca and 100 nm Ag were deposited at a rate of 0.2–0.6 nm/s by thermal evaporation at a pressure of $\leq 2\times10^{-4}$ Pa. The active area of devices was 9 mm^2. The current–voltage (*I–V*) characteristics and the write–read–erase–reread cycles were performed by Keithley 2400 sourcemeter controlled by a computer. All electrical measurements on the device were carried out in ambient without encapsulation.

3. Results and discussion

Typical current–voltage (*I–V*) characteristics of the device with a structure of ITO/PEDOT:PSS (50 nm)/PVK:$Eu_3(DBM)_9$(TMMB) (100 nm)/LiF (0.5 nm)/Ca (20 nm)/Ag (200 nm) are shown in Fig. 1. Repeatable electrical bistability is observed when using ITO as the cathode, Ca/Ag as the anode, and the initial voltage is swept from a negative value. It can be seen that the current increases progressively with bias voltage from negative to positive, representing a high-conductance ON state [region (2)]. As the voltage increases further, a sharp decrease in the current from 10^{-2} A to 10^{-4} A takes place at the critical voltage of 6 V, and the current keeps the low conductance OFF state [region (4)], indicating the transition of the devices from the ON state to OFF state. The transition from the high current state to the low current state is equivalent to the writing process in a digital memory device. After this transition, the state of the device still remains even after turning off the bias voltage. The low current OFF state can be recovered to a high current ON state by simply applying a negative bias. The *I–V* characteristics (such a reversible transition between ON and OFF states) define the electrical bistability of the devices and also reveal the non-volatile nature of the memory effect. It was found experimentally that the process shown in Fig. 1 is repeatable, indicating the rewritability of the device.

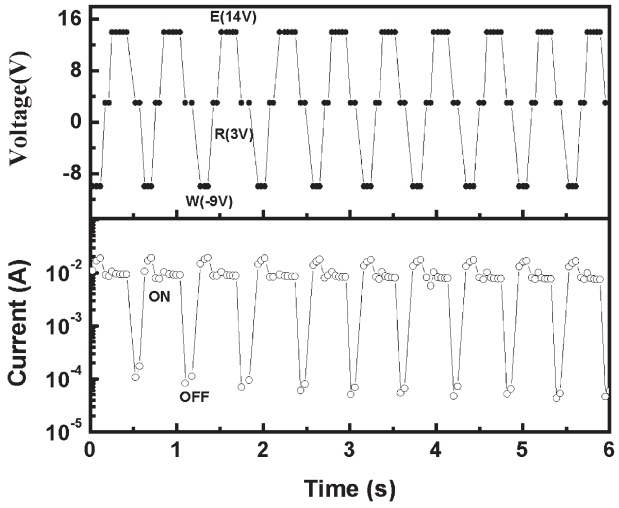

Fig. 2. Typical voltage responses and current responses of an OBMD during the write–read–erase–reread voltage cycles. The writing (W), reading (R), and erasing (E) voltages are − 9, 3, and 14 V, respectively.

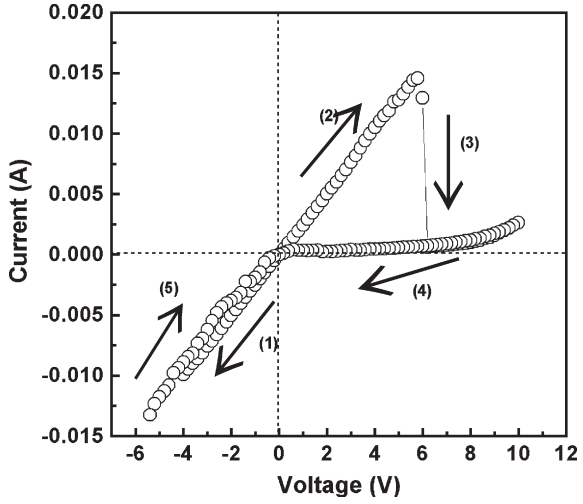

Fig. 1. *I–V* curves of an OBMD. The arrows in the figure indicate the voltage-scanning directions.

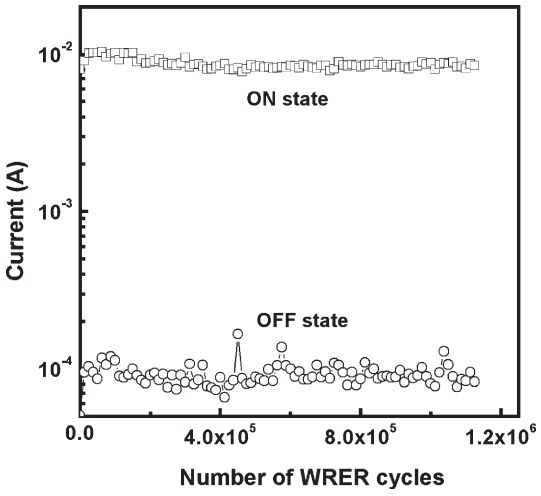

Fig. 3. Currents of the ON and OFF states as a function of the number of write–read–erase–reread cycles. 1×10^6 cycles have been tested in ambient conditions.

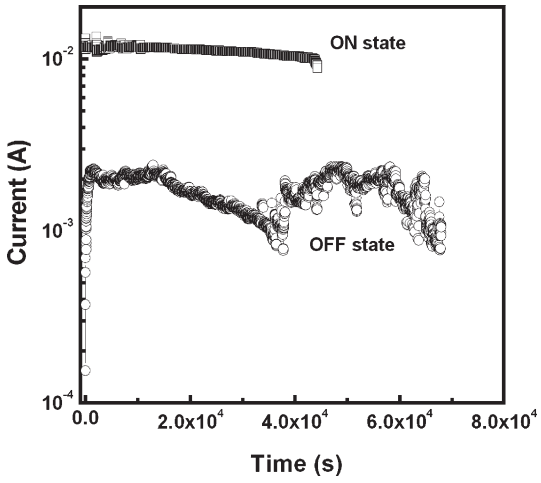

Fig. 4. The stability test of an OBMD in either the ON or OFF state.

Furthermore, write–read–erase–reread cycles are also important characteristic parameters to the performance of a memory device. Fig. 2 shows typical current responses of the device during the write–read–erase–reread voltage cycles. A 14 V pulse induces the device to be in the OFF state. This ON state is read by a 3 V pulse with a current of $\sim 10^{-4}$ A. A negative bias of − 9 V erases this OFF state to produce the ON state. The ON state is detected by a 3 V pulse with a current of $\sim 10^{-2}$ A. It can be seen that the current response of the device followed the applied write–read–erase–reread cycles very well. The difference between the read and reread currents demonstrates the ON and OFF states of the bit stored in the bistable device. Moreover, once the device switches to either state, it remains in that state for a prolonged period of time. The stability of the devices under stress is measured under continuous-bias conditions. These write–read–erase–reread cycles and the duration test demonstrate that the devices meet the basic requirements which are necessary for binary-information storage and present the potential for operation as non-volatile memory.

In addition to the re-writing capability, other parameters that are important to the performance of a memory device were evaluated under ambient condition, including read cycles, ON/OFF ratio, switching time, and retention ability. It is found that more than one million write–erase cycles can be realized in the device with good rewritable characteristics, and no current degradation is observed for both the ON state and OFF state during the test, as shown in Fig. 3, where the currents on the ON state and OFF state as a function of the number of write–read–erase–reread cycle of the device are given. The ON/OFF current ratio reaches 100. To measure the retention time of the device, a writing voltage of − 14 V is applied. The ON and OFF states can still be read several days to weeks later. Furthermore, the memory device is quite stable under a continuous bias. As shown in Fig. 4, no significant change in current of ON and OFF states is noted, and the ON/OFF current ratio yet maintains about 10 after 11 h stress test, although the current in OFF state increases sharply in the initial period. As an organic electrically bistable memory device, all parameters to the performance of a memory device are wonderful, showing potential applications as a memory cell. These features allow the application of the dendrimers europium(III) complex as an active medium in non-volatile memory devices.

It is well known that PVK is a typical hole-transporting polymer and the carbazole group in PVK is a better electron-donor. On the other hand, the $Eu_3(DBM)_9(TMMB)$ acts as an electron acceptor. In the donor–acceptor composite system, charge transfer (CT) is easy to occur and generally considered as main transit mechanism between the ON state and OFF state. For the case of $Eu_3(DBM)_9(TMMB)$ doped with PVK, therefore, it is concluded that the electronic transit is attributed to an electrical-field-induced charge transfer between PVK and $Eu_3(DBM)_9(TMMB)$. The high-conductance state of the device is due to the higher hole mobility of PVK. When a forward voltage is applied, the carbazole groups are oxidized and holes are generated (ON state). The current increases with the increase of bias voltage, and when the bias reaches the threshold voltage, the reduced $Eu_3(DBM)_9(TMMB)$ can form a CT complex with surrounding oxidized carbazole groups. The CT complex is basically insulating, leading to the sharp decrease in the current of the device. Now the device is in its low-conductance state (OFF state). Actually, the formed CT complex is not very stable; a reversal voltage can result in the return of the carbazole group and $Eu_3(DBM)_9(TMMB)$ to their original state. The electrically reversible processes are greatly crucial to repeat the transit between the ON state and OFF state. It can be sure that the interaction between PVK and $Eu_3(DBM)_9(TMMB)$ should play an important role on the electrically switching characteristics in the device.

4. Conclusions

We have designed and synthesized a soluble dendrimers bistable Eu(III) complex and presented their potential applications in the organic memory for binary information storage. In the devices, the ON and OFF states can be written in or erased by voltage. More than 10^6 write–read–erase–reread cycles have been performed in the ambient conditions without current degradation. Furthermore, the fabrication process of the OBMD described above involves quite a simple and low-cost technology, compatible with established organic electronic device construction processes. It is believed that with the help of puposely designed dendrimers metal complexes, OBMD performance could be further improved by means of molecular engineering and optimal architectures, and we are in the progress of exploring these possibilities.

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