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Memory Devices Based on Lanthanide (Sm^{3+}, Eu^{3+}, Gd^{3+}) Complexes

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Memory effects in single-layer organic light-emitting devices based on Sm^{3+}, Gd^{3+}, and Eu^{3+} rare earth complexes were realized. The device structure was indium–tin-oxide (ITO)/3,4-poly(ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT)/Poly(*N*-vinyl carbazole) (PVK): rare earth complex/LiF/Ca/Ag. It was found experimentally that all the devices exhibited two distinctive bistable conductivity states in current–voltage characteristics by applying negative starting voltage, and more than 10^6 write–read–erase–reread cycles were achieved without degradation. Our results indicate that the rare earth organic complexes are promising materials for high-density, low-cost memory application besides the potential application as organic light-emitting materials in display devices.

Introduction

During the past 10 years, there has been a growing interest in organic optoelectronic devices such as organic light emitting diodes (OLEDs),[1−4] organic solar cells,[5,6] organic field-effect transistors,[7,8] and organic lasers[9] due to the unique electrical and optical properties of organic materials. Their advantages include low fabrication cost, high mechanical flexibility, and versatility of the chemical structure. Among organic semiconductor devices, organic electrical memory devices are a relatively new family and appear highly attractive, owing to their potential application in data storage. Generally, the memory devices show two different states of conductivities at the same applied voltage, namely, the high-conductance state (ON state) and the low-conductance state (OFF state). The electronic bistability is ideal as memory used in personal computers, digital assistants, digital cameras, etc. The switching effect in organic materials has been known since1970.[10,11] However, up to now, the realization of high-performance memory devices based on organic materials makes the use of organic memory devices in applications for information storage possible, and different memory devices based on organic molecules, polymers, and nanoparticle-doped polymers were reported.[12−34]

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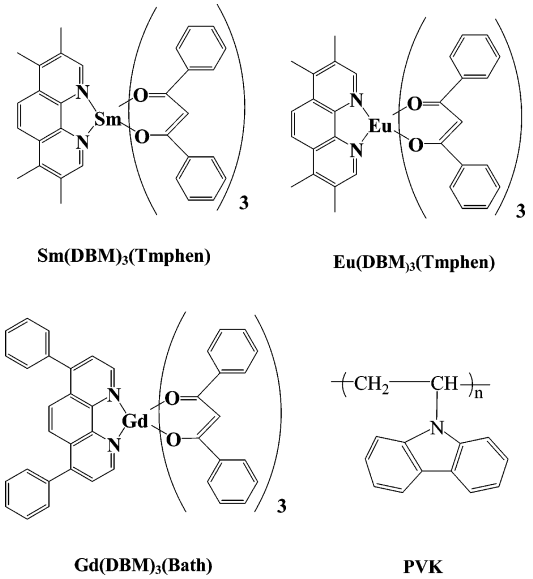

Figure 1. Molecular structures of $Sm(DBM)_3(Tmphen)$, $Eu(DBM)_3(Tmphen)$, $Gd(DBM)_3(Bath)$, and PVK.

It is well known that rare earth (RE) organic complexes show narrow emission and theoretically high electroluminescence (EL) efficiency originating from the emission of both singlet and triplet excitons, thus a promising light-emitting material system in organic light-emitting diodes.[35−37] In this paper, we doped a series of RE complexes $Eu(DBM)_3(Tmphen)$, $Sm(DBM)_3(Tmphen)$, and $Gd(DBM)_3(Bath)$ (DBM= dibenzoylmethanato, Tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline, Bath = 4,7-diphenyl-1,10-phenanthroline)[36−38] into poly(*N*-vinylcarbazole) (PVK) as active medium to fabricate single-layer memory devices. It was found experimentally that all the devices showed electrical bistability in current−voltage characteristics when Ca/Ag was used as the anode, indium−tin-oxide (ITO) as the cathode, and the sweep started from a negative voltage. Two different conductance states (ON state and OFF state) were observed at the same bias voltage and were repeatable. More than 10^6 write−read−erase−reread cycles were achieved in ambient conditions without degradation, showing potential applications as a memory cell.

Experimental Section

The used RE complexes $Eu(DBM)_3(Tmphen)$, $Sm(DBM)_3(Tmphen)$, and $Gd(DBM)_3(Bath)$ were synthesized according to literature.[36−38] Figure 1 shows the molecular structures of $Eu(DBM)_3(Tmphen)$, $Sm(DBM)_3(Tmphen)$, and $Gd(DBM)_3(Bath)$. The device structure used in this study was ITO/PEDOT/PVK:RE complex/LiF/Ca/Ag (device A), PEDOT is 3,4-poly(ethylenedioxythiophene)−poly(styrenesulfonate). The devices were fabricated by spin-coating the materials onto a cleaned glass substrate precoated with a layer of ITO. First, a 50 nm thick layer of PEDOT was spin-coated on an ITO surface at 2000 rpm for 60 s. After the thin film was dried in an oven for 15 min (120 °C), an ∼80 nm thick RE complexes doped with a PVK (Aldrich, MW = 90 000) layer was prepared by spin-coating the chloroform solution (10 mg/mL, 10% concentration of RE complex) at 1200 rpm for 60 s. Finally, 0.5 nm thick LiF, 20 nm Ca, and 100 nm Ag were deposited in turn. The metallic cathode was evaporated at the rate 0.2−0.6 nm/s under high vacuum ($\leq 2\times10^{-4}$ Pa). 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 were done in ambient condition without any device encapsulation. The active area of the devices was 9 mm^2.

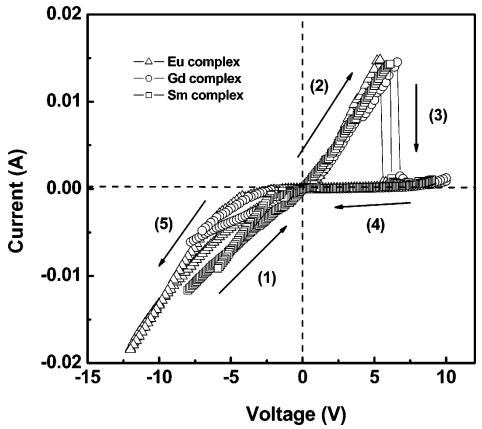

Figure 2. Current−voltage characteristics of the devices ITO/PEDOT/PVK: $Sm(DBM)_3(Tmphen)$/LiF/Ca/Ag, ITO/PEDOT/PVK: $Eu(DBM)_3(Tmphen)$/LiF/Ca/Ag, and ITO/PEDOT/PVK: $Gd(DBM)_3(Bath)$/LiF/Ca/Ag.

Results and Discussion

As we saw, the device (Sm^{3+}, Eu^{3+}) that emitted pure light originated from the electron transit of the RE ion from excited state to ground state when ITO was used as the anode and Ca/Ag as the cathode. However, it was interesting to note that repeatable electrical bistability was observed in current−voltage characteristics of all the devices when using ITO as the cathode, Ca/Ag as the anode, and the start voltage was swept from a negative value. Figure 2 shows the current−voltage characteristics of devices ITO/PEDOT/PVK: $Sm(DBM)_3(Tmphen)$/LiF/Ca/Ag, ITO/PEDOT/PVK: $Eu(DBM)_3(Tmphen)$/LiF/Ca/Ag, and ITO/PEDOT/PVK: $Gd(DBM)_3(Bath)$/LiF/Ca/Ag. It can be seen that the current increases progressively with the bias voltage from negative to positive and is high (high-conductance state, ON state, (2)). As the voltage is increased further, a sharp decrease in the current from 10^{-2} to 10^{-4} A occurrs at about 7 V, and the current keeps the low-conductance state (OFF state, (4)) with the current to decrease to 0, indicating the transition of the devices from the ON state to OFF state. This transition from the high-current state to the low-current state process

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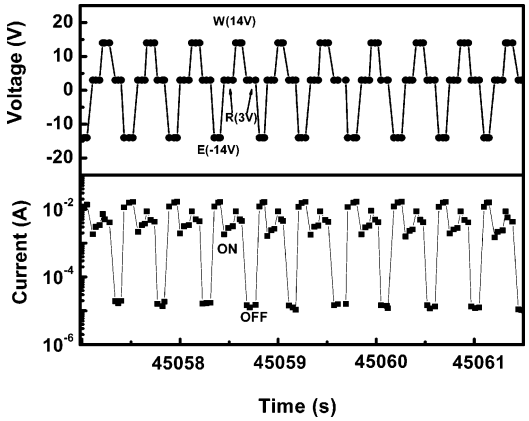

Figure 3. Typical current response of the device ITO/PEDOT/PVK: Sm(DBM)$_3$(Tmphen)/LiF/Ca/Ag during the write−read−erase−reread voltage cycles. The voltage for write, read, and erase are 14, 3, and −14 V, respectively.

is equivalent to the writing process in a digital memory cell. After this transition, the devices still remain in this state even after turning off the bias voltage. One of the most important features of the RE complex doped polymer films is that the low-current state can be recovered to a high-current state by the simple application of a negative bias. The $I-V$ characteristics define the electrical bistability of the devices and also reveal the nonvolatile nature of the memory effect. It was found experimentally that the shape of $I-V$ curves is repeatable, indicating the rewritability of the devices.

In addition to the rewriting capability, write−read−erase−reread cycles, ON/OFF current ratio, and retention time are also important characteristic parameters to the performance of a memory device. Figure 3 shows the write−read−erase−reread cycles for a ITO/PEDOT/PVK: Sm(DBM)$_3$(Tmphen)/LiF/Ca/Ag device. The voltages for write, erase, and read are 10, −14, and 3 V, respectively. The difference between the read and reread currents demonstrates the ON and OFF states of the bit stored in the bistable device. It can be seen that more than 10^6 write−erase cycles are conducted on 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 Figure 4a, where the currents on the ON state and OFF state as a function of the number of write−read−erase−reread cycle of ITO/PEDOT/PVK: Sm(DBM)$_3$(Tmphen)/LiF/Ca/Ag device are given. The ON/OFF current ratio reaches 2 orders of magnitude (10^2). For the retention time of the device, after applying a writing voltage of 14 V, and then waiting for several days to weeks, when again reading the device, the ON and OFF states are still observed. The approximately same write−read−erase−reread cycle capacity and ON/OFF current ratio are also achieved in the devices of ITO/PEDOT/PVK: Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag and ITO/PEDOT/PVK: Gd(DBM)$_3$(Bath)/LiF/Ca/Ag. The panels b and c of Figure 4 show the currents on the ON state and OFF state as a function of the number of write−read−erase−reread cycles of ITO/PEDOT/PVK: Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag and ITO/PEDOT/PVK: Gd(DBM)$_3$(Bath)/LiF/Ca/Ag, respectively. These features allow the application of the organolanthanide complexes as active medium in nonvolatile memory devices.

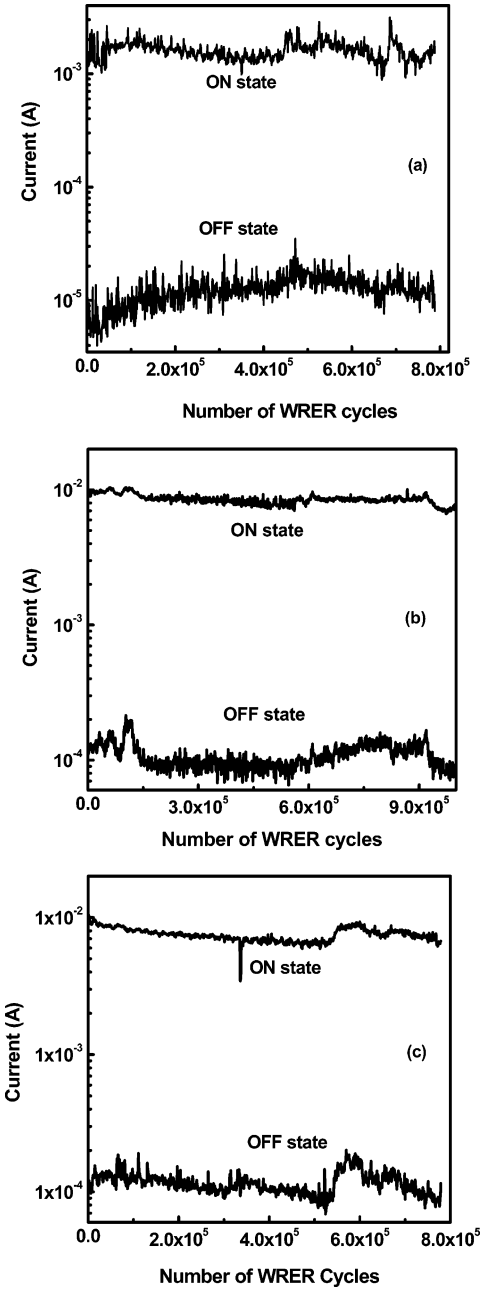

Figure 4. Write−read−erase−read cycles of the devices ITO/PEDOT/PVK: Sm(DBM)3(Tmphen)/LiF/Ca/Ag (a), ITO/PEDOT/PVK: Eu(DBM)3-(Tmphen)/LiF/Ca/Ag (b), and ITO/PEDOT/PVK: Gd(DBM)3(Bath)/LiF/Ca/Ag (c), respectively.

To determine the operation mechanism, the devices of ITO/PVK:Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag, ITO/PVK:Eu(DBM)$_3$(Tmphen)/Ag and ITO/PVK/Ag were fabricated. Figure 5 shows the current−voltage characteristics of ITO/PVK:Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag, ITO/PVK:Eu(DBM)$_3$(Tmphen)/Ag and ITO/PVK/Ag. It can be seen that ITO/PVK:Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag and ITO/PVK:Eu(DBM)$_3$(Tmphen)/Ag also show similar electrical switching properties to ITO/PEDOT/PVK: Sm(DBM)$_3$(Tmphen)/LiF/Ca/Ag. This indicates that the PEDOT and LiF/Ca layers do not play crucial role on the electronic transit between the ON state and OFF state. However, it was found experimentally that the introduction of the PEDOT and LiF/Ca layers improves significantly the stability of the fabricated memory

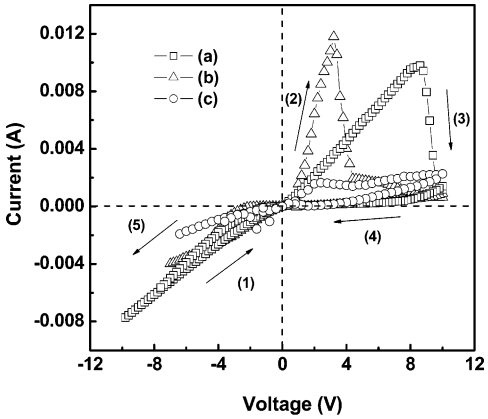

Figure 5. Current−voltage characteristics of devices ITO/PVK:Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag (a), ITO/PVK:Eu(DBM)$_3$(Tmphen)/Ag (b), and ITO/PVK/Ag (c).

devices. Furthermore, no obvious stable electronic transit phenomenon in the device ITO/PVK/Ag was observed, as shown in Figure 5. Therefore, it can be sure that the interaction between PVK and organolanthanide complexes should play an important role on the electrically switching characteristics in our devices. It was well known that PVK is a typical hole-transporting polymer and the carbazole group in PVK is a better electron-donor.[32] On the other hand, the organolanthanide complexes act as an electron acceptor.[35] 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.[30] For the case of RE complexes doped with PVK, therefore, it is concluded that the electronic transit is attributed to an electrical-field-induced charge transfer between PVK and RE complexes. The high-conductance state of the device is due to the higher hole mobility of PVK. The current increases with the increase of bias voltage, and when the bias reaches the threshold voltage, the reduced Eu complex can form a CT complex with surrounding oxidized carbazole groups.[32] 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 complex 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 seen that the conduction mechanisms in both the ON and OFF states exhibit bulk-limited characteristics. Panels a and b of Figure 6, respectively, show the $I-V$ characteristics of both ON state and OFF state in coordinates log(I) versus log(V) for the device ITO/PEDOT/PVK: Gd(DBM)$_3$(Bath)/LiF/Ca/Ag. Similar $I-V$ characteristics are also observed in the devices ITO/PEDOT/PVK: Sm(DBM)$_3$(Tmphen)/LiF/Ca/Ag and ITO/PEDOT/PVK: Eu(DBM)$_3$(Tmphen)/LiF/Ca/Ag. For the ON state, a straight line with slope of 1.3 is observed. The linear relationship suggests that the current conduction is Ohmic.[39] On the other hand, for

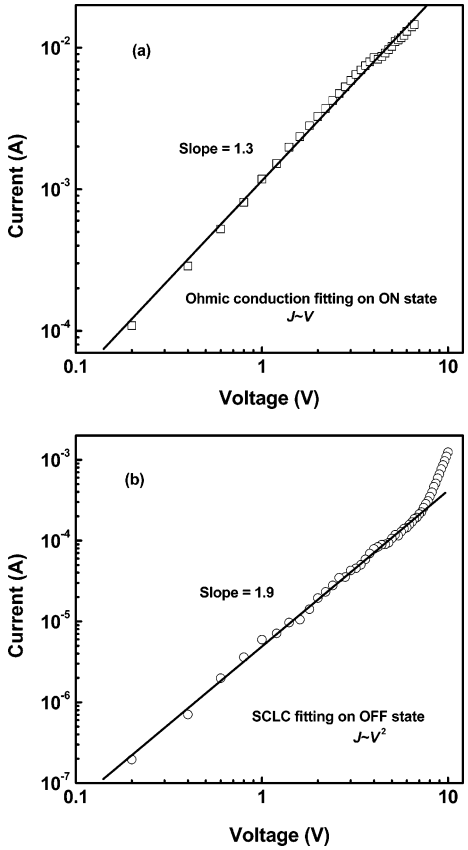

Figure 6. Current−voltage characteristics of the device ITO/PEDOT/PVK: Gd(DBM)$_3$(Bath)/LiF/Ca/Ag in the ON state (a) and the OFF state (b).

the OFF state, the $I-V$ characteristic shows a straight line with a slope of 1.9, indicating that the space-charge limited current (SCLC)[39] is probably the main conduction mechanism in the OFF state. Therefore, the change of the current conduction from the ON state to OFF state is only from Ohmic current to space-charge limited current.

Conclusion

We realized memory devices through a single-layer OLED structure with Sm^{3+}, Gd^{3+}, and Eu^{3+} RE complexes. The devices can be switched electrically between two states with a conductivity difference of about 2 orders of magnitude, and the switches are nonvolatile. Over 10^6 write−read−erase cycles have been realized, and no obvious current degradation was observed. Our results provided an interesting approach that simply dopes RE organic complexes into proper conducting polymers to form a novel material system as active medium in memory devices, which could have an important effect on the future information technology.

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