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Charge Transfer

Rewritable Multilevel Memory Performance of a Tetraazatetracene Donor–Acceptor Derivative with Good Endurance

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Abstract: A new tetraazatetracene derivative, 2,3-[4,4′-bis(*N*,*N*-diphenylamino)benzyl]-5,12-bis[(triisopropylsilyl)ethynyl]-1,4,6,11-tetraazatetracene (TPAs-BTTT), displays rewritable multilevel memory behavior, which is probably induced by multielectron intramolecular charge transfer (CT).

Organic resistive random-access memories (RRAMs) could be potential promising alternatives to traditional silicon-based memories owing to their flexibility, nanoscaling ability, high switching speed, and low power consumption.[1] Among various memory materials employed in sandwiched RRAM devices,[2] organic small molecules have received much attention owing to their well-defined structures; tunable band positions; and more accurate simulation–experiment matching; which is crucial to elucidate the structure–property relationship and charge-carrier transporting mechanisms.[3] In particular, multilevel memory materials could be developed through a reasonable molecule designing strategy to realize high-density data storage (HDDS). It has been demonstrated that introducing different electron “traps” into molecules could generate multiple resistive levels in one material when a potential is applied. However, most of these materials only show typical write once, read many times (WORM) behavior, or their performance needs to be induced by various excitation sources,[4] which has become a limitation for their practical application. Intramolecular CT induces rewritable memory behavior in donor–acceptor (D–A) molecules.[5] An interesting issue is whether multielectron intramolecular CT could occur, so that different charge injection could diversify the resistance of one material, and charge recombination could function as an “erasing” process, which would realize rewritable multilevel memory performance. To achieve this concept, more D–A units in one molecule could be a solution. However, this type of material is rare.

Recently, investigations into the synthesis and properties of large N-heteroacenes have attracted much attention,[6] and their potential applications in organic electronics, such as field-effect transistors, phototransistors, light-emitting diodes, photoelectrochemical cells, and photovoltaics, have been thoroughly investigated.[7] The electron-deficient pyridine or pyrazine units in N-heteroacenes could act as acceptors to realize good electron injection, especially, multielectron injection. On the other hand, the triphenylamine (TPA) unit has been widely employed as a donor moiety in memory materials, owing to its strong ability to stabilize a charge-separated state. By combining these two factors into one molecule, the synergistic effect could lead to a novel material with multilevel memory properties. Herein, we report a new tetraazatetracene derivative, TPAs-BTTT, which contains two TPA units as donors and 5,12-bis[(triisopropylsilyl)ethynyl]-1,4,6,11-tetraazatetracene (BTTT) as an acceptor. The memory devices based on TPAs-BTTT show a typical rewritable multilevel behavior with good endurance.

Figure 1 a shows the synthetic route for the preparation of TPAs-BTTT. The starting material, 4,4′-bis(*N*,*N*-diphenylamino)benzil (**1**), was prepared from TPA and oxalyl chloride through Friedel–Crafts acylation. TPAs-BTTT was obtained as a blue powder in 13 % yield by condensing 1,4-bis[(triisopropylsilyl)ethynyl]-2,3-diaminalphenazine (**2**) and **1** in acetic acid with a catalytic amount of IBX.[8] Block single crystals were obtained by slowly diffusing acetonitrile into a solution of TPAs-BTTT in toluene. As shown in Figure 1 b, in spite of the twisted conformation of TPA, TPAs-BTTT adopts good offset intersection face-to-face stacking among neighboring molecules. The interlayer distance of 3.626 Å is larger than that in common planar N-heteroacenes, but shorter than that of a van der Waals interaction;

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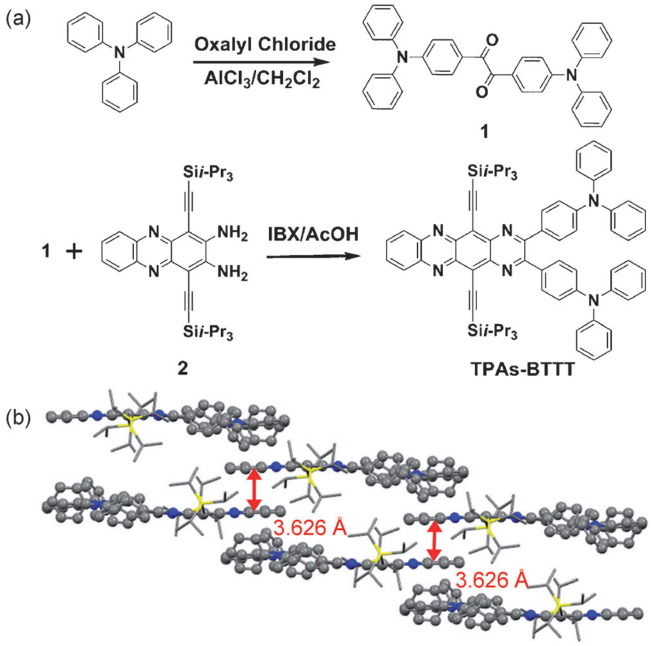

Figure 1. a) Synthetic route to TPAs-BTTT. IBX = 2-iodoxybenzoic acid. b) Molecular stacking of TPAs-BTTT.

this indicates that there are π–π interactions between adjacent molecules.

Figure 2a shows the UV/Vis absorption spectrum of TPAs-BTTT. Two absorption peaks in the visible region ($\lambda_{max} = 548$ and 594 nm) are observed in CH_2Cl_2, which suggests strong intramolecular CT. Redshifts of these absorptions occur ($\lambda_{max} = 548 \rightarrow 607$ nm and $\lambda_{max} = 594 \rightarrow 658$ nm) when the UV/Vis absorption spectrum was measured as a solid film; this corresponded to strong π–π interactions between adjacent molecules. The onset of the absorbance wavelength (λ_{onset}) in the solid film is $\lambda = 721$ nm, which is 26 nm redshifted relative to that at $\lambda = 709$ nm in CH_2Cl_2. The optical band gap of TPAs-BTTT is about 1.72 eV, as determined from λ_{onset} of the solid film.

Cyclic voltammetry was performed in CH_2Cl_2/0.1 M nBu$_4$NPF$_6$. As shown in Figure 2b, TPAs-BTTT first undergoes a reversible molecular reduction at a half-wave potential ($E_{1/2}$ versus $[FeCp_2]^+/[FeCp_2]$; Cp = cyclopentadienyl) of −1.03 V, followed by a less reversible reduction at $E_{1/2} = -1.28$ V. An irreversible oxidation at an onset potential of 0.30 V (E_{onset} versus $[FeCp_2]^+/[FeCp_2]$) and a reversible oxidation at $E_{1/2} = 0.73$ V can be observed, respectively. The different redox behavior suggests multielectron dissociation of TPAs-BTTT when excited by voltage potential, which could induce multilevel resistive states in memory devices. The HOMO energy level can be determined as −5.10 eV from the E_{onset} value of the first oxidation peak; the LUMO energy level is calculated to be −3.38 eV from the difference between the HOMO energy level and the optical band gap.

The sandwich-structured memory devices were fabricated on precleaned indium tin oxide (ITO) glass substrates. TPAs-BTTT in cyclohexanone (10 mg mL^{-1}) was spin-coated as an active layer with a thickness of 70 nm and high crystallization could be observed by AFM (Figure S6 in the Supporting Information). Gold was sputter-coated onto the TPAs-BTTT layer as the top electrode through an in situ metal shadow mask with a diameter of 100 μm and a thickness of 300 nm. The memory behavior of the ITO/TPAs-BTTT/Au device is demonstrated by current–voltage (I–V) characteristics (Figure 3a). In sweep 1, as

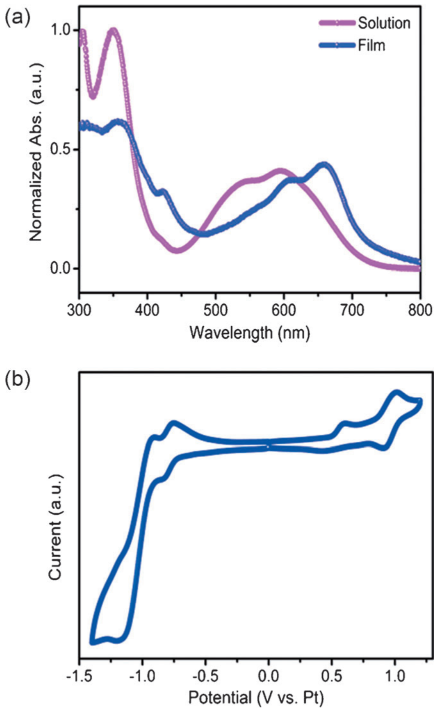

Figure 2. a) Normalized UV/Vis absorption spectrum of TPAs-BTTT. b) Normalized cyclic voltammograms of TPAs-BTTT in CH_2Cl_2/0.1 M nBu$_4$NPF$_6$.

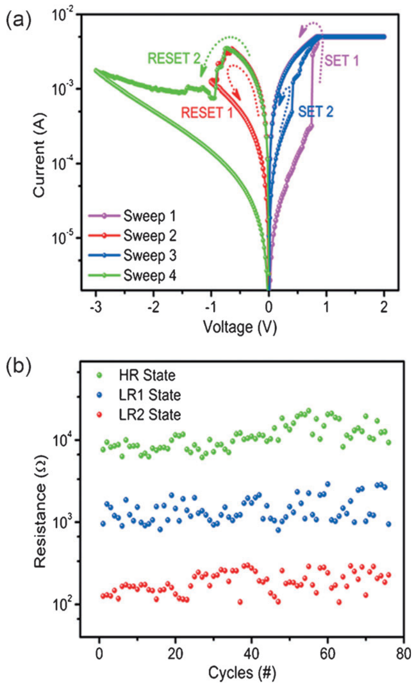

Figure 3. a) Current–voltage (I–V) characteristics of ITO/TPAs-BTTT/Au device. b) Endurance performance of the devices.

the potential goes from 0 to +2 V, the current is maintained in the low-magnitude region, the state of which is defined as a high-resistance state (HR state). An abrupt increase in the current can be observed with a threshold voltage at around 0.76 V; this indicates that the device switches to a low-resistance state (LR2 state) by SET 1 process (Figure 3 a). The device can retain the LR2 state both in the dual sweep from +2.0 to 0 V and after removal of the power supply; this suggests typical nonvolatile behavior. In sweep 2, from 0 to −1.0 V, the current drops and remains in an intermediate range, which is defined as the LR1 state; the process can be called RESET 1 (Figure 3 a). A positive sweep from 0 to 2 V (Figure 3 a, sweep 3) can further switch from the LR1 state to the LR2 state by SET 2. Another sweep (Figure 3 a, sweep 4) from 0 to −3 V can recover the initial HR state. The recovery of the device from the LR2 state to the HR state served as the RESET 2 process. Essentially, the HR and LR1 states could be generated by RESET 2 and RESET 1 operations, respectively. Starting from the HR or LR1 state, both SET 1 and SET 2 operations could result in the LR2 state. The three distinguished resistive states suggest that TPAs-BTTT has a multilevel memory performance. Each of these states could be switched to others through SET 1/SET 2 or RESET 1/RESET 2 operations, which can be defined as writing and erasing processes, respectively, and indicate that the as-fabricated memory device is rewritable. Cyclic switching operations have been carried out to investigate the endurance performance through the typical cycle of SET 1–RESET 1–SET 2–RESET 2. Generally, the device can be repeatedly switched between HR, LR1, and LR2 states for more than 70 cycles. Figure 3 b shows the resistance distribution of the three states for 76 cycles. The resistance values were read at 0.2 V in each state. The ON/OFF ratio between LR2 and LR1, and LR1 and HR is about eight, which indicates that the device would suffer much less from misreading. The SET 1 or SET 2 sweep from 0 to 2 V can switch the device to the LR2 state, and a reverse RESET 1 sweep from 0 to −1.0–1.5 V can result in the LR1 state. A larger reverse RESET 2 sweep of 0 to −3 V can give the HR state, which suggests that the multiple-states memory behavior is highly reproducible. The retention performance of the device was evaluated by applying a reading voltage of −0.2 V to the HR, LR1, or LR2 states under ambient conditions (Figure S7 in the Supporting Information). No clear current decay for each state was observed in 10^4 s during the test, which suggested that the multilevel states were retained.

Molecular simulation is employed to understand the switching mechanism and charge-carrier migration. As shown in Figure 4 a, the LUMO and HOMO energy levels are located at the BTTT and TPAs moieties, respectively, which could be helpful for intramolecular CT by combining good stacking with the low LUMO energy level. Figure 4 b shows the energy diagram of the ITO/TPAs-BTTT/Au system. The energy barrier from ITO (with a work function of −4.8 eV) to the TPAs-BTTT film is estimated to be 0.3 eV, which is smaller than that (1.72 eV) of gold (with a work function of −5.1 eV). Therefore, charge-carrier migration is dominated by hole injection. Interestingly, TPAs-BTTT has very close HOMO (−5.100 eV) and HOMO−1 (−5.093 eV) energy levels, which suggests that double-electron excitation could happen in one excitation process. In SET 1 (Figure 4 c), the charge-carrier concentration is very low and the device is in the HR state. As the voltage increases to the threshold voltage, double-electron excitation from the TPAs to the BTTT unit happens in the active layer and more free charge carriers are formed,[5a,9] and the device is set to the LR2 state. In the following RESET 1 sweep, a small reverse voltage (−1.0 to −1.5 V) possibly recombines one electron with one hole and the device is reset to the LR1 state. However, the LR2 state can be recovered by another positive sweeping, which is the SET 2 process, whereas a higher reverse voltage in the RESET 2 process can return the initial HR state.

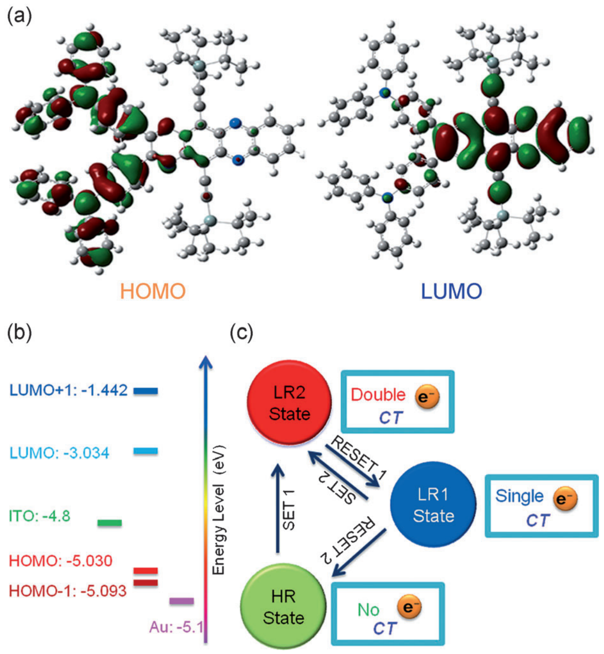

Figure 4. a) Calculated HOMO and LUMO energy levels of TPAs-BTTT. b) Energy diagram of the ITO/TPAs-BTTT/Au system. c) Schematic diagram of the switching process of the device.

In summary, a new tetraazatetracene derivative, TPAs-BTTT, containing two donors and one acceptor has been successfully prepared and characterized. The sandwich-like memory devices with TPAs-BTTT as the active layer exhibited nonvolatile rewritable multilevel memory behavior with good endurance and stability, which was probably induced by multielectron intramolecular CT. Our success could provide a useful strategy to develop novel organic small molecules for RRAMs.

Experimental Section

Data collection of crystals was performed on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized $\mathrm{Mo}_{K\alpha}$ radiation source ($\lambda = 0.71073$ Å). Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of the SHELXTL program package.

CCDC 1014927 (TPAs-BTTT) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: charge transfer · donor–acceptor systems · electrochemistry · heteroacenes · multilevel memory

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