Incorporating a redox active entity to attain electrical bistability in a polymer semiconductor†

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Owing to the advantages of 3-D printable stack, scalability and low cost solution state production, polymer-based resistive memory devices have been identified as the promising alternative for conventional oxide technology. Resistive memory devices based on the redox switch mechanism is particularly found to yield high precision with respect to the operational voltages. Reversible nonvolatile resistive state switching was realized with high device yield (>80%), with a redox-active chemical entity conjugated to the polymeric semiconductor, and the control experiments with the model compound confirmed the imperative role of the redox-active anthraquinone center in the polymeric backbone. Highly uniform nanodomains and the trap free layers excluded the possibilities of other known switching mechanisms. Optical studies and the molecular modelling data assert the presence of strong charge transfer characteristics upon optical excitation due to the insertion of the anthraquinone unit, which was detrimental in exhibiting bistable conductive states in electrical bias as well.

Introduction

To meet the global requirement of data storage under the evolution of technology, the efficiency of the basic data storage systems needs to be progressed.1–4 A mammoth augmentation in the digital data storage (more than 300%) over the last decade indicates the need of the hour.5,6 Power-efficient binary data storage devices are the most critical technology to meet the requirement.7 It is already known that the present data storage technologies have technical weaknesses that position them for replacement by upcoming resistive data storage technology.8–10 For example, HDDs drain battery life; and, although NAND (NOTAND) flash memory may offer nonvolatility, it suffers from slow writing speeds and a limited number of rewritable cycles.11–15 Today’s most promising alternative non-volatile memory technology is Resistive Memory, more precisely, Resistive Random-Access Memory (ReRAM), which is expected to inherit the market for NAND flash.16–20 These resistor-type memory devices offer simplicity in fabrication and allow the possibility for high data storage density via two-dimensional, or even three-dimensional crossbar arrays.21 This type of resistive memory devices can store data by defining the two states of electrical conductance (high and low) as “1” and “0” in response to an applied electric field. Hence, it is essential to investigate the underlying mechanism and the molecular level changes associated with the switching process, and it should be correlated to the chemical structure to develop efficient molecular materials with this aim. Organic small molecules, polymers, inorganic materials, and inorganic/organic hybrid materials have been successfully demonstrated for binary data storage in the literature.22–28 Most of the reports on polymeric active layer materials are composite active layer materials with suitable functional additives which may trigger phase segregation with time.29–32 Hence, single polymer active layer materials with the required functions are superior in fabricating memristor devices. The causing mechanisms of resistive state switching in such single polymer active layer materials are also important in obtaining the best output performance.33 Redox active (mostly strong acceptor) groups connected to the polymeric/small molecular backbone to achieve the Charge Transfer (CT) state mediated/redox mediated resistive state switching is known in literature (please see Table S4†). A detailed comparative analysis is provided in the ESI.† In most of the cases, the acceptor unit facilitates the charge transfer state formation with electrical excitation.34,35

In the present communication, we report the electrical bistability of a redox-active polymer (AQ2TDPP) in which the anthraquinone redox-active conjugate that acts as the acceptor...
centre is covalently connected to the thiophene-DPP monomer. Optical and electrical behaviour of its monomeric model compound 2TDPP (see ESI†) were also investigated to reach the conclusion on the switching mechanism. The synthetic procedure is as shown in Scheme 1. The detailed characterization procedures are provided in the ESI.† Polymer AQ2TDPP is synthesized by Stille coupling polymerization from compounds 1 and 2 (Scheme 1). AQ2TDPP was obtained with a moderate molecular weight ($M_n = 9.4$ kDa) and low dispersity ($D = 1.18$) index. Thermal stability of the polymer was studied using Thermogravimetric Analysis (TGA). Fig. S4† presents the thermogram of AQ2TDPP. It possesses high thermal stability with a decomposition temperature ($T_d$) of 218 °C.

Fig. 1a shows the geometry optimized structure and the orbital diagrams of the monomeric unit of AQ2TDPP. The Highest Occupied Molecular Orbital (HOMO) is localized over the 2TDPP unit, while the Lowest Unoccupied Molecular Orbital (LUMO) is confined to the anthraquinone conjugate. Hence, $S_0$-$S_1$ optical excitation is expected to possess charge transfer characteristics. Fig. 1b presents the optical absorption spectrum of a dilute solution and the spin-coated film of AQ2TDPP. The major absorption band centred at 590 nm is assigned to the $S_0$–$S_1$ (HOMO → LUMO) transition whereas the higher energy band centred at 380 nm is assigned to $S_0$–$S_2$ (HOMO–1 → LUMO). Solution state PL spectroscopy of both AQ2TDPP and 2TDPP also have been carried out. Monomer 2TDPP had a strong fluorescence band centred at 562 nm in chloroform whereas AQ2TDPP was non-fluorescent in solution. The non-fluorescent nature of the solutions of AQ and 2TDPP conjugate adduct also indicates the strong charge-transfer character to the excited state. The spin-coated films (of thickness ∼200 nm) of both the compounds were found to be non-fluorescent. The electrochemical characteristics of the polymer are depicted in Fig. 1c, which indicates the irreversible redox features of the polymer in dichloromethane (anhydrous). The irreversible reduction peak signifies the less favourable irreversible AQ moiety centred reduction process. The first reduction potential is observed to be at −0.71 V. HOMO–LUMO energy values of both the compounds are calculated from the reduction potential and the optical band gap (see the ESI† for more information). The optical and electrochemical properties of the model compound 2TDPP are well known in literature and are followed as such.36,37 The first oxidation and the reduction potentials ($E_{1/2}$) were 0.50 and −1.70 V againstFc/Fc⁺ as reference. Fig. 1d summarizes the relative energy level alignment of the various charge injection contacts and layers discussed later.

To understand the carrier transport behaviours of the neat films of AQ2TDPP and 2TDPP, single-carrier devices were prepared with the following device structure. The hole only and the electron only devices had ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/AI layer structures. The layers were chosen to facilitate/block certain carrier injections. For example, in electron-only devices, ZnO was used to prevent the hole injection at the ITO contact, and Au was chosen as the top electrode in hole only devices (instead of Al in resistive switching devices) to prevent electron injection at moderate bias voltage. The morphology of the active layer was characterised by Atomic Force Microscopy (AFM). The height image of the spin casted AQ2TDPP film and the characteristic cross-sectional height profile is depicted in Fig. 2b and c. The film exhibited a root mean square roughness of 1.77 nm, which confirms the minimum undulations on the surface and excludes the possibility of surface defects (see Fig. S5, ESI†). A film thickness of 200 nm was used for optical spectroscopic
techniques while the electrical characterizations were made using devices with 100–110 nm thickness. Thickness was monitored using cross-sectional SEM analysis (Fig. S5b†) while film deposition optimization process. The devices yielded characteristic ohmic as well as trap free space charge regime of the carrier transport in the case of the hole only devices, whereas the electron only devices exhibited strong field dependency at the lower bias voltage indicative of electron traps in the layer. As mentioned in Fig. 2a, the carrier mobilities were obtained from Mott–Gurney relation (ESI†) of the single carrier devices. The hole mobility was calculated to be $1.13 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, whereas the obtained electron mobility was $1.23 \times 10^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$. The electron mobility is an order less in comparison to the hole mobility of the films. This is attributed to the charge trapping nature of the AQ units in the active layer polymer matrix. The $J$–$V$ curves clearly indicated the trap free electron and hole transport across the active layer. Interestingly, none of the single carrier devices exhibited the bistable conductive responses. This confirms the involvement of both the carriers in exhibiting bistable conductivity in devices. Hence, we have chosen ITO and Al as the injection contacts in resistive memory devices.

The resistive memory devices of both AQ2TDPP and 2TDPP were fabricated on patterned glass/ITO substrates with a device area of $2 \times 2$ mm$^2$. Detailed fabrication procedure is provided in the ESI† All the fabrication and the electrical characterizations were conducted at ambient atmospheric conditions. To compare the dependence of atmospheric moisture, inert conditions are maintained during the fabrication process and probing. A total of 32 devices of each molecule was fabricated, and the current–voltage ($I$–$V$) characteristics of these devices have been investigated.

More than 81% of the devices in the case of AQ2TDPP are found to exhibit characteristic bistable resistive states, whereas none of the devices of 2TDPP is found to be successful in terms of its resistive bistability. A representative $I$–$V$ response of a AQ2TDPP device is depicted in Fig. 3a. It clearly indicates the existence of reversible non-volatile bi-stable states. For the best performing device of AQ2TDPP, in the first positive sweep from 0 to 3 V, the current showed an abrupt increase from $2.67 \times 10^{-2}$ mA to $2.01 \times 10^{-1}$ mA at a switching threshold voltage ($V_{th}$) of $\sim 2.5$ V. This type of switching process presented a transition from a low-conductivity (OFF) state (state-I) to a high-conductivity (ON) state (state-II) and can be regarded as the “writing” process in memory devices. The device is found to remain in the ON state (state-II) until a certain negative bias is applied. Keeping the device in state-II, if the applied bias is turned off, it is observed to remain in the ON state (state-II) itself. This clearly indicates the existence of the non-volatile nature of the data stored in the device. In the reverse sweep from 0 V to $-3$ V (sweep 2), the device is found to be in the ON state (state-II) until the voltage is below $-1.8$ V, and at $-1.9$ V the ON state is observed to relax back to the OFF state (state-I). The observed current ratio corresponding to these states is 12.5 for the best performing device. The log scale plot of the $I$–$V$ response indicates the switching between two Ohmic states characterised by two linear conductive states with slope $\sim 1$ (Fig. 3d). This observation indicates that the conduction process is primarily Ohmic in both the states, which exclude the possibility of mechanisms of conductive filaments. In addition, upon applying a constant stress of 0.5 V, there was no significant degradation in the current for the two different states for more than 30 000 s, as shown in Fig. 3b. To ensure the ability to switch the states, more than 100 cycles of switching were monitored (Fig. 3c), which ensures the rewritable efficiency of the device. On the contrary, 2TDPP devices yielded no characteristic bistability, as shown in Fig. S10 (ESI†), as a representative example. The homopolymer of 2TDPP is quite known in the literature for its use in organic photovoltaic devices, but no report on the electrical bistability is available yet. Hence, it is concluded that the resistive state switching is imparted to the polymeric active layer due to the incorporation of the anthraquinone acceptor unit to the backbone, which induces the irreversible reduction feature to the entire polymeric chain, and the recombination of electronically excited molecules upon bias would be due to the strong charge transfer characteristics as it is localized over AQ (electrons) and 2TDPP units (holes) exclusively. Consistent performance of the device is also supported by the narrow distribution of the threshold voltages of these devices (Fig. 4b) unlike the other underlying mechanisms of the bistable charge transport. Fig. 4b displays the distribution of the turn-on voltage of the 26 devices fabricated out of AQ2TDPP.

The proposed underlying mechanism of the resistive state switching in the redox conjugate AQ linked semiconductor polymer is as follows. Fig. S9 (ESI†), shows the molecular electrostatic potential (MEP) surface. The transparent blue area indicates the positive centres that facilitate the hole migration through this open channel. However, there are some negative ESP regions (red), which arises from amide and carbonyl groups of DPP core and the anthraquinone moiety, respectively. These negative regions, especially the AQ centre, act as a
in the control sample (AQ2TDPP) and (c) proposed mechanism of switching pathways.

Fig. 4 Set (a) and reset (b) voltage distribution and the proposed mechanistic pathway of switching process of the resistive memory devices of AQ2TDPP and (c) proposed mechanism of switching pathways.

deep “electron trap” (as discussed in cyclic voltammetry) to localize the charge, leading to charge retention, which needs reverse bias condition to detrap the charges. The electrically generated electron–hole pair has to undergo a CT state mediated recombination as the electrons will be localized over the AQ unit and the holes are localized over the 2TDPP unit (Fig. 4c). From the energy level diagram of different layers of the device, the energy barrier for the electron and the hole injection process at Al and ITO contacts in forward bias is 0.49 and 0.66 eV, respectively.

The HOMO/LUMO energy levels and electrode work function alignment suggests that the electron injection is more favourable over the hole injection in forward bias. Yet, at low bias voltage, the electric field is low, charge carriers will not possess sufficient energy to overcome the Schottky barrier at the ITO/AQ2TDPP interface, and the small current as observed is likely due to the tunnelling of the charge carriers. When the applied voltage exceeds the Schottky barrier height of ~0.22 eV, holes are preferentially injected into the polymer layer and migrate through the continuous positive ESP channel of the polymer backbone (in the light blue colour of Fig. S9, ESI†). When the applied voltage reaches the reduction potential of the acceptor unit (anthraquinone) determines the threshold voltage of the “ON” state. The transport process of neutral and the reduced state of the acceptor unit was found to be the cause of electrical bistability in the device. In summary, the elucidation of the resistive state switching is as proposed in the schematic diagram (Fig. 4d).

Conclusions

Observation of resistive state switching in polymers with a redox-active acceptor unit has been demonstrated. The control model compound, monomer unit deprived of the acceptor group, was a fiasco in its response. This ensures the mechanistic course of the process. The Schottky injection barrier at the respective electrodes and the reduction potential of the acceptor unit (anthraquinone) determines the threshold voltage of the “ON” state. The transport process of neutral and the reduced state of the acceptor unit was found to be the cause of electrical bistability in the device. In summary, the elucidation of the resistive state switching is as proposed in the schematic diagram (Fig. 4d).

Author contributions

NGG and CK carried out the synthesis and the characterization of all the compounds. BKB has performed the electrical characterization and the microscopic analysis. IG conducted the optical and electrochemical analysis. SSZ supervised the synthesis and RV designed the project, supervised and analysed the data in consultation with all the authors. RV drafted the manuscript with input from all the authors.

Conflicts of interest

There are no conflicts to declare.

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