

Organic bistable memory device based on a novel pyrrolo-pyrrole derivative, PPbAN

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Because of its interesting possibilities organic electronics has recently gained tremendous attention among researchers. New polymers and conjugated molecules are being synthesized and studied for organic electronic applications. Here we are reporting a bilayer organic bistable memory device based on a pyrrolo-pyrrole derivative, 3,3'-(5',5''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5',5'-diyl))bis(2-(4-nitrophenyl)acrylonitrile) (PPbAN) which is highly conjugated and having the donor property. A known and widely used acceptor methano fullerene, [6,6]-phenyl C61 butyric acid methyl ester (PCBM) has been used as the acceptor. Device fabrication is carried out on an Indium tin oxide substrate by spin coating technique, aluminum is used as the top electrode. The device exhibited good bistability with a low conducting state having thermionic emission behavior and a high conductivity state following ohmic nature.

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1. Introduction

With the possibility of large area light emitters and photo voltaic devices [1-4] with organic semiconductors, organic electronic has gained attention of the researchers because of its potential to realize high performance devices by tailoring the material properties. By modifying the device structure or semiconductor material properties one can realize a high performance device. Further there are possibilities of material tuning also. Compared to the conventional silicon based electronics where the material choice are limited to elemental semiconductors like silicon, germanium, and compound semiconductors like GaAs, InP etc., possibilities of organic electronics are huge. Because of the availability of a large number of polymers especially conjugated and organic molecules having high conjugation there is a wide spectrum of materials available for organic electronics. The ease of custom modification of polymers or molecules by chemical engineering makes the spectrum much wide.

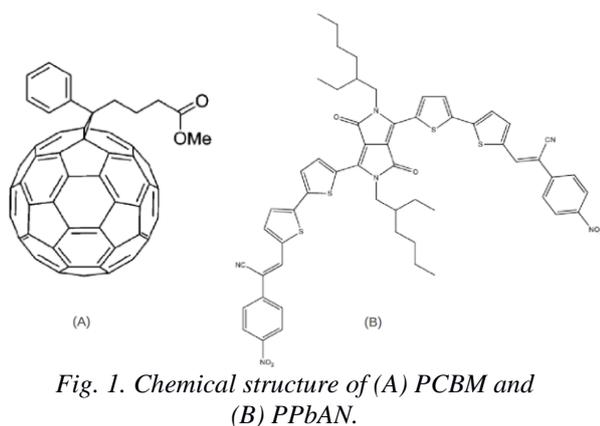
Organic bistable memory is a relatively new entry to the group of organic electronic devices by the demonstration of L. Ma [5] in 2002. Being two terminal devices with switchable electrical property, the resistance of these devices can be switched from an initial low value to a higher one by applying suitable voltages. Recently there are reports [6,7] based on the charge trapping by various metal nanoparticles or nano clusters embedded in insulating or conjugated organic matrices. Memory device based on the electron acceptors such as fullerene and its derivatives are investigated [8-10] by various groups.

Electric field induced charge transfer in donor acceptor systems are also studied [11-13] for bistable memory application. Compared to acceptor type molecules a large number of donor type conjugated molecules have been synthesized and studied by various groups [16]. Fullerene and its derivatives are widely used as electron acceptors organic electronic devices. Out of them the methano fullerene, [6,6]-phenyl C61 butyric acid methyl ester (PCBM) has gained much attention [14,15].

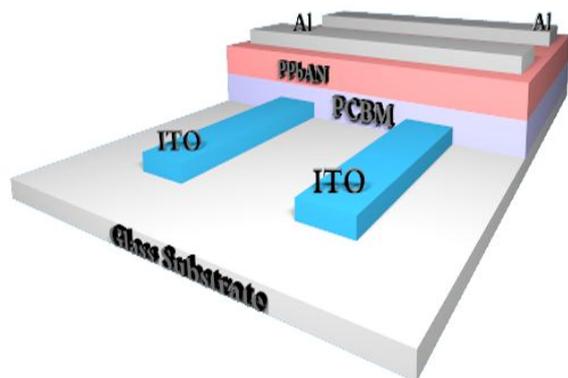
Here we are reporting for the first time the use of a Pyrrolo-Pyrrole derivative, 3,3'-(5',5''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5',5'-diyl))bis(2-(4-nitrophenyl)acrylonitrile) (PPbAN) in memory switching application. The structure of this donor type molecule is shown in the Fig. 1. Also given in the same figure is the structure of the acceptor molecule used for making the device along with PPbAN.

2. Experimental

PCBM, and Indium tin oxide coated (ITO) PET sheet are procured from Sigma Aldrich while PPbAN is supplied by our collaborating group at Jaipur Engineering college, Jaipur, India. The chemical structures of these materials are shown in the Fig. 1.



For fabricating the memory device, Indium tin oxide (ITO) coated PET films are patterned to form parallel strips with 5 mm width each through chemical etching of the ITO sheet in a mixture of dilute HNO_3 and HCl through suitable masks. Patterned substrates are thoroughly cleaned by first washing with detergent and then sonicating successively in isopropanol and deionized water for 20 minutes each. They are then vacuum dried and exposed to oxygen plasma for 5 minutes to improve the hydrophilicity of the substrate surface. Device structure employed is shown in Fig. 2. Both the donor and acceptor molecules are coated over the substrate by spin coating from a 10 mg/ml solution of PPbAN in Acetonitrile and PCBM in Chlorobenzene respectively. Each layer is vacuum dried before the application of next layer. The final bilayer structure is dried in a vacuum oven overnight for the removal of solvents. Top, aluminum (Al) electrodes are deposited by thermal evaporation at a base pressure of 10^{-5} mbar, through a shadow mask in the form of strips having 5 mm width running in perpendicular direction to the bottom ITO contacts resulting in a final cross bar structure as shown in the Fig. 2. Switching characterization of the device is made using an automated setup consisting of a Keithly 2400 Source Meter Unit.



3. Results and discussion

From the absorption spectrum of PPbAN (Fig. 3), it is clear that the absorption starts at around 760 nm

corresponding to an optical band gap of $\sim 1.62\text{eV}$. A typical current voltage curve for the device showing the bistable switching and hysteresis is shown in Fig. 4. Initially the device is in high resistance state or OFF state as indicated by the low current during the beginning of first scan (indicated as S1 in Fig. 4) from 0 to 10 V.

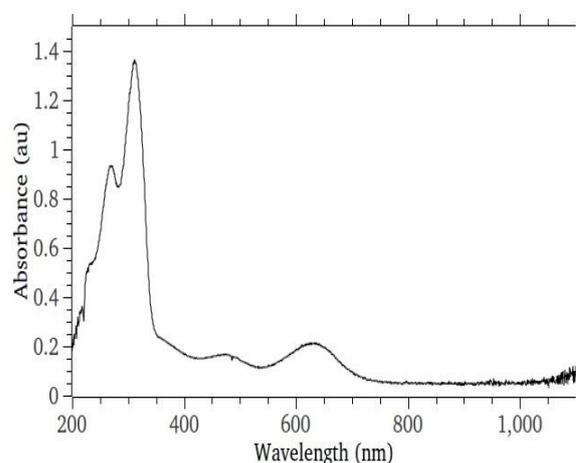


Fig. 3. UV-Visible spectra of PPbAN solution in acetonitrile.

The current is seen increasing monotonously at low voltages and at 5 V the current jumps to a high value and continues at this high current (low resistance) path or ON state during the rest of the voltage changes. During the reverse scan (as indicated by S2 in Fig. 4) of 10 V to -10 V the current follows a new path of low resistance and it stays in that state until the negative bias reaches -5 V, and then switches back to the initial high resistance state. It can also be seen from the Fig. 4 that device switches to high-conductivity state again on applying the positive sweep. However this case switch - ON occurs at a slightly higher voltage.

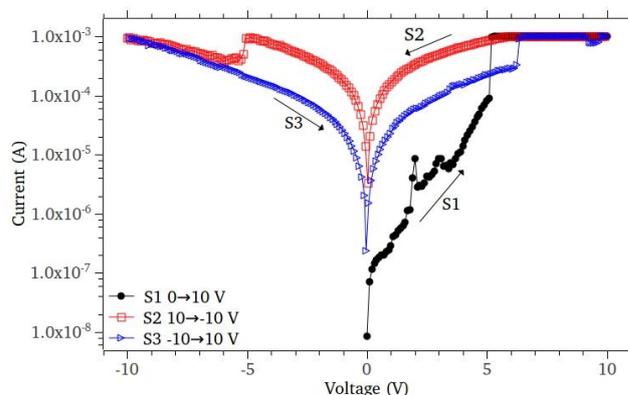


Fig. 4. Current - voltage characteristics of ITO/PPbAN/PCBM/Al device; S1, S2, S3 are the consecutive scans applied to the device.

The switching action observed here can be explained on the basis of the concept of electric field induced charge transfer between PPbAN and PCBM. At low applied

voltages the current in the device can be attributed [17] to the thermionic emission of charge carriers from the electrodes. In the case of thermionic emission, current through the device is proportional to the exponential of the square root of applied voltage. The OFF state current of the device and the fairly good exponential fit made to it (Fig. 5), again indicate the suitability of the thermionic emission model to the observed switching of our device.

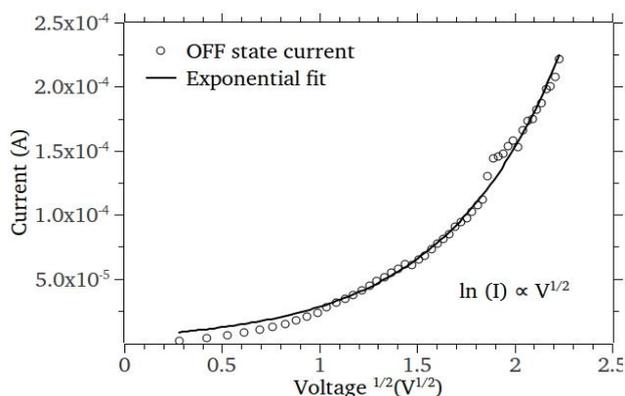


Fig. 5. Plot of OFF state Current vs $(\text{Voltage})^{1/2}$, an exponential fit is also shown.

Further it can be assumed that when the field attained enough strength there will be injection of electrons from the HOMO of PPbAN to the LUMO of PCBM with the HOMO of PPbAN and LUMO of PCBM being partially occupied. This leads to the generation of charge carriers because of the positively and negatively charging of PPbAN and PCBM. These charge carriers can be considered to be responsible for the switching of the current to the observed high value. The ON - state current exhibits an ohmic behavior as seen from the Fig. 6, where a linear fit is made to the ON state current.

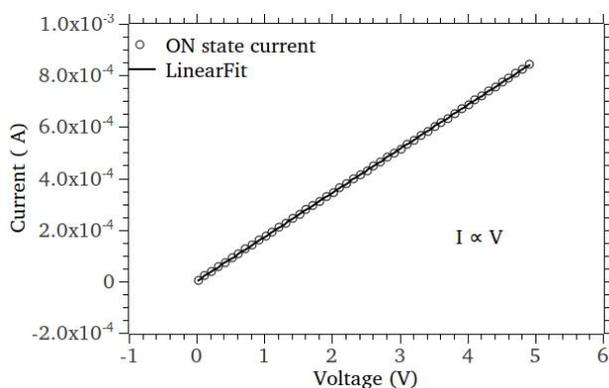


Fig. 6. ON state current response of the device; a linear fit is also shown.

Finally, the application of the negative bias causes charge transfer to reverse direction bringing the device back to the initial high resistance state.

4. Conclusion

The studies revealed that the PPbAN with its low band gap (1.62eV) is a potential candidate material for organic electronic applications. Bilayer memory device investigated with PPbAN is showing bistability with nonvolatile nature. Conduction mechanism in OFF state is found to exhibit thermionic emission nature and ohmic model is suitable for the ON state current. Even though the memory performance is promising there exists problems like instability in switching voltages which needs attention.

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