



# Memory devices based on small organic molecules donor-acceptor system

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## ABSTRACT

For the last a few decades the interest in using organic materials in electronic applications (light emitting diodes, field effect transistors, solar cells, etc) has increased rapidly. Recently, organic materials have also been used to realise electronic memory devices. These devices show two electrical conductance states (“high” and “low”) when voltage is applied. The memory effect in these devices with simple structure based on a thin film of nano-sized particles and/or small molecules embedded in an organic layer was demonstrated. This work investigates organic memory devices based on organic materials–blend between small organic molecules (TTF and TCNE) and polymer (PVAc).

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## 1. Introduction

Organic materials exhibit remarkable properties and in recent years the interest in using these materials in electronic device has shown a rapid increase. For example, numerous organic materials have been proposed and demonstrated for their possible applications in solar cells [1], thin film transistors [2] and light emitting diodes [3]. Recently, the use of organic materials has been demonstrated in electronic memory devices. A memory effect has been reported in a large variety of organic materials and device configurations. The simplicity of the structure, low-temperature processing and the low fabrication cost are same important characteristics of this category of devices. The structure of such polymer memory devices (PDMs) consists of cross-point elements with two parallel top and bottom electrodes between them an active organic layer (an admixture of polymer and small organic molecules or/and nanoparticles). These devices show electrical bistability, “low” and “high” electrical conductive states, when voltage is applied attest that it can be used as data storage cells.

A numerous combination of metallic [4–6], ferroelectric [7], semiconducting [8] nanoparticles and organic small molecules [9–19] in a polymer matrix have been shown to exhibit memory behaviour.

In some cases the physical origin of the switching mechanism is clear (for example in devices based on a blend between polymer and ferroelectric nanoparticles) but in other reported polymer memory devices; there are many hypotheses but ambiguous explanations.

Paul [9] and Kanwal et al [10], demonstrated, for the first time, a fully-organic bistable memory device based on a blend of polyvinyl phenol (PVP) and small organic molecules (fullerene  $C_{60}$ ). In this type

of memory device  $C_{60}$  plays an essential role as the charge storage medium.

The effect of  $C_{60}$  concentration on a capacitance–voltage (C–V) curve for organic memory devices using a poly(4-vinyl phenol) (PVP) layer was presented in [11]. Electrical proprieties and working mechanism in memory structures fabricated using the poly(N-vinylcarbazole-PVK) and  $C_{60}$  are reported in [12].

Devices with gold nanoparticles in combination with small organic molecules (8HQ) embedded in a polymer matrix have been demonstrated by Ouyang et al. [13,14] and Prime et al [15,16].

Memory devices based on polystyrene (PS) as the matrix and methanofullerene6,6-phenyl  $C_{61}$ -butyric acid methyl ester (PCBM) as an organic electron acceptor and tetrathiafulvalene (TTF) as an organic electron donor has been demonstrated. They explain the bistability of the devices by electrically-induced charge transfer between conjugate organic compounds [13,17].

In 2007 [18] Paul proposed a model to clarify the switching mechanism in devices where in the polymer matrix (polystyrene) an electron donor 8 hydroxyquinoline (8HQ) and fullerene ( $C_{60}$ ) as electron acceptor were embedded and the memory behaviour was explained on the basis electric dipole formation in the matrix.

In our recently published work [19] we have demonstrated successfully a new D–A (donor–acceptor) small organic molecule pair, tetrathiafulvalene (TTF) as an electron donor and tetracyanoethylene (TCNE) as an electron acceptor, as element that determined memory behaviour. In this work, we investigate the effect on the device performance and stability of a D–A pair of the small organic molecules the effects of their concentration has also been investigated in detail.

## 2. Experimental details

In this study, we used polyvinyl acetate (PVAc), as a host material and tetrathiafulvalene and tetracyanoethylene organic molecules, all supplied from Sigma Aldrich. The solution for the organic active layer

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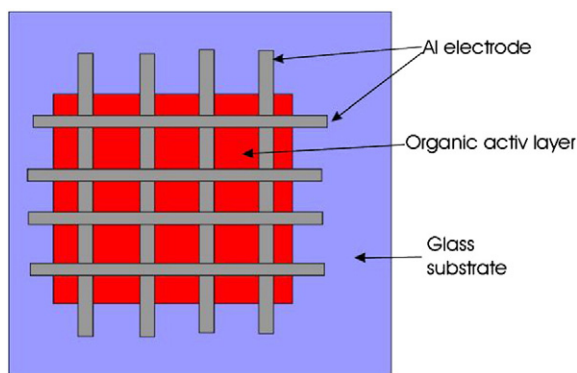


Fig. 1. Schematic diagram of metal/polymer blend/metal (MPM) structure.

was prepared as follows: firstly, small organic molecules (TCNE) was dissolved in methanol and kept continuously in ultrasonic bath. After visual conformation that TCNE had dissolved fully methanol then a second organic molecule (TTF) was added and in finally PVAc. The concentration of the PVAc was kept constant (30 mg/ml) and the concentration of organic molecules was varied (2.5; 5 and 10 mg/ml). For electrical measurements ( $I$ - $V$  characteristics, write/read/erase cycles and retention time), metal/polymer blend/metal (MPM) structures, as shown in Fig. 1, were fabricated. In order to realise these structures, the aluminum bottom and top electrodes were deposited by thermal evaporation in vacuum and the polymer blend layer was deposited by spin coating. A glass slide was used as a substrate.

The metal/insulator/semiconductor (MIS) structures investigated in this work consisted of an ohmic Al bottom contact to p-type Si, a polymer blend (polystyrene(PS) and TCNE and TTF) followed by polyvinyl acetate (PVAc) and in top aluminium (Al) electrode.

The current-voltage ( $I$ - $V$ ), write-read-erase-write and retention time characteristics of the memory device structures were measured in a screened chamber, in the dark, at room temperatures, using a PC-driven picoammeter (HP4140B). Capacitance-voltage measurements were conducted on an HP4192A impedance analyser at a frequency of 1 MHz.

### 3. Results and discussion

The chemical structures of the polyvinyl acetate (PVAc), tetracyanoethylene (TCNE) and tetrathiafulvalene (TTF) are shown in Fig. 2.

Previously, we have investigated extensively the charge transfer between organic molecules, TCNE (electron acceptor) and TTF (electron donor) [19]. The existence of the charge transfer between organic molecules was confirmed by the FTIR spectra band around  $2200\text{ cm}^{-1}$  related to the  $\text{C}\equiv\text{N}$  stretching mode (not show here) (Fig. 3).

Based on FTIR results, we believe that charge transfer occurs between TCNE and TTF, giving rise to electric dipole formation in the polymer matrix. The TTF-TCNE dipoles play a key role in the switching behavior of memory devices. Individual small organic molecules (TTF, TCNE), and also as a D-A complex, have been studied by other workers [20–27]. In order to investigate the essential role played by the molecules complex (donor and acceptor types) in the switching

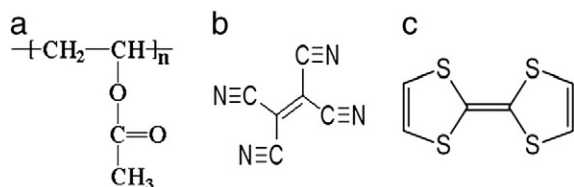


Fig. 2. Chemical structures of (a) polyvinyl acetate (PVAc); (b) tetracyanoethylene (TCNE); (c) tetrathiafulvalene (TTF).

mechanism, the influence of their concentration on the performance of these memory devices was investigated. It is well known [20–27] that TTF is an electron donor molecule and TCNE is an electron acceptor molecule. When these two organic molecules are incorporated in a polymer matrix it is expected that charge transfer will occur. Once the charge is transferred, the molecular combination becomes similar to a “salt”, in which one component is positively charged and other is negatively charged. This creates a dipole structure in the polymer matrix, which results in an internal electric field in the device. The switching mechanism between the low conductivity state and the high conductivity state in our devices is determined by this internal electric field. This working mechanism, based on the displacement of charges of opposite polarity on the application of an external electric field, has been reported previously in [7,18,19,28,29].

The study was conducted for three different concentrations 2.5; 5 and 10 mg/ml respectively of small organic molecules (Fig. 3).

Fig. 4 compares  $I$ - $V$  characteristics of structures where active layer contains a polymer polyvinyl acetate (PVAc) (30 mg/ml) and with organic molecules (1:1 ratio) with three different concentrations. The concentrations of PVAc were kept constant to study the effect of different concentrations of small molecules on the switching-behaviour of the memory devices. It is evident from these results that concentration has significant effect on the hysteresis observed in the  $I$ - $V$  behaviour.

Current-voltage behaviour of a metal/polyvinyl acetate only/metal device shows a small hysteresis (not shown).

The current-voltage characteristics of the sample consisting of TCNE and TTF (2.5 mg/ml) embedded in the polymer matrix reveals a flat hysteresis. For the samples which contained 5 and 10 mg/ml TCNE and TTF, the large current-voltage curves were observed. This result was expected (in the  $I$ - $V$  behaviour and in on/off ratio respectively) because the internal electric field is directly proportional to the number of charges in the dipole system. Also, from the current-voltage curve the on/off ratio was measured and it has been observed that the samples with 5 mg/ml of organic molecules (TCNE, TTF) show the highest value. A possible explanation is that by increasing the concentration of small organic molecules changes occur in the segregated (stacking) type (dimmer or mixed) or/and in the stacking geometry (distortions of molecules). This may have a direct effect on the electric dipole formation and thus may cause an increase in the on/off ratio with an increase in the concentration of small molecules in PVAc.

The write-read-erase cycles of the sample which contained small organic molecules (TCNE, TTF) with 5 mg/ml and 10 mg/ml are shown in Fig. 5. It is evident that for the sample with 5 mg/ml the on/off ratio remains constant after many cycles in comparison with the sample with 10 mg/ml which decreases after few cycles. We are taking further study to understand fully the observed behaviour. It is very clear from Fig. 5a that the devices are switching between a high conductivity (“0”) to low conductivity (“1”) states. The difference between the “0” and “1” state is around  $0.1\text{ }\mu\text{A}$ .

Additionally, a multicycle stability test on these devices (admixture of PVAc and 5 mg/ml TCNE and TTF) was investigated (Fig. 6). The devices exhibit a distinguishable two conductivity state for over 5000 cycles.

All write/read/erase and stability tests suggest that the memory devices containing a small organic molecules complex using a 5 mg/ml concentration has an excellent performance.

In order to confirm that charge transfer is taking place the capacitance-voltage ( $C$ - $V$ ) behavior of metal/insulator/semiconductor (MIS) structure was investigated.

The  $C$ - $V$  curves for devices p-Si/PS/PVAc/Al without small organic molecules show a flat band voltage shift of about  $0.2\text{ V}$  (Fig. 7a). The samples which contained both molecules TCNE and TTF show clearly a hysteresis with a flat band voltage shift around  $10\text{ V}$ . Thus indicating the essential role played by small organic molecules in our devices and the results sustain our hypothesis that the mechanism is determined by dipole formation and rotation under external an electric field.

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