Write-Once-Read-Many-Times (WORM) Memory Applications in a Monolayer of Donor/Acceptor Supramolecule

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We demonstrate write-once-read-many-times (WORM) memory in a monolayer of a donor/acceptor (D/A) composite. Both molecular layer and multilayer films show irreversible memory-switching to a high-conducting state. The ratio between the conductivities of the two states is around 1×10^4. Although the individual components show a reversible nonvolatile memory or no memory at all, the composite system exhibits irreversible switching for WORM applications with a long retention time. Monolayer of a composite system as memory elements provides newer directions to introduce organic molecules in integrated electronic circuitry.

1. Introduction

As an alternative to the post silicon technology, molecular electronics is aiming toward the use of a single molecule or an assembly of molecules as an active element in integrated electronic circuitry. Aviram and Ratner were the first to propose a D-σ-A molecule connecting an electron donor moiety (D) to an electron acceptor (A) one through a saturated sigma bridge (σ) as an electronic component, a rectifier.[1] Metzger et al. experimentally confirmed a molecular rectifier with a molecule connecting D and A moieties by a π-bridge (D-π-A).[2] Now, with the success of several electronic and opto-electronic devices based on (bulk) conjugated organics, research is focusing on molecular switches and memory elements.

Memory elements are generally based on electrical bistability of organic molecules. Bistability can result from threshold or Ovshinsky switching[3] and memory switching.[4] In the former type of switching, a bias is needed to maintain the higher conducting state. In memory switching, both the conducting states have an associated memory and hence do not require a bias to sustain them. In both the cases, the two conducting states are observed at an applied voltage. Some of the mechanisms for electrical bistability are (1) voltage-activated alignment of Fermi levels of the contacts with molecular orbitals,[5] (2) structural rearrangement (conformational change),[6,7] (3) electroreduction,[8−10] or (4) electroreduction with conformational change.[11] In all the cases, conjugation in the backbone of the molecule is presumably extended and/or the HOMO−LUMO gap is reduced to result in the high-conducting state. Regardless of the mechanisms put forward in the literature, the two types of switching, namely threshold and memory, could not be predicted in one system. Instead of using a single material as an active element, donor/acceptor assemblies have also been an approach.[12] Advantages of such assemblies are the ability to tune its electronic and transport properties through either of the components to achieve unique devices. Additionally, improvement in the signal-to-noise ratio can be realized in such D/A systems.[13] Molecules adsorbed on the surface of carbon nanotubes have been an approach to achieving addressibility.[14]

Though the ultimate aim is to use a single molecule as an active component in electronic circuits, available systems cannot characterize a nanoscale object (<10 nm) at ease within a nanogap with stable electrical contacts.[15] Instead of using a single molecule as an active element, a donor/acceptor assembly (or a monolayer of the assembly) may be an alternative approach to addressing and characterizing nanoscale structures. In this article, we aimed to achieve

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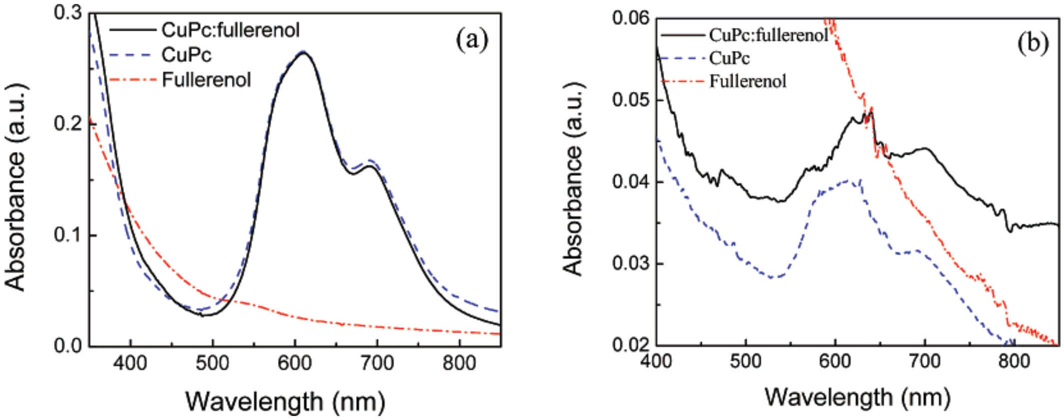

Figure 1. (a) Electronic absorption spectra of CuPc:fullerenol, CuPc, and fullerenol solution. (b) Corresponding spectra of one monolayer film.

electrical bistability and memory phenomenon in a molecular layer of a D/A system. With the ease in addressing the hybrid systems, we focus on how the electrical properties compare with those of the components.

2. Experimental Section

As a D/A composite system, we choose copper(II) phthalocyanine and buckminsterfullerenes (C_{60}). Because we targeted to use the molecular layer of the composite, we deposited a layer-by-layer (LbL) electrostatic assembly from tetrasodium salt of copper(II) phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid (CuPc) and polyhydroxyfullerene, $C_{60}(OH)_x$, $x = 22-26$ (fullerenol), with poly(allylamine hydrochloride) (PAH) as the intermediate polycation. Whereas CuPc and PAH were purchased from Aldrich Chemical Co., fullerenol was purchased from MER Corporation, Tucson, Arizona. We deposited LbL films of CuPc, fullerenol, and CuPc:fullerenol (9:1 weight ratio) composite from 5×10^{-3} M solutions in deionized water (Milli-Q of Millipore, resistivity = 18.2 MΩ cm), which acted as anionic baths; a 5×10^{-3} M PAH solution served as the polycationic bath for LbL film deposition. Indium tin oxide (ITO)-coated glass and doped silicon wafers were used as substrates. The polished Si(111) wafers were phosphorus-doped (N-type) with a resistivity of 5−10 mΩ cm. The substrates were deprotonated in a mixture of H_2O, H_2O_2, and NH_4OH (5:2:2) for 1 h. Sequential dipping in polycationic and anionic baths resulted in single and 10 bilayer LbL films. To deposit a monolayer, we first dipped Si substrates in the PAH bath for 15 min, followed by rinsing in three deionized water baths. The substrates were then dipped into the anionic solution (of either CuPc, fullerenol, or CuPc:fullerenol composite) for 15 min, followed by the same rinsing protocol in a separate set of water baths. This resulted in one molecular layer (monolayer) of the material. Ten-layer LbL films were grown on striped ITO substrates by repeating the dipping sequence. The thickness of the films varied between 50 and 60 nm for 10-layer films. The thickness of the monolayer was hence less than 6 nm. The films were annealed at 110 °C in a vacuum (1×10^{-3} Torr) for 6 h. For multilayer films, aluminum (Al) was vacuum-evaporated on top of the annealed films from a tungsten filament basket at a pressure below 1×10^{-5} Torr. A mechanical shutter protected the films from excess heat before and after Al deposition. The active area of each of the sandwiched cells, as determined by a mask during evaporation, was 6 mm^2.

For electrical characteristics, sandwiched structures were placed in a shielded vacuum chamber (1×10^{-3} Torr). Monolayer films were kept with the film facing downward. A syringe with a Hg blob on the tip of a metal needle was raised slowly from outside the chamber by a micrometer screw till the blob just touched the film. The diameter of the blob was below 0.5 mm. The contact between the film and the blob was monitored through a microscope. Bias was applied with respect to the top (Hg or Al) electrode. Current−voltage ($I-V$) characteristics were recorded at room temperature and during both sweep directions and also in voltage loops. The voltage step was 0.01−0.05 V with a scan speed of 20 mV/s. The $I-V$ characteristics were recorded with a Yokogawa 7651 dc source and a Keithley 486 picoammeter or a Keithley 617 electrometer. The instruments were controlled by a personal computer via a general-purpose interface bus (GPIB). $I-V$ characteristics of the monolayer films were also recorded with the Pt/Ir tip of a scanning tunneling microscope (STM) as an electrode. Such measurements were carried out with a Nanosurf easyScan2 controller (constant current mode) under ambient conditions. To study the deposition of the materials in LbL films, we recorded electronic absorption spectroscopy of monolayer and multilayer films deposited on quartz substrates.

3. Results and Discussion

Electronic Absorption Spectra. Electronic absorption spectra of CuPc:fullerenol, CuPc, and fullerenol are shown in Figure 1a. Figure 1b shows the spectra of a monolayer of the respective system/material. The spectra of CuPc:fullerenol solution and monolayer film show that a charge-transfer complex did not form in the excited state of the supramolecular assembly. For both solution and monolayer films of CuPc:fullerenol, the absorption spectrum is an algebraic sum of the spectra of individual components. The spectra of the monolayer films further confirm transfer of the materials on the substrates during adsorption of each layer in the LbL deposition process.

Ten-Layer Systems. $I-V$ characteristics were recorded in devices based on 10 layers of CuPc, fullerenol, and CuPc:fullerenol composite. For all the devices, $I-V$ characteristics were measured by scanning the bias in a loop, e.g., a sequence from 0 to $+V_{\mathrm{Max}}$ to $-V_{\mathrm{Max}}$ to $+V_{\mathrm{Max}}$ repeatedly. We have also varied the amplitude of V_{Max} to generate a range of $I-V$ characteristics. The devices based on the CuPc:fullerenol composite show a jump in current at a reverse bias (Figure 2). Device current at any voltage during the voltage scan from $-V_{\mathrm{Max}}$ is several orders higher in magnitude as compared to that during the initial sweep from $+V_{\mathrm{Max}}$. Because the high-conducting state is sustained even at no-bias condition, electrical bistability here can be termed as memory-switching phenomenon. The ratio between the

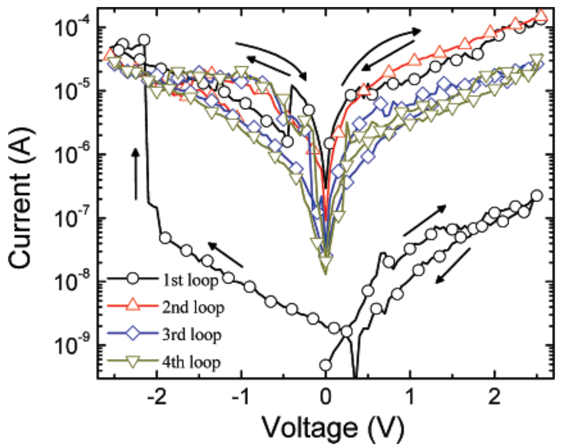

Figure 2. Current−voltage characteristics of 10-layer LbL film of CuPc:fellerenol composite system sandwiched between ITO and Al electrodes under four consecutive voltage loops. Arrows show the direction of voltage sweep.

conductivities, which depends on V_{Max}, reaches up to 1×10^4. The higher conducting state is retained in the subsequent voltage scans. The irreversible nature of switching from a low-conducting off state (in an as-fabricated device) to a high-conducting on state is itself of interest. Such a switching shows possible applications in write-once-read-many-times (WORM) memory applications.[16,17]

As control experiments, we have characterized devices based on 10 layers of CuPc and fullerenol. $I-V$ characteristics of the devices are presented in panels a and b of Figure 3, respectively. In each of the cases, characteristics under three consecutive voltage loops are presented. The device based on CuPc displays reversible bistablity with associated memory phenomenon. This is in contrast to the CuPc:fullerenol system, where switching is irreversible in nature. During the sweep from $+V_{\text{Max}}$ to $-V_{\text{Max}}$, the device based on CuPc remains in the low-conducting off state. At a particular reverse bias (around −1.7 V), the device shows a transition to a high-conducting on state. The high state is retained in the $-V_{\text{Max}}$ to $+V_{\text{Max}}$ scan, leading to nonvolatile memory characteristics. At some $+V_{\text{Max}}$, the device switched to the off state, making it a reversible switching element. The fullerenol-based device shows rectifying $I-V$ characteristics without any switching or memory phenomenon.

Fullerenes in nonconjugated polymer matrices exhibited WORM[18] memory or flash memory[19] at moderate voltages. Charge confinement in fullerenes has been proposed to result in the high-conducting state in such systems. In the present work, we have used a D/A supramolecule in which the fullerene molecules are surrounded by a number of CuPc molecules via electrostatic interaction. It has been shown by ab initio calculation[20] that the LUMO energy level of the supramolecule matches with that of fullerene, whereas the HOMO of the composite matches with that of CuPc. Under a suitable reverse bias, when the fermi energy of the outer electrode (Si or ITO) matches the LUMO of the supramolecule, an easy electron transfer may occur from the electrode to the molecule, leading to a high-conducting state. Now, because fullerenol is a strong electron acceptor and CuPc an efficient electron donor, intramolecular electron transfer (from CuPc to fullerenol) is favorable in the CuPc:fullerenol system. With the electron transfer, it is trapped in the supramolecule. Reverse bias (in the experimental range) is not sufficient enough to extract the electron. The supramolecular device hence retains the high-conducting state in the subsequent bias scans. In the individual components, a possibility of electron transfer (and trapping in the acceptor) does not occur. The switching hence becomes reversible in CuPc.

Monolayer Systems. With an aim to achieve memory applications from molecular scale elements, we have characterized the monolayer of CuPc:fullerenol supramolecules. For comparison, we have also characterized the monolayer of the components, namely CuPc and fullerenol. Here, because the monolayer was adsorbed on the substrate via electrostatic interaction, we could measure $I-V$ characteristics with Hg or a STM tip without any peel-off of the monolayer. Figure 4a depicts $I-V$ characteristics for the monolayer of the CuPc:fullerenol composite (on polished Si) with a Hg blob as the other electrode. Seven consecutive loops are shown in the figure. As in the 10-layer device, the monolayer was initially in the low-conducting off state. By a voltage sweep to a reverse bias, an increase in conductivity occurs. At any voltage, the current remains at least four orders of magnitude higher than that in the initial scan. The higher level of current is retained even when the bias is scanned in loops. The switching phenomenon in the monolayer of CuPc:fullerenol is also irreversible in nature, making it suitable for WORM memory applications. Switching time, measured by the time lag between a square wave voltage

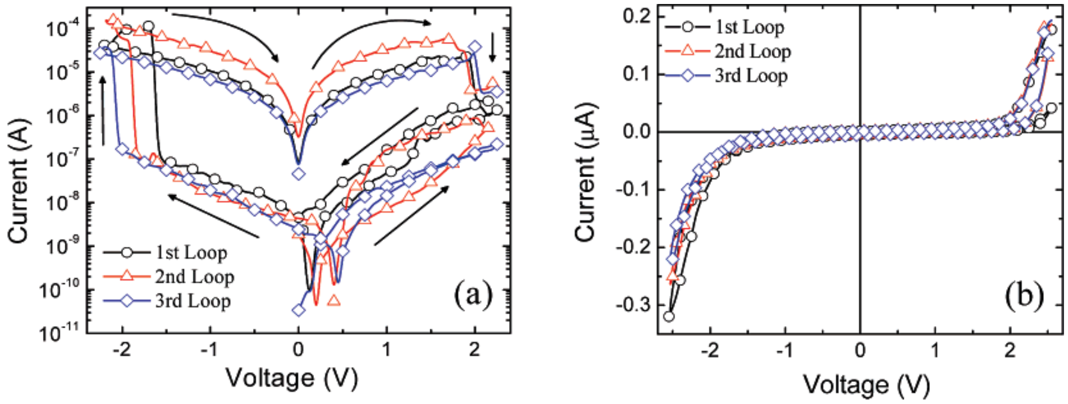

Figure 3. Current−voltage characteristics of 10-layer LbL film of (a) CuPc and (b) fullerenol sandwiched between ITO and Al electrodes under three consecutive voltage loops.

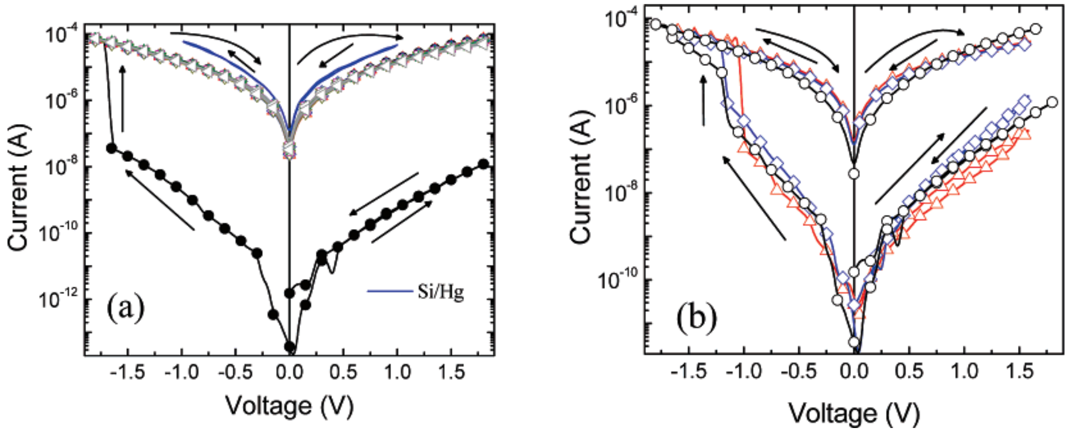

Figure 4. (a) Current−voltage characteristics of CuPc:fullerenol monolayer on Si substrate with Hg blob as the other electrode under seven consecutive voltage loops. First loop is shown with filled symbols. The subsequent loops are shown as different open symbols. Current without the monolayer is shown as Si/Hg. (b) Current−voltage characteristics of the monolayer at three different spots on the film showing the degree of reproducibility of irreversible memory switching. Only the first voltage loop is shown in the figure. Arrows in the figures show the direction of voltage sweep.

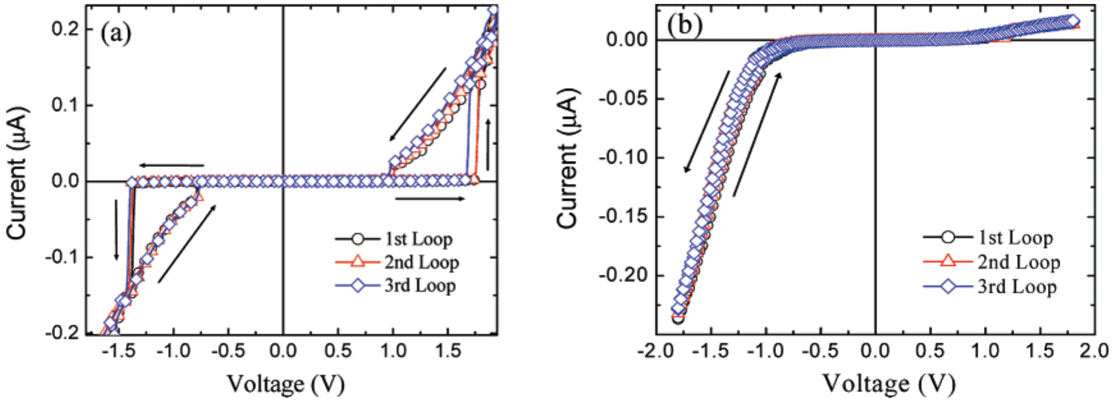

Figure 5. Current−voltage characteristics of (a) CuPc and (b) fullerenol monolayer on Si with Hg blob as the other electrode under three consecutive voltage loops. Arrows show the direction of voltage sweep.

pulse and the transient current, is around 90 ns, which is comparable to the value reported in the literature.[19]

We have carried out several control experiments to establish the results. First of all, we checked the contributions of the 1−1.5 nm native SiO_2 on Si. The current due to the oxide layer under the same experimental conditions (Si/Hg case), as shown in Figure 4a, is symmetric and is higher in magnitude than the on-state current with CuPc:fullerenol monolayer. This shows that when a Hg contact was made on the monolayer, there was no short circuit. The characteristics in Figure 4a hence truly reflect the properties of a monolayer of CuPc:fullerenol supramolecular composite. To study the reproducibility of the memory switching in the monolayer of the composite, we have probed different spots on the films. Figure 4b shows $I-V$ characteristics of the monolayer at three different points on the monolayer. The nature of the $I-V$s remained mostly identical at different spots on the film. Current at a voltage varied to some extent (12% for the high state). The variation in current could be due to different size Hg blobs being used in each of the cases or different tip-molecule distances.[5]

As further control experiments, we have characterized a monolayer of the individual components of the D/A composite, namely CuPc and fullerenol. $I-V$ characteristics of a monolayer of CuPc and fullerenol on a Si wafer (with Hg as the other electrode) are shown in panels a and b of Figure 5, respectively. In contrast to the 10-layer CuPc film, in which memory switching was observed, the CuPc monolayer yielded threshold switching in the $I-V$ characteristics. That is, in both bias directions, the current switched to a high value when the magnitude of voltage increased and exceeded a threshold one. The critical voltage for threshold switching is around 1.4−1.6 V. Below the threshold voltage, the $I-V$ is nonlinear and symmetric in nature.[21] Beyond the threshold voltage, the magnitude of the current increases almost linearly with voltage. During the sweep toward 0 V, the device loses the high-conducting state. The switching between the two states is reversible in nature. Measurements were carried out at various spots on the film with a new Hg blob for each position. The results were crosschecked with only one PAH layer on Si, which produced no such switching in $I-V$ characteristics. The fullerenol monolayer, similar to the 10-layer film, shows rectifying $I-V$ characteristics without any switching or memory phenomenon (Figure 5b).

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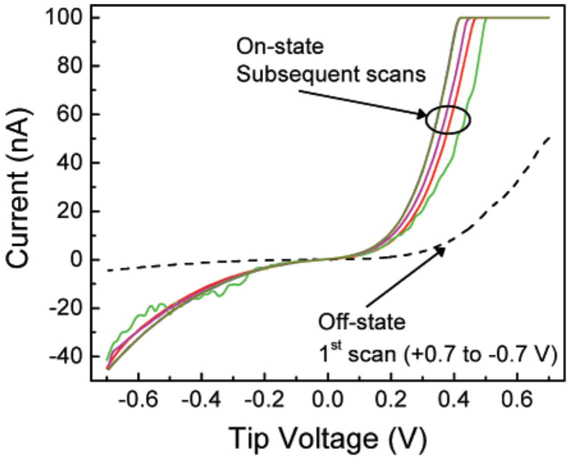

Figure 6. Current−voltage characteristics of a monolayer of CuPc:fullerenol composite on Si measured with a STM tip. The second and subsequent voltage sweeps were carried out in both scan directions.

The results for three consecutive voltage loops show the reproducibility of the measurements.

To exclude the effect of electrode oxidization, electromigration, or metal filament formation within the active organic layer, we have used the Pt/Ir tip of a STM for measuring the $I-V$ characteristics of a monolayer of CuPc:fullerenol composite on Si electrode. Here, electrons tunnel from the STM tip to the organic layer and then cross the SiO_2 barrier into the substrate. Two different $I-V$ characteristics were obtained for the first and subsequent scans (Figure 6). During the initial scan from $+V_{Max}$ to $-V_{Max}$, the device current was low (off state). In the subsequent voltage sweeps, the magnitude of the current at any voltage is higher than that in the initial scan. The higher magnitude persists regardless of the direction of voltage scan. The endurance of the high-conducting state in the subsequent voltage scans is a clear evidence that the composite switches to a high-conducting on state irreversibly. Such results on a monolayer of CuPc:fullerenol composite probed with a Pt/Ir tip further confirm that the electrical bistability with associated memory phenomenon are molecular in nature and do not arise because of metal diffusion.

Memory Applications. Because the 10-layer and monolayer films of CuPc:fullerenol switch irreversibly to a high-conducting state, they can be considered for WORM applications. To measure retention time of the high-conducting state, we first "pumped" the device/monolayer film with a suitable bias, which induced the high-conducting state. We then "probed" them by measuring current under a small voltage pulse. To reduce the additive effect of the "probe" or "read" voltage on the existing state, we applied the "read" voltage in a pulse mode. Duty cycle was only 9%. Before inducing the high state, the pristine film in its low-conducting state was also read by applying the same "probe" voltage. Current as a function of time have been compared in the two cases. Panels a and b of Figure 7 show such plots for a 10-layer and a monolayer film of CuPc:fullerenol, respectively. Both the figures demonstrate that the current under the probe voltage for the high-conducting state is several orders higher in magnitude compared to the current when the low state is probed by the same voltage. Although the response of the low state remains almost steady, the response of the high-conducting state shows some decay after 11 h. The two states are clearly distinguishable even after hours of probing, demonstrating WORM applications. The figure further shows that the on/off ratio obtained from the voltage scans is translated in the time response of the two conducting states.

Transport Mechanism. We have further attempted to fit the on- and off-state currents of the CuPc:fullerenol films with existing conduction models. Transport mechanism in the low-conducting off state follows thermionic emission model. A plot of ln(I) versus $V^{1/2}$ shows a linear fit in the higher bias region. In the on state, carrier transport through the device obeys the Poole−Frankel model, exhibiting a linear fit of the log(I/V) versus $V^{1/2}$ plot. We hence find that in the electrical bistable devices, electrical switching is associated with a change in the conduction mechanism process. In the off state, the device current is limited by injection from the electrodes, whereas the conduction process in the high state is dominated by charge transport through the bulk of the device.

4. Conclusions

In conclusion, we have introduced a donor/acceptor composite system based on a metal phthalocyanine and a

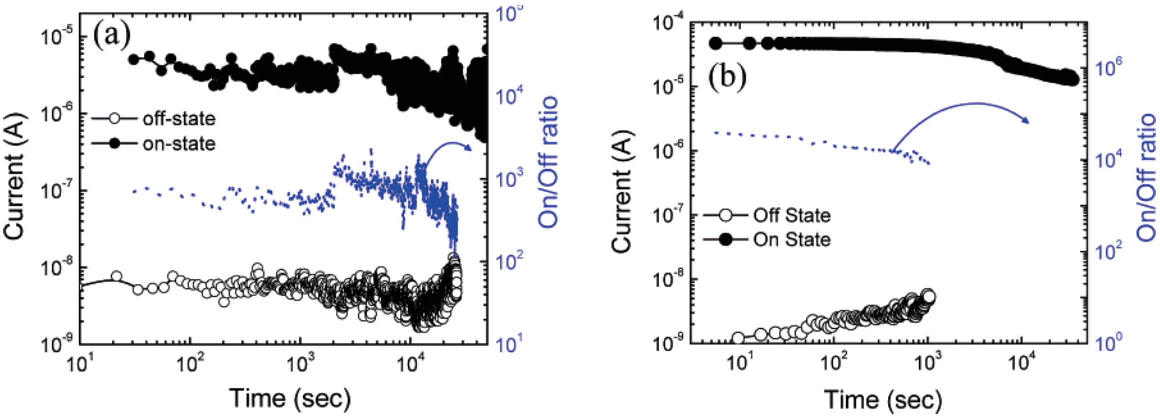

Figure 7. Retention time for WORM application of (a) 10-layer and (b) monolayer film of CuPc:fullerenol. (a) +2.5 and −2.5 V induced the low- and high-conducting states, respectively. For the monolayer case, the corresponding voltages were +1.4 and −1.4 V, respectively. Probe voltage was −0.9 and −0.7 V in (a) and (b), respectively. Absolute values of current are plotted for comparison. The figures additionally show time response of ratio between the high- and low-state currents (on/off ratio) under the same probe voltage.

fullerene derivative for switching and memory applications. Under a suitable bias, the supramolecular system switches irreversibly to a high-conducting state. Whereas the donor component of the composite exhibits reversible electrical bistability, the acceptor part show no switching at all. Apart from the multilayer of the composite, the monolayer of the donor/acceptor system displayed an irreversible switching with associated memory phenomenon. The retention time of the write-once-read-many-times memory elements is more than 11 h. Memory elements based on the monolayer of donor/acceptor composites provides an alternate route to achieving molecular memory in an addressable scale.

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