

Large Conductance Switching and Binary Operation in Organic Devices: Role of Functional Groups

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We have realized tuning of electronic memory-switching property via functional group modification in solid-state devices. Apart from their large ON/OFF ratio and long memory retention time, solid-state devices sustain repetitive switching between the two ON/OFF states at high frequencies. We have chosen several molecular systems with same backbone structure and tuned ON/OFF ratio from 4 to 300 000 simply by increasing the number of deactivating groups. A key to the large ON/OFF ratio in these devices has been the presence of acceptor groups in the molecules and consequently low OFF state current. We analyzed the appearance of ON state in terms of conjugation restoration of the molecules. A redox active group has been found to be necessary in the molecules for continuous flip-flop between “1” and “0” states for random access memory (RAM) applications.

1. Introduction

The incorporation of a single molecule in basic switching devices and, finally, the fabrication of ultradense integrated circuits are necessary for advanced computation. Working speed has to be faster and the size has to be orders smaller than the present state of the art transistors. The journey toward molecular electronics begun in 1974 with the molecular rectifier,¹ which consisted of a π -bonded donor–acceptor system separated by a σ -bonded tunneling bridge. The organic electronics now aim toward binary logic circuits, which are the basic elements of molecular computer.^{2,3} As the industry moves from bulk to molecule-based electronics, there is a growing trend to revisit voltage-induced switching phenomena in conjugated organics,^{4–15} which was first observed more than 30 years ago.^{16,17}

In switching devices, two different conducting states are observed at the same applied voltage. A number of possible mechanisms have been discussed to explain the existence of two states, which includes conformational twisting of the molecules or bundles,^{4,10,14} electronic or electrochemical mechanism,^{5–9} rotation of functional groups,¹⁵ etc. In a complicated trilayer structure, an additional metal layer has been introduced between two active organic layers to store charges and to provide large conductance switching¹⁸ (current ratio between the two states, ON–OFF ratio = 10^6). In these high-performing devices, where switching mechanism is a bulk property, their miniaturization is restricted.

In single layer switching devices, the current ratio between the two states (ON/OFF ratio) is generally low (<100) and memory lasts only for minutes (nearly 15 min, in nitro-amine based systems).⁹ The current ratio between the ON and OFF states, should be high for their effective use in high-frequency binary computation. The aim is therefore to achieve low OFF state current keeping ON state current under control in organic molecules.

With such an aim, we have looked for a new series of molecules, which can block the OFF-state leakage-current

completely. We have chosen molecules which possess electron-acceptor groups. In addition, presence of any donor group has been avoided so that the acceptor groups can perturb conjugation in the backbone and results in very low OFF state current. Though details of the mechanism of conductance switching are not yet fully understood, electrochemical reduction to restore conjugation could be a viable mechanism in these types of molecules. We aimed to tune the nonconjugation/conjugation in the molecular backbone by inducing/reducing perturbation to the electronic wave function. As we attach deactivating groups (having positive Hammett constant¹), such as nitro, chlorine, cyano, etc., in a controlled way, molecular orbital becomes localized due to presence of the electronegative moieties. The conjugation throughout the molecule is thus perturbed, and quantum-tunneling probability through the molecule is decreased. In this article, we have shown how the controlled presence of acceptor groups can perturb the conjugation and hence the OFF-state leakage-current in the device. We stressed on the design of organic molecules with suitable functional groups for future molecular switching devices with a high ON/OFF ratio.

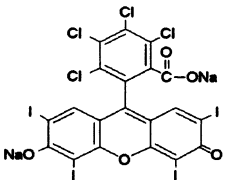
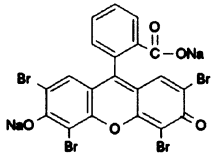
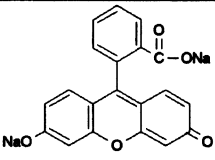
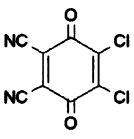
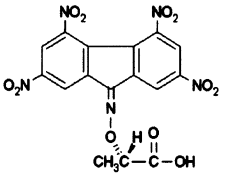
2. Experimental Section

The molecules of interest in the present work are Rose Bengal; 2',4',5',7'-tetrabromofluorescein, disodium salt (Eosin Y); fluorescein sodium; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); and (+)-2-(2,4,5,7-tetranitro-9-fluorenylidene-aminoxy)propionic acid (TAPA). The first three molecules have identical structure and electrochemistry. The molecular structures of the materials are shown in Table 1. To obtain devices based on Rose Bengal, Eosin Y, and fluorescein sodium, methanol solution of the material (2 mg/mL) was spun on indium tin oxide (ITO) coated glass substrate at a rotating speed of 2000 rpm for 30 s. For DDQ and TAPA, acetonitrile solutions were used. Cyclic voltametry was carried out in acetonitrile solution for all the molecules except fluorescein sodium.

ITO coated glass substrate used here had a hydrophilic surface. They were chemically treated with 3-aminopropyl)-

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TABLE 1: Different Molecules Used to Fabricate the Devices and the Correlation between Their Functional Groups and Switching and Data-Storage Properties of the Devices

Name of molecule	Structure	Number of planes	Number of planes with acceptor groups	Maximum ON/OFF ratio	Redox Group	Binary flip-flop
Rose Bengal		2	2	340000 ^a	Yes	Yes
2',4',5',7'-tetrabromofluorescein, disodium salt (Eosin Y)		2	1	9,800	Yes	Yes
Fluorescein sodium		2	0	4	Yes	No
2,3-Dichloro-5,6 dicyano-1,4-benzoquinone (DDQ)		1	1	10 ⁴	Yes	Yes
(+)-2-(2,4,5,7-tetranitro-9-fluorenylidene-aminoxy)propionic acid (TAPA)		1	1	10 ⁴	No	No

^a When donor group is attached to Rose Bengal, the ON/OFF ratio decreases to 100.

triethoxysilane so that the amine groups are tailed out of the surface. The amine groups were further deprotonated by applying 0.1 M HCl. When Rose Bengal, Eosin Y, or fluorescein sodium was spun on ITO surface, electrostatic bond formed between the electrode and the first layer of molecules. Subsequent layers were attached via van der Waals interactions. For DDQ and TAPA, no surface treatment was done prior to spin the films.

To obtain layer-by-layer electrostatic self-assembled (ESA) films^{19,20} of Rose Bengal, a weak polyelectrolyte, namely, poly-(allylamine hydrochloride) (PAH) (molecular weight = 70 000), has been used as polycation. Rose Bengal (5×10^{-3} M) and polymer (5×10^{-3} M, based on the repeat unit) solutions in milli-Q water (18.2 M Ω) were used as anionic and polycationic baths, respectively. The pHs of the solutions were adjusted by adding NaOH or HCl, respectively. ITO-coated hydrophilic glass

substrates (treated in pH = 7 buffer solution to keep the inherent negative charges on the surface) were first dipped into the polycationic electrolyte (pH = 2.5) for 15 min followed by rinsing in the milli-Q water baths for 2, 2, and 1 min, respectively. The slides were then dipped into the anionic bath (pH = 8.8) for 15 min followed by the same rinsing protocol in a separate set of water baths to result one bilayer of ESA films of Rose Bengal. The whole sequence was repeated to get 10 bilayers of ESA films of Rose Bengal.

The thin films were annealed in a vacuum oven (10^{-3} Torr) following standard protocol. Temperature of the oven was allowed to cool to room-temperature slowly. Thickness of the organic layer was less than 100 nm in all the films, as measured by a Planar Products Limited SF101 surfometer. On top of the annealed film, aluminum (Al) from a tungsten filament basket

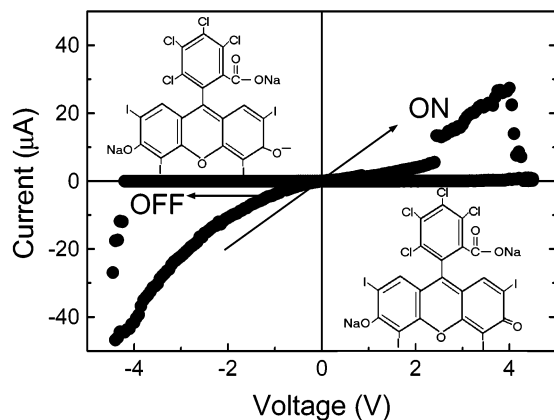


Figure 1. Current-voltage characteristics of devices based on spin-cast films of Rose Bengal for two sweep directions (shown by arrows) showing presence of two conducting states. The ON and OFF state configurations of Rose Bengal have been shown in the second and fourth quadrant, respectively.

was vacuum-evaporated at a pressure below 10^{-5} Torr. The active area of each of the devices was 6 mm^2 .

The devices were kept in a shielded vacuum chamber (10^{-3} Torr) at room temperature for 10 h before sets of current-voltage (I - V) characteristics were taken. The I - V characteristics (ITO positive) were recorded at two sweep directions ($+V$ to $-V$, and $-V$ to $+V$) and also in voltage loops (0 to $+V$ to $-V$ to $+V$). The I - V characteristics were recorded with a Yokogawa 7651 dc source and a Keithley 486 picoammeter. Voltage scan rate was varied between 2.5 and 0.25 mV/s. For pulsed mode measurements, the dc voltage source was coupled to fast switching transistors to generate voltage pulse of different widths and amplitudes. The rise and fall times of the voltage pulse were less than 100 ns. The voltage pulse sequence for "write-read-erase-read" measurements at frequencies up to 50 kHz was generated by a Hewlett-Packard HP3245A Universal Source, which led us to study device performance at frequencies up to 0.2 MHz. The instruments were controlled with a PC via a general-purpose interface bus (GPIB).

3. Results and Discussion

Devices Based on Rose Bengal. As we have tried to look beyond the presence of donor groups, we have chosen double planar Rose Bengal molecule, which has no donor groups but has acceptor groups in both of its planes. We have recorded I - V characteristics of Rose Bengal based devices for two sweep directions. The amplitude of maximum voltage has been varied to collect a wide range of characteristics. A typical case is shown in Figure 1. The figure shows that when the voltage was swept from a positive voltage ($V_{\text{max}} = 4.5 \text{ V}$), the device current was very low till -4.3 V . The state of Rose Bengal can be termed as OFF state, which switches to ON state at -4 V . During the sweep from a negative voltage (-4.5 V), Rose Bengal retained the high-conducting ON state. The device current has been several orders higher in magnitude than that during the previous sweep. The material finally switches to its OFF state at $+4 \text{ V}$. The voltages at which the material switches ON or OFF depended on the maximum voltage of sweep. The OFF state and one of the ON state conformations of Rose Bengal have been shown in the inset of Figure 1.

We have aimed to explain conductance switching phenomenon in these organics in terms of conjugation modification by oxidation/reduction of the molecules.^{6,8} Initially, conjugation of the molecules is perturbed due to the electron acceptor groups

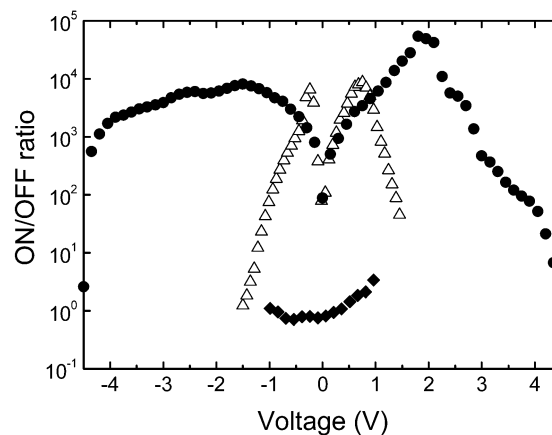


Figure 2. Ratio between the ON and OFF state current as a function of applied voltage in devices based on spin-cast films of Rose Bengal (circles), Eosin Y (triangles), and fluorescein sodium (diamond).

and the molecules are in nonconducting state. Under suitable reverse bias, the molecule is reduced; an electron is provided to the molecule which neutralizes the effect of the deactivating groups. Conjugation in the molecule is restored, and quantum-tunneling probability in the molecule increases. Rose Bengal molecules switch to the high-conducting ON state. Again applying certain forward bias, an electron is removed from the molecule to break the conjugation in the molecule. The molecule and hence the device therefore returns to its low-conducting OFF state.

Normalized density of states (NDOS) obtained from the I - V characteristics of the OFF and ON states and its corresponding d^2I/dV^2 spectra (vibrational) showed that in the two conducting states, switching molecules have two dissimilar conformation. In oxidized state, Rose Bengal has no available energy state, while the reduced state has sharp peaks of resonance with outer electrodes in both sides of bias polarity. Reduction adds electrons to increase available energy density of states between HOMO and LUMO for higher conduction to occur. Higher density of states of the molecules in the ON state basically "completes" the circuit via resonance with outer electrode Fermi level and allows large conduction in the device.

Devices Based on Eosin Y and Fluorescein Sodium. To check the hypothesis of conjugation modification and role of acceptor groups in the switching devices, we have chosen a series of molecules and recorded their I - V characteristics. Eosin Y and fluorescein sodium have identical backbone as in Rose Bengal. In these molecules, the number of deactivating groups has been decreased to 4 and 0, respectively, from 8 (in Rose Bengal). The degree of perturbation of the molecular orbital is tuned here by modifying the presence of electron accepting groups. In the following, we describe their contributions in the I - V characteristics and switching behavior, which is also listed in Table 1.

In Figure 2, we have shown the current ratio between the ON and OFF states (ON/OFF ratio) as a function of applied voltage for devices based on the three molecules. The ratio in Rose Bengal is as high as 10^5 . Such a high ratio, especially at room temperature and in single layer sandwich structures, is itself of interest. In Eosin Y, the ON/OFF ratio decreases to 10^3 , and Fluorescein sodium did not practically show any switching (ON/OFF ratio = 4). The results show that as the number of deactivating groups in the molecule is decreased, the devices' capability to show conductance switching decreases. Increased number of deactivating groups here means increased degree of perturbation of the electronic wave function and

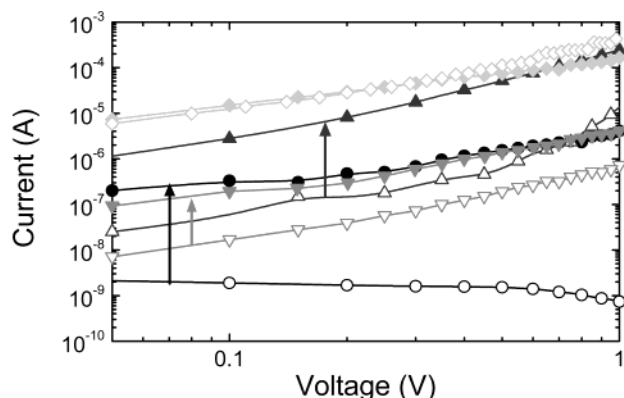


Figure 3. A comparison of I - V characteristics of devices based on spin-cast films of Rose Bengal (circles), Eosin Y (triangles), and fluorescein sodium (diamond) in the forward bias direction for two sweep directions. The arrows indicate transitions from OFF (open symbols) to ON (filled symbols) state in each of the devices. A case for devices based on ESA films of Rose Bengal is also shown (down triangle).

consequently higher barrier height for electron tunneling. The molecules in such cases provides a low density of states and hence offer a high resistance in the device, and results in a low OFF state current.

We have compared the OFF state current in the three devices (Figure 3). The figure shows that increased number of deactivating groups leads to a strong decrease in OFF state device current. The device current in the ON state also depended on the number of acceptor groups (Figure 3), but not as strongly as the device current in the OFF state. Such dependences resulted in a higher ON/OFF ratio between the current in the two states in devices with molecules having more acceptor groups. A lower ON state current in the Rose-Bengal- and Eosin-Y-based devices could be due to incomplete conjugation restoration in the ON state of the molecules by the application of the voltage.

The proposition of conjugation modification has further been verified by supramolecular chemistry. In ESA films, amino groups of polycation get attached to Rose Bengal. The I - V characteristics of ESA-based devices in the ON and OFF state are shown also in Figure 3. The lone pair electrons of free amino groups release the stress of Rose Bengal and restores conjugation to some extent. This leads to an increase in OFF-state current and consequent decrease in the ON/OFF ratio to 100, which mimics the design and switching characteristics of present day switching devices based on donor-acceptor groups. The results that a donor group in a molecule leads to lower ON/OFF ratio further show the advantage of using materials with only acceptor groups in fabricating switching devices.

Devices Based on Single Planer Molecules (DDQ and TAPA). The three molecules we have reported here so far have two planes. DDQ have a semioxidized or semireduced state (semiquinone) between fully oxidized (quinone) and fully reduced (quinhydrone) states, and TAPA follows two-electron oxidation-reduction process, in the positive direction of voltage scan only. All the three cases are reversible. DDQ have large delocalized systems in both oxidized and reduced states. In the semireduced stage, the single electron is strongly delocalized. Our results in devices based on DDQ and TAPA, which have only one plane and deactivating groups, show that two planes are not necessary to observe conductance switching phenomenon. In Figure 4, we have shown I - V characteristics of DDQ for two sweep directions. The two conducting states are clearly represented, with an ON/OFF ratio of 10 000 (inset of Figure 4). The results support the need of acceptor groups in molecules

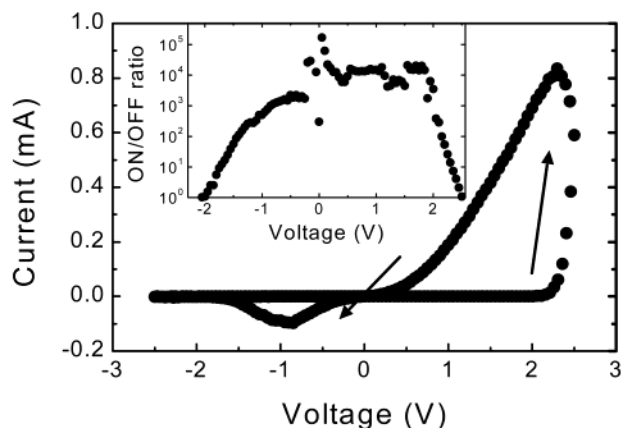


Figure 4. Current-voltage characteristics of devices based on spin-cast films of DDQ for two sweep directions (shown by arrows). Inset shows the ratio between the ON and OFF state current as a function of applied voltage of the device.

to observe switching phenomenon and consequent conjugation modification in observing high conducting state. The results further rules out any need of double plane in observing such an effect.

Cyclic Voltammetry. We have carried out cyclic voltammetry (CV) of the molecules (except fluorescein sodium) to obtain oxidation and reduction potentials. The critical voltages at which devices start to switch between ON and OFF states should however not match exactly with the oxidation-reduction potentials obtained from the CV measurements. Such measurements offer potential at which single molecule is reduced or oxidized. In the devices, since a large number of molecules are incorporated as bulk, a dipole-dipole interaction between the neighboring molecules generates a strong local field, which stretches intermolecular bond length and deforms charge distributions in the molecule. Consequently, the energy level of the molecules is shifted and sudden transitions between the ON and OFF states occur at modified oxidation/reduction potentials. As the number of deactivating groups in a molecule increases from 4 to 8, the local electric field becomes stronger, and hence, the difference between the switching voltage and the reduction (or oxidation) potential obtained from the CV measurements increases (Figure 5). Furthermore, the work-functions of the dissimilar electrodes used in the device modify the effective bias in an asymmetric way in the forward and reverse bias modes. The respective barrier heights for electron and hole determined the organic/metal interface, at which predominant reduction or oxidation is supposed to take place. In Rose-Bengal-based devices, where single electron oxidation-reduction process occurs, dominant electroreduction of the molecules in the devices occurs under reverse bias which could be due to a lower barrier height for electrons from ITO than that from the Al electrode.

Data Storage and Computation Applications. In the four molecules that depicted presence of two conducting states, an associated memory effect has also been observed. The materials retained the ON state until a reverse bias erases it and restores OFF state in the device. Such memory effects can lead to the devices for data-storage applications. Three of the devices show possibilities of "rewritable" memory for random access memory (RAM) applications (Table 1). The devices showed that "write-read-erase-read" sequence^{18,21} can be performed in these devices for many hours. A negative voltage pulse switches the device to its high conducting state, which can be considered as writing ON state. A small probe voltage pulse reads the state.

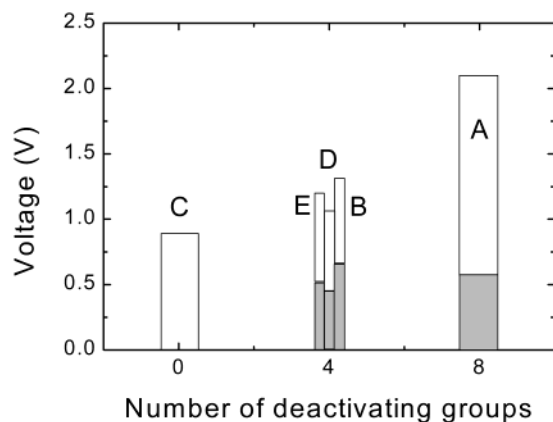


Figure 5. Reduction potential obtained from cyclic voltammetry (gray part) and switching voltage to ON state (whole column) for different molecules studied with 0, 4, and 8 deactivating groups. The figure shows the deviation of switching voltage from the reduction potential for molecules with different number of deactivating groups. The deviation between the two voltages increases when the number of deactivating groups present in the molecule increased from 4 to 8. Molecule C is insoluble in acetonitrile and hence cyclic voltammetry was not carried out for comparison. A, B, C, D, and E columns represent the cases with Rose Bengal, Eosin Y, fluorescein sodium, DDQ, and TAPA molecules, respectively.

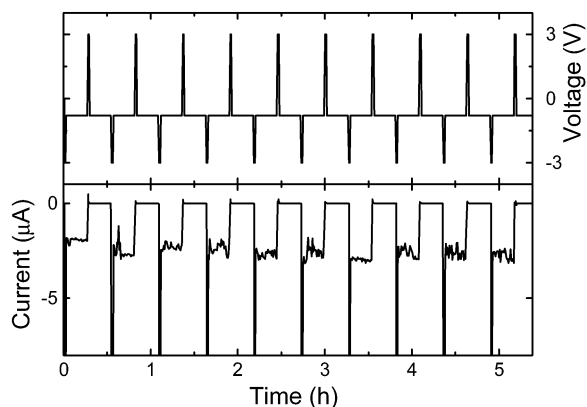


Figure 6. Switching performance of a pristine Rose Bengal based device during a “write-read-erase-read” sequence for data storage applications. The sequence of voltage pulse is shown in the upper trace, while the current response is shown in the lower one. The ON state has been induced (write) by -3 V pulse, while the OFF state has been reinstated (“erase”) by $+3$ V. Between switching, the states have been probed (“read”) by measuring current under a probe voltage (-0.8 V). The ratio between the probe current during the ON and OFF states has been as high as 10^3 .

Consequently, a positive voltage erases the ON state and recovers the OFF state, and finally another probe voltage reads the OFF state of the device (Figure 6). The current under the probe voltage has been different for the ON and OFF states of the device. Their ratio has been 10^2 – 10^3 in the three different molecules we have studied. The ratio is about one order lower in magnitude than the ON/OFF ratio at the same voltage (Figure 2). This could be due to storage of space charges in the devices under continuous operation. Also, as the device was undergone “write-read-erase-read” sequence for many hours, the stored space charges start to hinder reduction and hence result in lower current ratio under probe pulse.

The high and low conducting states can be converted to voltage for binary logic elements by measuring the voltage drop across a resistor. More than 72 million ON–OFF cycles were conducted in our devices showing good rewritable nature of the devices on the basis of the conductance switching of the

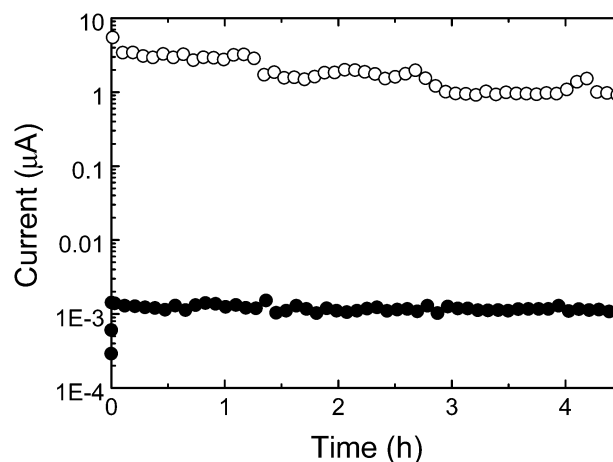


Figure 7. Long-time response of the ON (open symbols) and OFF state (filled symbols) of a Rose-Bengal-based device as probed by (modulus of) device current under -0.8 V. The ON and OFF states have been induced by -3 and 3 V, respectively.

molecules. The time response of the “write-read-erase-read” sequence is limited by the RC time constant, and has been less than $2.4 \mu\text{s}$, which is the limit of our measurement setup.

Apart from the rewritable nature, the devices’ capability to retain its ON or OFF states has also been studied. The molecules were found to retain their ON state nondestructively for several hours without applying any bias (Figure 7). The figure shows device current under a probe voltage as a function of time after ON or OFF state has been induced by applying a negative or positive voltage pulse, respectively. The probe current in the ON state has been higher by several orders of magnitude than that in the OFF state. One can therefore use the probe current or the voltage drop across a resistor to “read” the state of the device. The figure shows that once we “write” ON or OFF state and leave the device without any bias, the device retains the state. The state can be “read” by applying a small probe voltage. The plots show nonvolatile nature of memory in devices based on Rose Bengal, Eosin yellow, and DDQ for data-storage or read-only memory (ROM) applications. The probe current in the ON and OFF state started to merge in a staircase fashion in about 10 h, which however increases with decrease in the number of acceptor groups present in the molecule. Our preliminary studies further show that the devices based on molecules with more number of acceptor groups can show rewritable nature for longer times.

Although four of the materials (Table 1) showed presence of two conducting states, one of them, TAPA, did not show rewritable nature of ON and OFF states. Though TAPA has deactivating groups all over its surface, the molecule does not have similar redox active groups in its structure. Once the molecule switches to ON state, it returns to its OFF state only after tens of hours. The results show the necessity of redox active group in the molecule for rewritable data-storage applications.

4. Conclusions

In conclusion, we have studied conductance switching phenomenon in several organic molecular devices. Our results in a series of molecules with same backbone showed that as the number of acceptor groups in a molecule increases, the OFF-state current in the device decreases and hence the ON/OFF ratio increases. We also have shown that only one plane in a molecule is enough for observing such switching phenomenon. The appearance of high-conducting states in these molecules with acceptor groups and without any donor group has been

explained in terms of conjugation restoration via electroreduction. Our work provided a generalized path to design molecules with right functional groups for memory-switching and computational logic elements for future molecular electronics. An associated memory effect has also been observed in these devices. The materials retained the ON state until a reverse bias erases it and restores the OFF state. Such memory effect led to the devices for data-storage applications. Devices based on molecules with acceptor groups and a redox-active group showed "rewritable" states for random access memory (RAM) applications. The devices performed "write-read-erase-read" sequence for hours. The devices further retained a state for more than 10 h showing their applications in data-storage components. Our work provided a generalized path to design molecules with right functional groups for future molecular electronics as memory-switching and computational logic elements.

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