Memory-Switching Phenomenon in Acceptor-Rich Organic Molecules: Impedance Spectroscopic Studies

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We have studied memory-switching phenomena in terms of impedance spectroscopy in a series of xanthene-class fluorescein molecules. Frequency response studies have revealed that the electronic conduction mechanism was largely tuned by increasing the number of acceptor groups attached to the molecular backbone. In molecules with weak intermolecular interactions, the transition between a low- and a high-conducting state has been associated with a change in bulk resistance and dielectric properties. The devices in the two states remained a parallel combination of a resistor and a capacitor (C_P−R_P) network. In devices based on Rose Bengal, which exhibits a strong dipole−dipole interaction due to its acceptor groups, the switching between the states has been modeled as a transition between a C_P−R_P network in the off-state and a distributed resistor−capacitor (R−C) line network in the on-state. Instead of isolated clusters, a highly coupled network of reduced Rose Bengal molecules with strong dipole−dipole interaction yielded the high-conducting state. Under a "write−read−erase−read" sequence, the device switched between the two networks reversibly for many cycles.

1. Introduction

Impedance spectroscopy gathers the statistical distribution of resonances of a system as a function of space frequency. It has been a powerful tool to study the physical processes that are going on in the material in different devices.[1] In most of the cases, the electrical analogue of a device can be identified.[1−3] In the frequency range from microhertz to megahertz, alternating current measurements distinguish individual contributions from electrical conduction or polarization arising from different sources. Many different parameters, including adsorption or reaction kinetics,[4] diffusion constant, ionic and electronic conductivities,[5] or interface properties, such as grain size, resistance, and capacitance of grain boundaries,[6] have been studied.

In switching devices, two different conducting states of a conjugated semiconductor are observed at the same applied voltage. A number of possible mechanisms have been proposed to explain the existence of two conducting states.[7−13] The origin of the high-conducting state has been proposed to be due to conjugation modification via electroreduction of the molecules.[10−12] The radical anions of highly polar organic molecules generated in the bulk of the semiconductor are expected to modify the basic physical processes of conduction through the device.[11] Intermolecular interaction, molecular polarizibility, dipole moment, etc. will hence be largely modified during the transition from a neutral to an anionic state. The reaction kinetics of the switching process, creation of ionic diffusion channel, and dramatic change in the grain boundary capacitance during switching process should therefore be reflected in the impedance spectrum.[13] In this paper, we report how these fundamental parameters are modified during the conductance switching of organic memory-switching devices based on fluorescein-derived semiconductors.

In the present work, we have studied the effect of the functional groups of fluorescein on the conduction-switching mechanism. Semiempirical quantum mechanical computation following the AM1 model shows that acceptor groups in a molecule increase electron affinity and modify the LUMO to change the band gap and intermolecular interaction of a material. By keeping the backbone of the molecular structure the same, we have chosen molecules with an increased number of acceptor groups and studied corresponding memory-switching phenomenon. We have studied how functional groups can generate different pairs of electrical analogues during conductance switching.

2. Experimental Section

We have fabricated devices based on spin-cast films of disodium salts of 4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein (Rose Bengal), 2′,4′,5′,7′-tetrabromofluorescein (Eosin Y), and fluorescein. The dyes, whose molecular structures are shown in Table 1, were obtained from Aldrich Chemical Co. and were used without further purification. Indium tin oxide (ITO) coated, clean, hydrophilic glass substrates were treated with (3-aminopropyl)triethoxysilane. Amine groups were electrostatically bound with the first layer of active molecules. The spin-cast films were obtained from an acetonitrile solution of Rose Bengal and Eosin Y and from a methanol solution of fluorescein. Concentration of the solution was 2 mg/mL in each of the cases. Solutions were spun on ITO-coated glass at 200 rpm for 5 s followed by 1000 rpm for 30 s. The final speed was 2000 rpm for 20 s. The thin films were dried in a vacuum (10^{-5} Torr) at room temperature for 8 h. The thickness of the active layer was around 50 nm in each of the cases. On top of the film, aluminum (Al) from a tungsten filament basket was vacuum-evaporated at a pressure below 10^{-5} Torr. The active area of the devices was 6 mm².

The devices were kept in an evacuated metal chamber (10^{-3} Torr), which was further kept in a shielded box, so that all the

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TABLE 1: Different Molecules Used To Fabricate the Devices and the Correlation between Their Functional Groups and Switching and Electrical Analogue of the Devices

Name of molecule	Structure	Number of acceptor groups	Maximum On/Off ratio (from I-V)	Electrical analogue	
				Off state	On state
4,5,6,7-Tetrachloro-2',4',5',7'-tetraiodo fluorescein, disodium salt (Rose Bengal)		8	340000		
2',4',5',7'-Tetrabromo fluorescein, disodium salt (Eosin Y)		4	9,800		
Fluorescein, disodium salt (Fluorescein Sodium)		0	4		

cables were shielded against any stray noise. The impedance of the devices was characterized at room temperature. The real versus imaginary part of complex impedance, with frequency (f) of 100 mV rms ac signal as the independent variable, was measured in parallel mode by a Solartron 1260 impedance analyzer. The frequency range was from 1 Hz to 12 MHz (eight points/decade). Short-circuit and open-circuit corrections for the external leads were carried out with a standard normalization procedure. The instruments were controlled by a PC via a general-purpose interface bus (GPIB) and measurement was carried out with SMaRT software. In voltage variation studies up to a voltage V_{max}, $0 \rightarrow +V_{max} \rightarrow -V_{max} \rightarrow +V_{max}$, and $0 \rightarrow -V_{max} \rightarrow +V_{max} \rightarrow -V_{max}$ schemes were followed. Applied dc bias was increased by a step of 0.5 V during each of the scans.

3. Results and Discussion

Impedance Spectroscopy and Conductance Switching. Impedance characteristics of devices based on Rose Bengal, Eosin Y, and fluorescein were measured in a "write−read−erase−read" sequence of dc bias. That is, impedance characteristics were first recorded with a dc bias above critical switching voltage, which electroreduces the molecules to "write" or switch to its high-conducting state. To "read" the state, impedance was measured without any dc bias. Similarly, an equal reverse dc bias was applied during the frequency scan of impedance characteristics to "erase" the high state (and switch a to low-conducting one). The off-state was again "read" without any dc bias. Figure 1 shows the impedance characteristics at 0

V dc in the two "read" cases after switching to high- and low-conducting states, respectively.
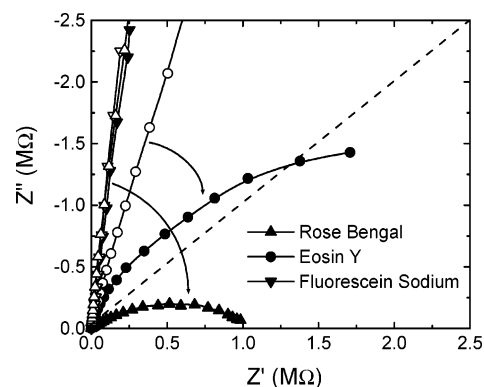

Figure 1. Z'−Z'' plots from 1 Hz to 12 MHz (eight points/decade) for devices based on Rose Bengal, Eosin Y, and fluorecein at 0 V dc bias after switching to high-conducting (filled symbols) and low-conducting (open symbols) states. Arrows indicate the transition between high and low states. The broken straight line is inclined at an angle of $\pi/4$.

The figure shows that the Cole−Cole plots for the devices exhibit semicircles (or signs of a semicircle). There has been a small shift from the origin. The devices in their off-state can hence be represented as a parallel combination of a resistor (R_P) and a capacitor (C_P) with a small resistance in series. In Rose Bengal and Eosin Y based devices, the radius of the semicircle,
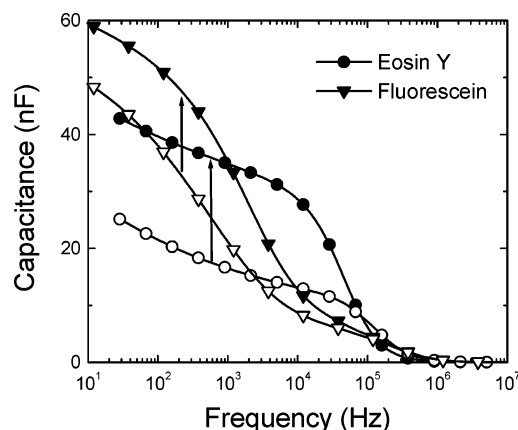
Figure 2. Variation of capacitance with frequency at 0 V dc bias in the off-state (open symbols) and on-state (filled symbols) of Eosin Y and fluorescein. Arrows indicate the transition from a low to a high state.

Figure 3. (a) Variation of capacitance with frequency at 0 V dc bias in the off-state of Rose Bengal. (b) Ratio of capacitance per unit length, c, and resistance per unit length, r, in the on-state of Rose Bengal calculated from the real and imaginary part of admittance, Y' and Y'', respectively.

which represents the bulk resistance of a device, has changed in the two "read" cases. While probing the high-conducting state (on-state), the diameter was smaller as compared to that in the low-conducting off-state. Since the impedances were measured without any dc bias, the change in the diameter could be related to the switching of the material with an associated memory. In an earlier report,[12] we showed that when the "write" pulse amplitude was greater than the critical switching voltage, the device switched to the high-conducting state. Equal reverse bias can "erase" the on-state state. In the case of fluorescein, the change in the diameter was very small. The ratio between the device current of the two states at any voltage, the on/off ratio, and the change in the diameter of the $Z'-Z''$ plot hence depended on the number of acceptor groups present in the molecule.

In the low-conducting state, interaction between molecular clusters is very weak and a lumped circuit element very well describes capacitive and resistive response in the Cole−Cole plot. The dipole−dipole interaction of neutral molecules forms the most stable couple structure with $\Delta H_{\text{dimer}} = -66.74, -63.97$, and -19.54 kcal[14] for neutral states of the dimer of Rose Bengal, Eosin Y, and fluorescein, respectively. To transform to the high-conducting state, Rose Bengal dimers reduce by accepting 83.08 kcal during the $H_{\text{RB}_2} \rightarrow H_{\text{RB}_2^-}$ transition.[15] For Eosin Y and fluorescein sodium, such a calculation could not be carried out due to the presence of Na^+. Due to fewer or no acceptor groups in Eosin Y and fluorescein, ion−dipole interaction could become predominant in such devices to restrict formation of reduced dimer species.

C_P-R_P to C_P-R_P Switching in Eosin Y and Fluorescein. To study if the conductance switching in Eosin Y and fluorescein is associated with a change in dielectric properties of the material, we have plotted the capacitance of devices based on Eosin Y and fluorescein as a function of frequency for the on- and off-states. Figure 2 shows that both the devices based on Eosin Y and fluorescein, which have strong dipole moments, showed a change in dielectric properties in their neutral off-state and reduced on-state. The change in the dielectric constant could be more in fluorecein due to its higher dipole moment than Eosin Y (dipole moment of Eosin Y and fluorescein is 16.93 and 20.06 D, respectively). The results showed that both resistive and capacitive properties change during conductance switching. The electrical network, however, remained a C_P-R_P type in the high- and low-conducting states of the two materials.
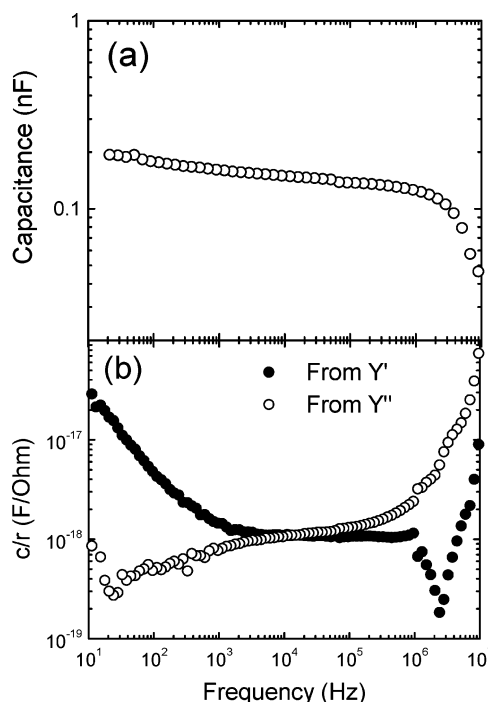
C_P-R_P to Distributed R−C Line Switching in Rose Bengal. The $Z'-Z''$ plot of the Rose Bengal off-state can also be represented as a C_P-R_P network. The plot for the high-conducting state, on the other hand, exhibited a semicircle inclined at an angle of $\pi/4$ at the origin of the $Z'-Z''$ axes (Figure 1). Such a plot represents a distributed R−C network. The origin of such a network can be explained in the following manner. In the high conducting state, radical anions generally dominate the matrix. Instead of isolated clusters, individual molecules behave as pseudocapacitors and intermolecular charge transfer dominates conduction. As the dipole−dipole interaction is a long-range one, the whole matrix becomes a highly coupled network and behaves as a distributed R−C line. The deviation from a straight line at an angle $\pi/4$ to a semicircle inclined at an angle of $\pi/4$ (53° experimentally) indicates a presence of a parallel dc conductor with the distributed R−C line. The schematic circuits[1] for the on- and off-states of the materials have been summed up in Table 1. The correlation between the number of acceptor groups and the on/off ratio has also been enlisted in the table.

To verify the thesis of switching from a C_P-R_P to a distributive R−C line network, we have calculated C_P and c/r for off- and on-states, respectively. Here c and r are the capacitance and resistance per unit length, respectively. Since the two states of Rose Bengal are to be represented as two different network systems, one cannot calculate dielectric constant or dielectric properties of the material in the two states in an identical manner. For the off-state of Rose Bengal, following C_P-R_P network, we have plotted C_P as a function of frequency in Figure 3a. For the high-conducting state, on the other hand, angular frequency (ω) response of complex admittance is described as[1,16]

$$Y(\omega) = (1 + i)(c/2r)^{1/2}\omega^{1/2}$$

with conductance G_0 as an additional component in parallel.

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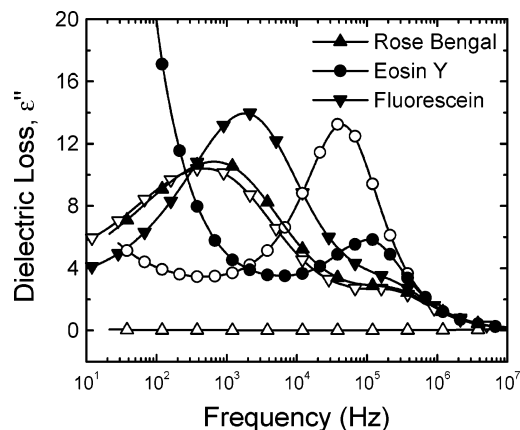*J. Phys. Chem. B, Vol. 109, No. 13, 2005* **6087**

Figure 4. Dielectric loss spectroscopy at 0 V dc bias of the on-state (filled symbols) and off-state (open symbols) of Rose Bengal, Eosin Y, and fluorescein.

Figure 5. Switching in terms of $Z'-Z''$ plot in Rose Bengal based device during the "read" cycles of "write−read−erase−read" sequences. Impedance characteristics were recorded to "read" the state at 0 V dc bias. Measurements were carried out 6 min after applying −3 V to "write" and +3 V to "erase" the high-conducting state.

The basic parameter for the device, c/r, has been calculated from Y'' and Y' and plotted against frequency in Figure 3b. The plot shows that c/r calculated from Y'' and Y' matched in the high-frequency region. The plot suggests that the distributive network is valid in the frequency range where dipolar polarization dominates the matrix.

When we compare the results in the three molecules, we find that due to the high electron affinity of Rose Bengal (−9.1 eV) and Eosin Y (−7.0 eV), acceptor groups act as carrier trapping sites. For Rose Bengal with acceptor groups in both of its planes (dipole moment = 17.39 D), which are nearly perpendicular to each other, the on-state has been associated with strong dipolar interactions among the molecules. This resulted in a change in electrical network configuration in its on-state. In Eosin Y, on the other hand, where only one of the two mutually perpendicular planes is surrounded by acceptor groups (dipole moment = 16.93 D), capacitance in the on- and off-state changed reversibly without any change in circuit network. Fluorescein has no dipole−dipole interaction (long-range order), and hence, only space charge polarization dominated the two states.[17]

Relaxation Processes in the Molecular Clusters. Dielectric loss takes into account the transition points of different dielectric mechanisms. With increasing frequency, slower mechanisms fail to respond and are overshadowed by faster mechanisms. In the devices we studied, the transition between ionic regimes to dipolar one depends on the acceptor groups attached to the molecular backbone. In Figure 4, we have plotted dielectric loss of three devices in their high- and low-conducting states. From the frequency at which the loss spectrum shows a peak, the relaxation time has been evaluated. The figure shows that in the off state, only space charge related leakage current dominates in the matrix of Eosin Y and fluorescein. In Rose Bengal, loss was very low (<0.07) and did not exhibit any peak in the frequency range of measurement. Hence, relaxation time could not be evaluated here. Such low dielectric loss in Rose Bengal is due to a very low off-state device current.[12] The bias dependence of dipolar relaxation (τ = 3.7 μs at 0 V) in the on-state is almost absent in Rose Bengal based devices, while it is present in the other two cases. In Eosin Y based devices, during transition from the on- to the off-state, dielectric loss maximum corresponding to dipolar relaxation (τ = 0.9 μs at 0 V) diminishes and that of space charge relaxation increases.

Flip-Flop between two Network Circuits. A continuous transition between the two states has also been studied by impedance spectroscopy. In Eosin Y and Fluorecein, a sequence of "write−read−erase−read" performed many times showed
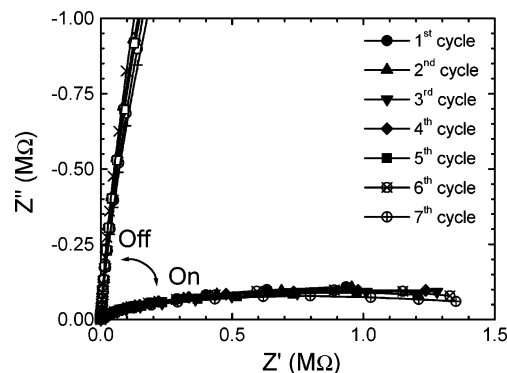
that the conductivity and dielectric properties switch between two levels. The electrical network for the two states however remained the same, a C_P-R_P network. In Rose Bengal, on the other hand, the results in Figure 5 under the sequence showed that the device could undergo a continuous transition between two networks, namely, a C_P-R_P and a distributed R−C line. In the figure, we have plotted $Z'-Z''$ without any dc bias after a negative and a positive voltage, which induced a high- and a low-conducting state, respectively. The results for the two networks looked identical for many sequence (Figure 5) showing that the matrix could switch between weakly interacting lumped clusters and a highly coupled network. The conduction mechanism should accordingly follow a transition between hopping nature in the low-conducting state and diffusion type in the high-state.

4. Conclusion

In conclusion, we have conducted detailed impedance spectroscopic studies of devices that undergo conductance switching. We have shown that conductance switching is associated with dielectric changes of the material. The change in dielectric properties is also related to the number of acceptor groups associated with the molecules, or their permanent dipole moment. In molecules with weak dipolar interactions, the matrix remained weakly interacting lumped clusters in both high- and low-conducting states. In Rose Bengal, the reduced high-conducting molecules form strongly coupled network. Such a network is normally used to explain diffusion of carriers in contrast to hopping transport in the low-state. The impedance spectroscopy of the two states showed that the device switched between two equivalent circuits: a C_P-R_P network in the off-state and a distributed R−C network in the on-state. Such switching between the two network systems, i.e., switching between two independent conduction mechanisms, has been observed reproducibly for many cycles.

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