Chapter 7

Organic Bistable Electrical Switch in tris, 8-Hydroxyquinoline Aluminum

7.1 Introduction

Switch is a basic component that can be rapidly and reversibly toggled between two distinct states and is commonly used in all kinds of applications. Modern digital memory is based on either electrical, or optical, or magnetic bistable switches. Since the discovery[114] of bistable switching in organometallic charge transfer(CT) complex based on copper tetracyano quinodimethane(Cu-TCNQ), there are several demonstrations[115, 116, 117, 118, 119, 120] of some kind of switching phenomena in different types of organic molecules or molecular solids. Recently, a neutral radical organic conductor that can exhibit bistability in all three physical channels simultaneously from a paramagnetic, insulating and IR-transparent to a diamagnetic, conducting and IR-opaque situation has been reported[118].

Ever since the first report[1] of efficient OLED, tris, 8-hydroxyquinoline Aluminum (Alq3) continues to be the most promising organic molecular semiconductors(OMS) for optoelectronic devices[121] based on small molecules. In this chapter, a possibility of realizing molecular switch based on Alq3 is offered by a phenomenon similar to electrical bistability in which a device exhibits two states of different conductivities at the same electric field. Hence, a seamless integration of electrical and optical devices for multifunctionality on a
single device may be achieved using Alq3 molecules.

7.2 Bistable Switching

The fundamental building block for the system required for information processing and storage is solid-state electrical switch, which is generally based on the ability to produce and control changes in one of the physical properties of a material. In some cases this modulation of physical property, induced by some external perturbation, such as optical, electrical or magnetic, results in two distinct states, which can be retrieved reversibly and used as bistable switch. The storage and processing of digital information employ this kind of bistable switches with “non-linear” input-output responses. The mechanism of threshold switching in disordered materials has been studied[122, 123] in details. A molecular electric switch is fabricated using molecules, being able to exist in two different states, having two different properties. The two distinct states are (i) ON state that allows electron transfer to occur and (ii) an OFF state that does not allow electron transfer. It has been attempted to explain the switching action in organic molecules or solids by three physical processes, which are (i) tunneling switch - works on excitation of the molecule, which can be turned OFF by either changing the barrier height or the depth of the potential well, (ii) torsion process - twists the molecule around a single bond to achieve decoupling in the OFF state and (iii) saturation/unsaturation - a double bond is transformed into a single one therefore breaking conjugation, which is accomplished by reduction or molecular reorganization and ON-OFF states are obtained by deprotonation or protonation of the intervalence bonds.

7.3 Experimental Details

The device in our investigations consists of a thin layer of Alq3, sandwiched between two metal electrodes. The device fabrication procedure using vacuum deposition technique(VDT)
is same as our previous metal-phthalocyanine based single layered organic devices[73] and is given in Chapter-II. High purity, sublimed Alq3 has been procured from Aldrich Chemical Co. Alq3 was evaporated either on ITO coated glass substrates, or on thin film of metals(Au, Cu, Al) thermally evaporated on glass substrate. Each layer was deposited in a vacuum chamber at a rate of 5-10Å/s and subsequently characterized by absorption spectroscopy and atomic force microscopy. Thickness of the resulting organic films was between 25 to 500nm. The metals for the top and bottom electrodes(Au, Cu and Al) were placed in a resistively heated tungsten filament and evaporated in a vacuum chamber. All evaporation were done at a base pressure of 2×10^-6 Torr. The current-voltage(J-V) characteristics are studied for Alq3 based single layered devices(metal/Alq3/metal devices) using different metal electrodes. We have measured the J-V characteristics by continuously varying the bias and also by interrupting the bias between each voltage step and in both cases, we have found same results. The J-V characteristics for the metal/Alq3/metal structures with different thickness of Alq3 layers were reproducible at all temperatures and showed no hysteresis.

7.4 Switching Effect in Al/Alq3/Metal Structures

Fig.7.1 shows the room temperature J-V characteristics of Alq3 based single layer devices with fixed cathode electrode(Al) and different anode electrodes(AI, Au, and ITO). In the first bias scan, current increases slowly with bias, but above some threshold voltage current increases abruptly by several order of magnitudes. At this threshold voltage, the device undergoes a change from a high impedance(∼ GΩ) state(OFF-state) to a low impedance(∼ KΩ) state(ON-state). In the second bias scan, the device stays in the high conduction state by displaying high current even at low bias below the threshold voltage, which persists in the third and subsequent bias scans showing a bistable behavior at the same electric field. In this conducting state current shows Ohmic behavior(J ∝ V), which indicates efficient charge
Figure 7.1: Room temperature J-V characteristics of Alq3 based single layer devices with different thicknesses of Alq3 layers sandwiched between Al cathode and different anodes. Current increases by several order of magnitude at a threshold bias of ~ 3 - 8V is observed for (a) Al/Alq3/Al, (b) Al/Alq3/Au, and (c) Al/Alq3/ITO structures. Empty circles with connecting lines(for a guide to eye) represent the first bias scan, empty squares and empty triangles show the second and third bias scans, respectively. The cross and plus symbols represents the conducting(low impedance) state for Al/Alq3/Au devices with 200 and 400nm Alq3 layers, respectively. In all devices, after crossing the threshold voltage, the devices remain in the conducting state which is observed in second, third and subsequent bias scans. The straight line fit(solid lines) to the conducting state J(V) data shows the linear dependence of J on V, showing an Ohmic behavior.
carrier transport and does not show any significant change for devices with different thickness of the Alq3 layers. The J-V characteristics were reproducible in the low bias region (below the threshold voltage) for several bias scans. Similar behavior is observed for devices with different thicknesses of Alq3 layers, is shown in Fig. 7.1. Increasing the thickness of the Alq3 layer does not show any significant change in the impedance of the conducting state but the threshold voltage shifts toward the lower bias. As the thickness of the Alq3 layer increases, (i) threshold voltage shifts toward lower value and (ii) ON-OFF ratio decreases.

7.4.1 Al/Alq3/Al Structures

In Al/Alq3/Al devices, (i) a transition from a high impedance state of 60GΩ to a low impedance state of 6KΩ at threshold voltage of 5.5V with ON-OFF ratio of 10^5 for devices with 100nm Alq3 layers and (ii) from 320MΩ to 30KΩ at threshold voltage of 2.1V with ON-OFF ratio of 2 × 10^4 for devices with 400nm of Alq3 layer, are observed, which is shown in Fig. 7.1(a). Resistance of the samples in the insulating states is calculated from the linear portion of the J-V characteristics.

7.4.2 Al/Alq3/Au Structures

Au/Alq3/Al devices show (i) a transition from a high impedance state of 100GΩ to a low impedance state of 12KΩ at threshold voltage of 4.74V with ON-OFF ratio of 1 × 10^5 for 100nm Alq3 layer, (ii) a transition from 5GΩ to 30KΩ at 2.8V with ON-OFF ratio of 1.3 × 10^4 for 200nm alq3 layers, which is shown in Fig. 7.1(b). Resistance of the samples in the insulating states is calculated from the linear portion of the J-V characteristics.

7.4.3 Al/Alq3/ITO Structures

ITO/Alq3/Al devices show (i) a transition from a low impedance state of 600GΩ to a conducting state of 30KΩ at threshold voltage of 8.6V with ON-OFF ratio of 3.2 × 10^6 in
100nm sample and (ii) from $2G\Omega$ to $30K\Omega$ at 7V with ON-OFF ratio of $4.5 \times 10^4$ in 200nm sample, which is shown in Fig.7.1(c). Resistance of the samples in the insulating states is calculated from the linear portion of the J-V characteristics.

### 7.5 Absence of Switching Action in Devices with High Work Function Cathode

Fig.7.2 shows the J-V characteristics of Au/Alq3/Au and Cu/Alq3/Cu structures with 400nm thick Alq3 layers. The switching behavior is absent in these devices. The efficiency of carrier injection in OMS can be controlled by varying the work function of the contacting metals. The energy barriers that control the hole and electron injections at the metal/OMS interface are $\phi_{Bh} = I - \Phi_{anode}$ and $\phi_{Be} = \Phi_{cathode} - \chi$, where $\Phi$ is the work function, $I$ is the ionization potential and $\chi$ is the electron affinity of OMS. Alq3 has $\chi = 2.7eV$ and $I=5.8eV$ and is an electron transport OMS. Electron injection will be efficient when a low work function metal is used as cathode to have a smaller barrier height to the electrons at the cathode/Alq3 interface, but a high work function metal cathode introduces a larger barrier to the electron flow at the interface resulting inefficient electron injection into the devices. Hence, electron injection is efficient when Al($\Phi=4.2eV$) contact is chosen to be the cathode, compared to Au($\Phi=5.1eV$) or Cu($\Phi=4.6eV$) cathode, since there is a barrier of $\phi_{Be}=1.5eV$ at the Al/Alq3, $2.5eV$ at the Au/Alq3, and $2.0eV$ at the Cu/Alq3 interfaces. In Au cathode based devices, the magnitude of the current density is very small even at high applied bias($\sim 10^{-9}Amp/cm^2$ at $1.5 \times 10^6V/cm$) and much less compared to the Al cathode based devices(from Fig.7.1 and Fig.7.2).
Figure 7.2: Room temperature J-V characteristics of Au/Alq3/Au and Cu/Alq3/Cu devices, which shows no switching effect.

7.6 Recovery to Insulating State

In the first bias scan, after transition from a high to a low impedance state at a threshold voltage, the device persists in the conducting state for further bias scans. Again the high impedance state is regained by keeping the device at zero electric field for several hours to days. The recovery of the switching behavior with time is shown in Fig.7.3. It is seen that the device comes to the original low conduction state in 12hrs and the device again shows the same transition from the high to low impedance state at the same threshold voltage but with a less ON-OFF ratio ($10^3$ compared to $10^5$ in the virgin devices). Further experiments with more waiting time reproduces the conductance transition more efficiently with high ON-OFF ratio, but with a shift in threshold voltage to higher bias. The impedance of the conducting state is also increased with waiting time.

Fig.7.4 shows the switching action in thicker (600nm) Alq3 samples in Au/Alq3/Al devices. Switching behavior is observed in both the forward and reverse bias conditions. As
Figure 7.3: Recovery of insulating state in room temperature J-V characteristics of Al/Alq3/Al organic switching device. Empty circles with connecting lines (for a guide to eye) represent first bias scan and empty squares represent second bias scans. Initially ON-OFF ratio was $\sim 10^5$ and after 12 hours it becomes $\sim 10^3$ and device also remains in the conducting states after first bias scan. Increasing the recovering time shifts the threshold voltage toward the higher bias with ON-OFF ratio of $\sim 10^5$.

mentioned Chapter-III, when positive bias is applied to metal electrodes with high work function (ITO, Cu, Au), the device is under forward bias condition and when ITO electrode is negatively biased, the devices is under reverse condition. Current in the reverse bias is less than compared to that in forward bias due to larger barrier for electron injection at Au/Alq3 interface. Threshold voltage shifts to higher value in reverse bias condition. After achieving the conducting state in forward direction, the device stays in the same state for reverse bias too. The most interesting feature in the Fig.7.4 is that the switching behavior can be instantly recovered from a low impedance to the high impedance state by applying the same amount of threshold voltage in the reverse direction, but this has been possible only thicker device ($\geq 600nm$).
Figure 7.4: J-V characteristics of Au/Alq3(600nm)/Al showing that (i) there is a difference of two orders of magnitude of current flowing through the device when forwardly biased (with Al cathode) than when in reversely biased (with Au cathode) (ii) switching action is present both in forward and reverse bias situation with reverse threshold voltage is more than that of forward threshold voltage (iii) application of the negative potential equal to the threshold voltage, the device come to the original condition of OFF state.

7.7 Proposed Mechanism for Switching in Alq3

There are several mechanisms proposed[122, 123] for the explanation of this type of transition between conducting and insulating states. The most appealing one for this type of conductance transition in single or aggregate of organic molecules is the electric field induced conformational changes[124, 125, 126]. Alq3 might undergo an internal rotation into an excited molecular conformation or isomer, under application of electric field above some threshold. Alq3 has an octahedral symmetry and occurs in two geometrical isomers: meridan(mer-Alq3) and facial(fac-Alq3), which is more insulating than mer-Alq3 due to larger gap between lowest unoccupied molecular orbital(LUMO) and highest occupied molecular orbital(HOMO) in fac-Alq3. There are three hydroxyquinoline legends containing extended π-conjugated structures in Alq3. It has been shown theoretically[127] and
experimentally[125, 126] that in organic molecules, having several closed rings (which is the case in Alq3), the resistance can increase by several orders of magnitude ($10^4 - 10^5$) when the angle between the planes of the adjacent rings is changed from 0 to 90° and may result in greatly enhanced conduction ("ON-state") in the excited conformation of Alq3.

![Figure 7.5: The (a) meridian (b) facial form of Alq3. The darker circles about the central Al represent Oxygen atoms.](image)

This conductance transition is also observed at low temperature (shown in Fig.7.6) with a shift in the threshold voltage toward higher values. It is observed that conductance transition is observed only when Alq3 is sandwiched between two electrodes, at least one with lower work function (Al) than the other electrode (Au, Cu, ITO) and the highest ON-OFF ratio is observed when both electrodes are Al. No such conductance transition has been observed in Au/Alq3/Au and Cu/Alq3/Cu, i.e. when both electrodes with higher work function are used. Alq3 is an electron transport OMS with ionization potential and electron affinity[40] of 5.7eV and 2.9eV, respectively, so efficient electron injection is possible when a low work function metal is used as cathode such that barrier to the electrons at the cathode/Alq3 interface is reduced. The Al/Alq3 interface gives rise to a barrier of 1.3eV to the electron flow, leading to injection limited current conduction[128], whereas Cu/Alq3 and Au/Alq3 interfaces give
Figure 7.6: J-V characteristics of Al/Alq3(200nm)/Al at 50K and 325K. The threshold voltage shifts to higher value at lower temperature (i.e. 12.2V with ON/OFF ratio of $10^4$ at 50K compared to 5.5V with ON-OFF ratio of $10^5$ at 300K). Empty circles with connecting lines (for a guide to eye) represent first bias scan and empty squares represent second bias scan.

rise to barrier heights of 1.8eV and 2.3eV, respectively and lead to very inefficient electron injection from cathode to Alq3. Thus, efficient electron injection may be responsible for this type of conductance transition, though we cannot rule out the role of interface between Al and Alq3 on this conductance transition.

Weak temperature dependence of the conductance transition, as shown in Fig.7.6 and reverse bias induced recovery to OFF-state as shown in Fig.7.4, corroborates electric field induced conformational change to be responsible for the transition between insulating and conducting states.

7.8 Summary

In summary, we report a organic molecule based bistable electrical switch using conductance transition in single layer devices based on Alq3, with large room temperature ON-OFF
ratio (~ 10^5). At low threshold voltage (~5-10V), these devices undergo a change from insulating state (or high impedance ~ GΩ state) to conducting state (or low impedance ~ KΩ state). Switching behavior has been observed in devices with Al cathodes, but not in devices with high work function metal cathodes. After going to the low impedance state, again high impedance state can be regained by keeping the device at zero electric field for long time (≥ 12 hours). The threshold voltage decreases with thickness of the device and have a very weak dependence of temperature. These two-terminal reversible electrical switches have several device applications including molecule-based memory for molecular electronics.