Role of New Bis(2,2′-bipyridyl)(triazolopyridyl)ruthenium(II) Complex in the Organic Bistable Memory Application

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A significant amount of research has been done in the past few years using ruthenium metal complex for many different device applications. It is well-known that ruthenium complexes are promising candidates for high-efficiency, low-voltage devices, such as light emitting diodes (LEDs) and dye-sensitized solar cells (DSSCs).[1–4] Besides that, ruthenium complexes have another potential use in organic bistable memory application. However, only nonionic and few ionic compounds are known to exhibit good bistable memory phenomena.[5–11] Therefore, generation of an ionic coordination complex with a potential organic bistable memory application is a challenge. In this communication, a new ionic ruthenium dye with different charge transfer ligands was synthesized and used as a key element in organic bistable devices. We have observed high conductance switching of the complex with a large ON−OFF ratio and high rewritability with associated memory effect in the devices.

The *N*,*N*-chelated ruthenium complex in which *N*,*N* sites are part of a six-membered pyridine and five-membered triazolo rings in addition to two bipyridines(bpy) is used to improve the performance in the memory switching device. The details of the chemical synthesis and material characterization are shown in the Supporting Information. The complex shows moderately strong photoluminance (PL) due to the presence of quinoid form in the triazolopyridine ligand.[12,13] In addition to bands in the UV region, the complex (in acetonitrile) displays two $\pi(\mathrm{Ru})-\pi^*(\mathrm{L})$ metal to ligand charge transfer (MLCT) excitation bands of moderate intensity in the visible region near 420 and 444 nm. The solution is also luminescent, the peak lying near 603 nm. Excitation spectral studies have demonstrated that the luminescence is associated with the above-noted MLCT bands. A representative case is shown in Figure 1. The luminescence is believed to originate from the ^{3}MLCT state.

$\mathrm{Ru^{II}(bpy)_2(L)^{2+}}$ is moderate luminescent with quantum yield (Φ) ca. 0.008. The redox behavior in acetonitrile is characterized through a one-electron oxidation of the ruthenium center at 1.25 V and a one electron reduction of the ligand at −1.40 V versus saturated calomel electrode (SCE). The voltammogram is depicted in the Supporting Information, Figure S2.

In switching devices, two conducting states are observed at the same applied voltage, namely, the high-conducting state (ON state) and the low-conducting state (OFF state). Under some applied condition, the device can be switched from one state to the other, which is ideal for rewritable nonvolatile memory application.[5–11] For the memory device fabrication, acetonitrile (2 mg/mL) solution of ruthenium complex was deposited on the indium tin oxide coated substrate. Aluminum metal was evoporated above the ruthenium complex film to form another electrode. Thickness of the film is about ~80 nm.

The current−voltage ($I-V$) characteristics of the devices were recorded by scanning applied voltage from 0 to $+V_{\max}$ and then to $-V_{\max}$ followed by a reverse scan from $-V_{\max}$ to $+V_{\max}$. We have varied the amplitude of $V_{\max}$ to generate a range of $I-V$ characteristics. The characteristics were nonlinear in nature during repeated voltage cycles. A typical $I-V$ characteristic between ±2.5 V in devices based on ruthenium complex is shown in Figure 2.The characteristics in the reverse bias show electrical bistability. When the voltage was swept from a positive voltage, the material exhibited its low conducting state (OFF state), as due to very low leakage current. As the voltage approached $-V_{\max}$, the material switches on to its high conducting state (ON state). Device current at any voltage during the sweep from $-V_{\max}$ was several order higher in magnitude as compared to that during the sweep from $+V_{\max}$. The increase in conductivity at a suitable negative voltage, or conductance switching, was associated with a memory phenomenon. In other words, no bias was required to sustain the high conducting state, which was induced by a negative bias. Only a suitable positive bias could switch the high-conducting state to a low one.

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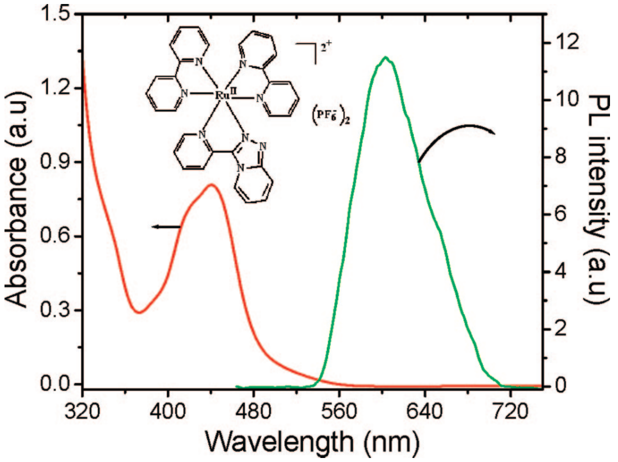

Figure 1. Absorbance and photoluminance spectra of the ruthenium complex in acetonitrile solution. Inset shows the molecular structure of ruthenium complex.

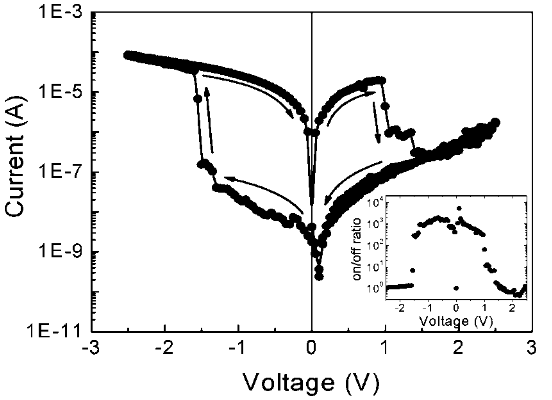

Figure 2. Current–voltage characteristics of a device based on spin-cast film of ruthenium complex for two sweep directions in log scale. The ratio between the ON- and OFF-state current as a function of applied voltage for the same sweeps as represented in the inset figure.

This transition from high-conducting state to low-conducting state is equivalent to the writing process in a digital memory. The voltages at which the device changed its states, however, is independent of $V_{\max}$. We also observed that the current values retraced during the voltage cycles. Hence, the transitions between the two states were reproducible indicating rewritability of the devices. Inset Figure 2 shows the variation of on/off ratio with applied bias. We have observed a 1×10^3 on/off ratio at -1.3 V. Such a high ratio, especially at room temperature and in single-layer sandwich structures, is interesting by itself. This is due to the electron accepting nature of the ruthenium and low OFF-state leakage current of the complex.

It is well-known that the ruthenium complexes act as high electron accepting materials and the appearance of high-conducting state, in general, has been explained in terms of electroreduction of the molecules.[5–8] Considering the difference in work-functions of the electrodes used, electron injection in reverse bias becomes favorable which consequently reduces the molecules to a high-conducting state. When a certain reverse bias close to the reduction potential of the ruthenium complex is applied, the bipyridine and bipyridine type ligands of ruthenium complex are reduced by receiving an electron from the respective electrodes. Therfore, the charge carrier trasport through the molecules is enhanced, and produces high current in the device. The reduction potential value is about -1.4V vs SCE, which is actually the switching voltage of the device. The device returns to its original state, when the voltage sweeps to a suitable forward bias (around 1.0 V). This oxidizes the one electron ruthenium center by removing the extra electron previously added. This switching mechanism is quite similar to the electroreductive polymerizations of the polyvinylpyridine monomer complexes of ruthenium.[14] The presence of large mobile $(PF_6^-)_2$ counteranions in the ruthenium complex do not play any important roles to the switching mechanism.

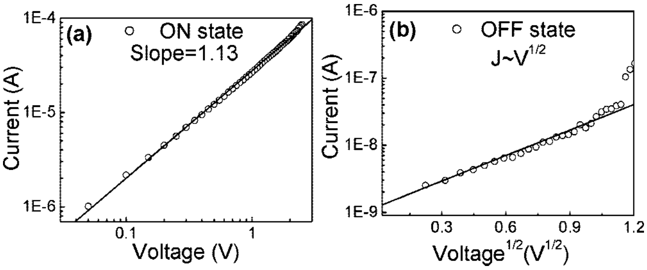

Figure 3. (a) Absolute value of current versus voltage plot of the ON state, and (b) absolute value of current versus square root of voltage amplitude plot of the OFF state of a device based on ruthenium complex film. Results from the reverse bias section of $I-V$ characteristics are plotted here. The lines are best fit to linear regime of the plot in each case.

Further the conduction mechanism of the device has been studied from the $I-V$ characteristics in the high- and low-conducting states. The ON-state current for the voltage sweep from -2.0 to 0.0 V can be plotted as $\log(I)$ versus $\log(V)$, which is shown in the Figure 3a. The plot fits to a straight line with slope of 1.13. This linear relationship suggests that the current conduction in the ON state is Ohmic in nature. On the other hand the OFF- sate current for the voltage sweep 0.0 to -2.0 V, is plotted as $\log(I)$ versus $V^{1/2}$ (Figure 3b). The plot also fits to straight lines suggesting that the conduction mechanism follows thermionic emission model.[15] Therefore the change of the current conduction from the high state to low state is due to transition from the ohmic to space charge limited current.

Reversibility of the associated memory phenomenon can best be studied under a voltage pulse sequence, namely "write−read−erase−read" cycle. In such a cycle, the high- and low-conducting states are induced ("write" and "erase", respectively) repeatedly and the states are monitored or "read" in between. We have characterized the devices under such voltage sequence up to 2 h. A section of the voltage sequence and corresponding current from the device is shown in Figure 4. Here, -2.0 and $+2.0$ V pulse (width = 15 s) were applied to "write" the high-state and "erase" to a low conducting one, respectively. The states were probed by measuring device current at -0.8 V. The figure shows that the magnitude of current under "read" voltage was much higher in the high-conducting state as compared to the low state. The results hence show that one can flip-flop the two

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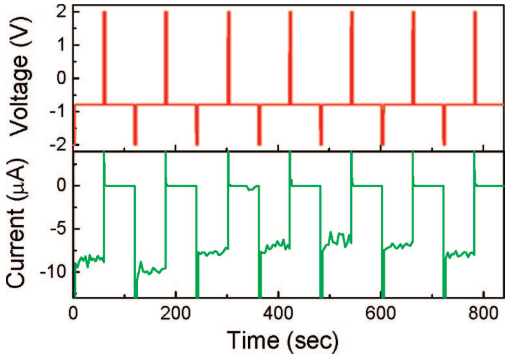

Figure 4. Switching performance of a pristine ruthenium complex device during a "write−read−erase−read" sequence for rewritable data storage applications. The sequence of voltage pulse is shown in the upper trace, whereas the current response is shown in the lower one.

states of the devices and probe them successfully as in rewritable or random-access memory (RAM) applications.

We have also studied the read only memory (ROM) of the devices. The devices could also remember its ON and OFF states for hours. Once the ON state (or OFF state) has been induced, we have probed the state by applying a small voltage for hours and measured the device current. Figure 5 shows such current while probing ON and OFF states. The current has been several orders higher when the ON state has been probed. The results clearly show that once the ON or OFF state state is induced, the device remembers the state for hours without any sort of degradation for data-storage applications. Here also, the ratio between the probe currents corresponded with the On/Off ratio obtained in $I-V$ characteristics.

In conclusion, a new ruthenium complex was synthesized with different charge transfer ligands and it functioned as an organic bistable memory device when sandwiched between two metal electrodes. The transitions between the two states were rewritable in nature and associated with memory phenomenon. The devices exhibited random-access memory applications under "write−read−erase−read" voltage sequence.

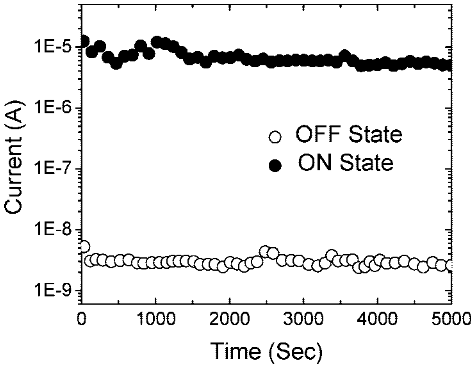

Figure 5. Long time response of the ON (filled symbols) and OFF state (open symbols) as probed by device current under −0.8 V. The ON and OFF states have been induced by −2.0 and 2.0 V, respectively. The sign of the probe current has been reversed to plot in logarithmic scale.

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Supporting Information Available: Details of chemical synthesis and characterization and device fabrication (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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