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Conductance switching mechanism of Rose Bengal organic thin films in ambient conditions*

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The molecular thin films of Rose Bengal (RB) embedded in polymethyl methacrylate matrix are fabricated by using the spin-coating technique. The macroscopic current–voltage (I–V) characterization of the film shows that the RB molecule has two conductance switching states with a high ON/OFF ratio in ambient conditions. The infrared spectra indicate that intermolecular hydrogen bonds can form in the RB thin films after their hydrolysis in air. With the first-principles calculations, we demonstrate that the hydrogen bonds will be destroyed in concomitance with the conformational change when the RB molecule switches to its high-conductance state after applying a voltage.

Keywords: Rose Bengal, conductance transition, mechanism
PACC: 7360

The organic functional molecules of bistable states are promising candidates for the next generation of information storage and future optoelectronic devices.[1−3] A number of mechanisms and strategies responsible for the two switching states in a variety of organic molecules have been proposed, such as conformational changing, rotation of functional group, charge transfer, and reduction–oxidation process. In the previous studies, a series of donor–acceptor (D-A) type charge-transfer complexes has been extensively explored to show stable, reversible conductance switching due to the intermolecular charge transfer.[4−9] In addition, the first conductance transition in a solid state film of rotaxane-based molecules was demonstrated to be ascribed to its structural change.[10−12]

RB molecule is of significance for potential applications in molecular switching or optoelectronics devices.[13−21] It has only electron acceptor groups in the absence of any donor group, so the acceptor groups can perturb the conjugation on the backbone and results in a very low OFF state current. The detailed mechanism of conductance switching in RB has not been fully understood yet, though generally it can be explained by both the electroreduction and electric field induced conformational changes.[13−15] On the other hand, from the practical viewpoint, the electrical switching molecules should provide stable and reproducible conductance transition properties in ambient conditions. RB molecule is prone to be hydrolysed and then can form intermolecular hydrogen bonds in air. The effect of these hydrogen bonds on the conformational change and conductance transition has not been ever investigated before.

In this paper, we study the conductance transition mechanism of RB molecules in ambient conditions. The molecular thin films of RB embedded in polymethyl methacrylate (PMMA) polymer matrix are fabricated. A conduction transition is observed in this film when a sweeping voltage between 0 to 3 V is applied. From the infrared (IR) spectrum measurements, we demonstrate that intermolecular hydrogen bonds can form in the RB thin films in air conditions. When the RB molecule switches to its high-conductance state after applying a voltage, the hydrogen bonds will be destroyed in concomitance with the conformational change.

In a conjugated molecule, the electric field will induce the conformation distortion and the conductance of the molecule can be changed according to the functional groups and dipole movements.[22,23] The PMMA polymer is used as a polymer matrix in the

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present work because it has different functional groups and dipole moments with RB molecules, so that the distortions of the molecular structures under an electric field are different. The structures of PMMA and RB are shown in Fig.1. To obtain the PMMA and the RB thin film, we prepared the PMMA and the RB solutions separately and then put them together. We chose acetone as the solvent of both solutions, and kept the ratio of RB to mono-PMMA be 1:25 while they were dissolving into each other. The solution was spun on an indium tin oxide (ITO) coated glass substrate at a rotating speed of 1800 rpm per 30 s, and repeated once. Before this, both solutions had been churned up for almost 10 h. After the spin coating, the samples were dried for more than 10 h. All of the steps except drying were taken at room temperature. The surface morphology and roughness of the thin film were then characterized by tapping mode atomic force microscopy (AFM) imaging (DI Multimode IIIa) in air.

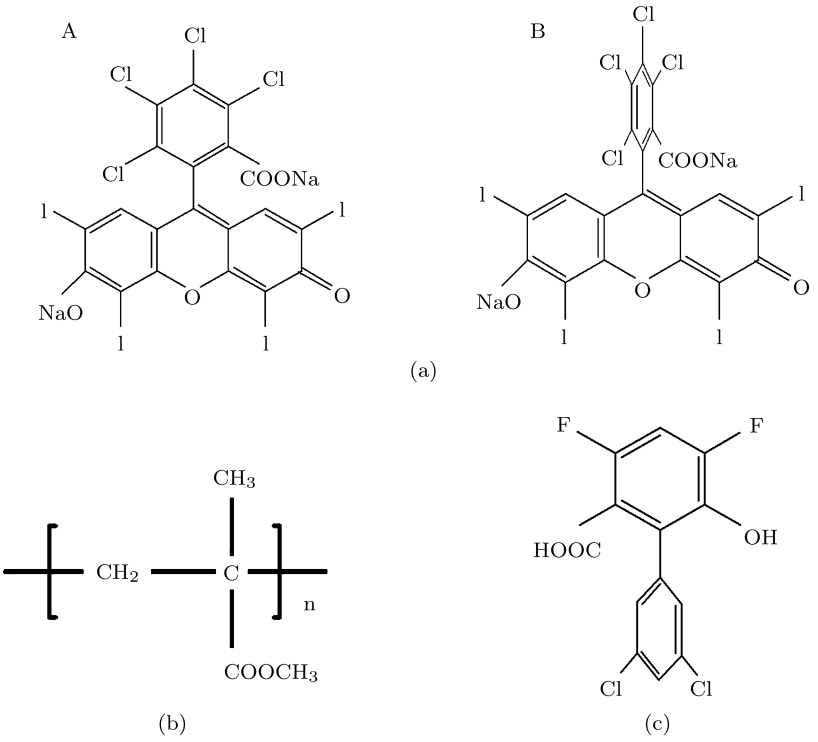


Fig.1. (a) The chemical structure of Rose Bengal molecule and its two configurations: A and B; (b) the chemical structures of PMMA; (c) a simplified molecule RB-s.

The current–voltage (I–V) characteristics were measured by using the Keithley 4200-SCS with a current resolution of 1 fA. A gold tip, which softly contacts the surface of thin films and serves as a top electrode, gave an active area of about 1 mm^2 for each device. During the experiment, the sample was not allowed to be irradiated by any light and always kept at room temperature in air. The sweeping voltage between 0 to 3 V was applied to the thin film at a voltage scan rate of 2.5 mV/s. Moreover, infrared (IR) spectra were measured from the organic thin film by using a spectrometer (Magna-IR 750, Nicolet Co.) before and after I–V measurement, separately.

Figure 2 shows an AFM topographic image of the PMMA/RB thin film. The substrate is covered by a thin layer of mixed PMMA and RB molecules with an average thickness of about 100 nm. The molecular film is formed by small particles with a rather uniform size of about several hundreds of nanometres, while the measured root mean square (RMS) roughness of the film, Rq, is only about 6.00 nm. The aggregating behaviour of the molecules to form molecular particles may give rise to some important qualities of the thin film, for example, acting as capacitor with high capacitance. Additionally, the acceptor groups in RB molecule has a great tendency to accept electrons dur-

ing the releasing of capacitance.

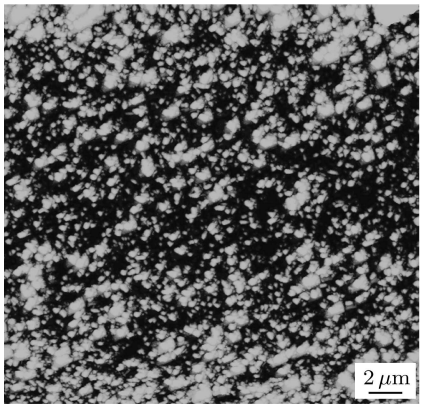


Fig.2. AFM topographic images of PMMA/RB thin films, with an imaging area of $20 \times 20\,\mu m^2$. The uniform film is formed from molecular nanoparticles with about several hundreds of nanometres in size. The measured RMS roughness (Rq) is 6.00 nm.

To start with, we measured the conductance properties of the pure PMMA thin film on ITO substrate prepared by using the spin-coating technique. Figure 3(a) shows the linear I–V characteristics in a range from 0 to 3 V, which displays a well Ohmic resistance. The calculated resistance is approximately $10^9\,\Omega$, and obviously the pure PMMA thin film has a very low conductivity in this voltage range.

The typical I–V characteristic of mixed PMMA and RB film is shown in Fig.3(b). During scanning the voltage from 0 to a positive voltage (2.0 V), the film exhibits its low conducting state (OFF state) initially with a resistance of about $10^7\,\Omega$, when the voltage approaches to the so-called threshold voltage (about 2.5 V), the current increases rapidly and the resistance drops down to about $10^5\,\Omega$, showing its high conducting state (ON state). So we can achieve two switching states on PMMA/RB films with a high conductance ratio (ON/OFF ratio) of about 100. Because the current increases up to 10^{-6} A smoothly, the possibility of the breakdown of electric potential can be excluded by repeating experiments.

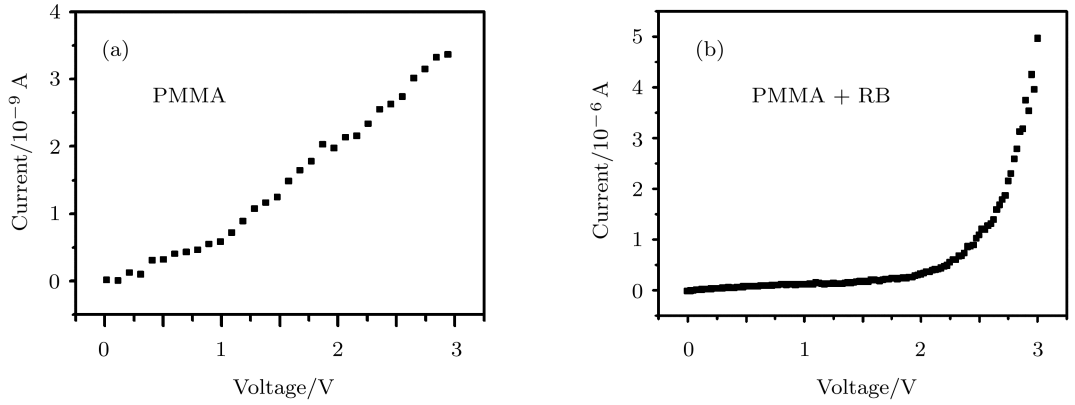


Fig.3. I–V characteristics of the devices based on spin-cast films. In (a) the I–V curve measured from a pure PMMA-based device shows a linear I–V relation in a range from 0 to 3 V and a very low conductance, and in (b) the I–V curve measured from a Rose Bengal-based device indicates two conductance switching states on PMMA/RB film and a threshold voltage of about 2.5 V for OFF-ON transition.

The conductances of PMMA/RB film at OFF state and ON state are about two and four orders of magnitude higher than those of pure PMMA thin film, respectively. The high conductivity observed in the PMMA/RB thin film should come from the RB molecules. It has been reported[14,15] that two mechanisms, namely electroreduction and conformational change of the molecules, resulting in conjugation modification can individually explain the switching between the low- and the high-conducting states. In the case of RB embedded in a polymer matrix, an RB molecule has two planes anchored in a supramolecular matrix. In the low-conducting state, the two planes present perpendicularly in the RB molecule, which have permanent dipole moments, allow a forward-bias induced conformation change to occur. After apply-

ing a voltage, electroreduction of RB molecules can facilitate conjugation restoration in the backbone of the molecule, hence resulting in switching to a high-conducting state.

In order to clarify whether the conductance transition of molecules comes from the conformational change after applying a voltage, IR spectra were measured from the PMMA/RB film. As shown in the curve (b) of Fig.4, before applying a bias voltage, a broad adsorption peak in a range of 3300–3650 cm^{-1} can be found, which comes from the O-H stretching mode of the intermolecular hydrogen bonds. It indicates that there are hydrogen bonds formed in PMMA/RB films. Since there exists no hydroxyl group in the PMMA and RB molecules (Fig.1), the hydroxyl groups should be generated due to the hydrolysing of –ONa or –COONa groups in RB molecules in ambient conditions. After applying a bias voltage, the broad adsorption peak disappears and very weak adsorption peaks spread in a wide range instead of distributing from 2500 to 3800 cm^{-1} (curve (a)). The disappearance of the broad peak indicates the break of hydrogen bonds. The weak peaks of 2500–3300 cm^{-1} originate from the O-H stretching mode of –COOH group, while the sharp peaks of 3300–3800 cm^{-1} arise from the stretching mode of free O-H bonds and the residuary hydrogen bonds.

From the IR spectra, we also find that the O-H stretching mode shifts toward short wavelengths. This is ascribed to the configuration change of the RB molecule. To confirm whether the peak shift results from the configuration change, *ab initio* calculations were carried out at B3LYP/6-31G* level[24,25] by using Gaussian 98.[26] As indicated in Ref.[14], the RB molecule might have two configurations (see Fig.1(a)), one is flat (A), the other is not (B). After structural relaxation, we found both *ab initio* configurations converged to configuration B. The flat configuration A is less stable than B. The molecules should be in configuration B before applying a bias voltage. Now we suppose that it transits to configuration A after applying a bias voltage. Because the RB molecule has only benzene rings with different functional groups, hydroxyl and carboxyl, we simplify the RB molecule into the RB-s (see Fig.1(c)). The most stable configuration is the configuration where two benzene rings are not in a plane. We measured the IR spectra of the stable configuration and calculated an artificial flat configuration. And we found that the O-H stretching modes of –OH and –COOH groups shifted toward higher wavenumber by about 5 cm^{-1} when the two benzene rings are almost in a plane. With both the break of hydrogen bond and the change of configuration taken into account, the calculated results are in good agreement with the experimental result.

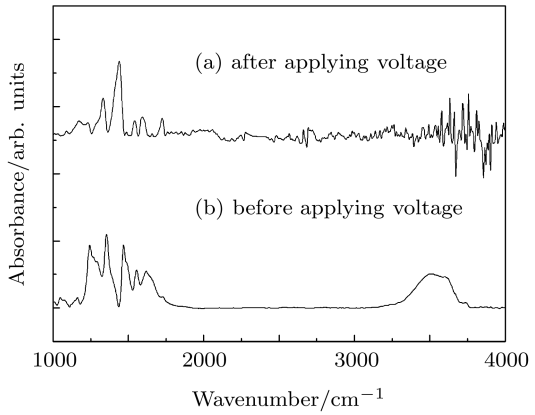


Fig.4. Infrared spectra of PMMA/RB thin films, where curve (a) shows the break of intermolecular hydrogen bonds after applying a voltage and curve (b) exhibits the broad adsorption peak located in a range of 3300–3650 cm^{-1}, indicating the presence of the O-H stretching mode of the hydrogen bonds before applying a voltage.

In summary, we have fabricated a simple device with RB molecules embedded in PMMA polymers. The film shows two conductance transition states with a high ON-OFF ratio. Based on the IR spectra obtained before and after applying a bias voltage, a new mechanism is proposed. The conducting transition is generated not only from the oxidation/reduction and configuration transition, but also from the break of intermolecular hydrogen bond, which is demonstrated by the IR spectra and first-principles calculations.

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