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A Memory Effect Controlled by a Pulsed Voltage in Photoinduced Conductivity Switching in an Organic Charge-Transfer Salt

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The photoinduced switching of material properties is an important practical functionality in optical devices and has been reported for a variety of molecular systems.[1,2] In conventional switching devices, such as light-activated thyristors and Shockley diodes, switching to a high conductivity (HC) state is induced by photoirradiation as well as by application of gate current or voltage.[3] Switching back to a low conductivity (LC) state takes place as the current is reduced below a holding level.

In this communication, we report that the photoinduced HC state in the organic charge-transfer salt α-(BEDT-TTF)$_2$I$_3$ can be repeatedly recovered without further photoirradiation by application of a pulsed voltage even after the current has been reduced to zero. The recovery to the HC state can be controlled by adjusting the pulse width and/or amplitude. By proper selection of pulsed voltage parameters, the switching can be made reversible or irreversible. Hysteresis loops in the current−voltage and current−irradiation intensity curves of the circuit demonstrate a memory effect with potential application in unconventional photoswitching operations. The characteristic of the hysteresis loop and current bistability can be flexibly varied by changing the width of the applied pulsed voltage. Such controllability is unprecedented and can be distinct advantages over conventional switching devices.

Molecular conductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are a family of compounds that have attracted intense interest.[4] α-(BEDT-TTF)$_2$I$_3$, which has a donor-layer arrangement classified as α-type, exhibits quasi-two-dimensional metallic conductivity on the crystal *ab* plane at room temperature, while the charge-ordered insulating phase appears at 135 K due to a first-order metal−insulator (M−I) phase transition.[5]

The electric circuit including the crystal of α-(BEDT-TTF)$_2$I$_3$ exhibited a switch in conductivity under an electric field and synchronous photoirradiation. Experimentally, a square-wave voltage pulse train with specified pulse height (ΔH) and width (ΔW) was applied to the sample via two electrical contacts on the sample separated by a distance (d) of 0.3−0.4 mm. For photoirradiation of the sample, a laser pulse train was applied in synchronization with the pulsed voltage via an optical fiber to illuminate the crystal between the two electrodes. Experiments were carried out mainly at 115 K. The circuit diagram and pulse scheme used in the experiments are shown in Supporting Information.

Figure 1a shows the time profiles of current in response to the application of a pulsed voltage (10 V, 2 ms) with and without photoirradiation. Figure 1b shows the current−voltage ($I-V$) characteristics with and without photoirradiation obtained by scanning the amplitude of the applied voltage in the positive and negative directions. As shown in Figure 1a,b, the HC state could not be obtained by application of a pulsed voltage alone. With synchronized photoirradiation, current switching to the HC state was observed, and the HC state was subsequently retained as long as the voltage was applied (Figure 1a). The switch from the LC to the HC state occurs in a discontinuous manner at a critical voltage (Figure 1b), and the reverse switching occurs at a lower voltage in the negative voltage scan, indicating hysteresis. Thus, two stable states of the crystal are possible over a certain voltage range. The current (I) is plotted against the voltage drop across the sample (V_S) in Figure 1c. This $I-V_S$ curve, calculated from the $I-V$ characteristic (see Supporting Information), shows that the bistability of the HC state can be ascribed to a differential negative resistance (DNR) in the photoirradiated crystal, demonstrating a light-activated thyristor-like behavior.

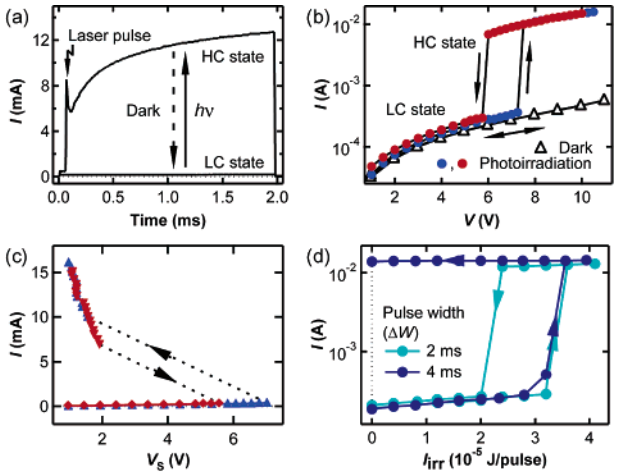

Figure 1. (a) Temporal profiles of the current measured with $R_L = 510$ Ω, $d = 0.35$ mm, and $I_{irr} = 3.4 \times 10^{-5}$ J/pulse. Upper and lower traces were obtained with and without photoirradiation, representing the HC and LC states, respectively. (b) $I-V$ characteristics obtained by scanning ΔH in the positive (blue) and negative (red) directions with photoirradiation (3.4×10^{-5} J/pulse), $\Delta W = 4$ ms, and $d = 0.30$ mm. $I-V$ characteristic without photoirradiation is shown by an open triangle. (c) $I-V_S$ characteristic observed with photoirradiation. (d) Current versus laser irradiation intensity ($I-I_{irr}$) characteristic curve. The data were obtained with $\Delta H = 10$ V, $\Delta W = 2$ or 4 ms, and $d = 0.35$ mm. Photoirradiation was performed regularly at a repetition rate of 8.3 Hz with scanning I_{irr}. Arrows indicate the direction of the scanning of I_{irr} and current I change.

The switching between the LC and HC states can be also controlled by the irradiation light intensity. Figure 1d shows plots of current I observed under the light intensity I_{irr} scanning in two cases of ΔW. Irrespective of ΔW, LC-to-HC switching was observed at essentially the same value of I_{irr}, indicating that ΔW does not affect the critical value of I_{irr} required to trigger the photoinduced HC state. In the reverse scan of I_{irr}, the $I-I_{irr}$ curves depended on ΔW. With $\Delta W = 2$ ms, the crystal returns to the LC state at $I_{irr} =$

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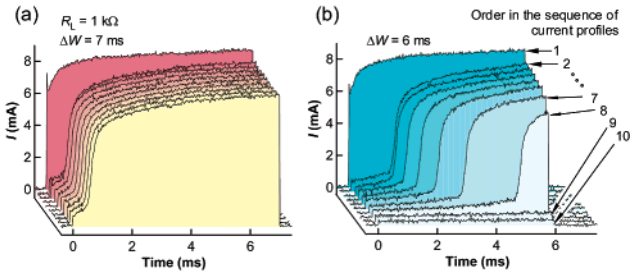

Figure 2. Sequences of current profiles obtained for 10 successively applied voltage pulses with 8.3 Hz with $R_L = 1$ kΩ; current profiles from 1 to 10. Photoirradiation was synchronized at the first voltage pulse only, i.e., in profile 1. Photoirradiation light was turned off for the second and the following pulses. Here, ΔH was 11 V, and ΔW was 7 ms (a) and 6 ms (b).

2×10^{-5} J/pulse, whereas the HC state is retained with $\Delta W = 4$ ms even after the irradiation was ceased. Such hysteresis observed in the $I-I_{irr}$ curves indicates a memory effect; the width of hysteresis increased with ΔW. The HC state can be thus sustained with appropriate voltage pulse widths (e.g., $\Delta W = 4$ ms) even without photoirradiation once the HC state is produced by a combination of pulsed voltage and photoirradiation. At small ΔW, while a bistability region is observed in the $I-I_{irr}$ curves, the crystal returns to the LC state without photoirradiation.

Figure 2 shows sequences of current profiles obtained for 10 successive voltage pulses, where photoirradiation was carried out at the first voltage pulse only. With $\Delta W = 7$ ms (Figure 2a), the HC state was obtained repeatedly without further irradiation. With $\Delta W = 6$ ms (Figure 2b), in contrast, the recovery to the HC state became weak, until the current completely disappeared after eight pulses. Thus when ΔW exceeds a certain threshold value (ΔW_T), the HC state produced by photoirradiation and applied voltage can be sustained without further photoirradiation. In other words, there is a memory effect in this phenomenon. Movie M1 in Supporting Information shows a real-time observation of this behavior on an oscilloscope. In the $\Delta W = 7$ ms run, the HC state was obtained continuously without further photoirradiation over more than 10 000 pulses without noticeable change, whereas the switching disappeared within approximately 1 s in the $\Delta W = 6$ ms run. The time required for the disappearance of the HC state depended on the experimental conditions; for example, in the case of $\Delta W < 1$ ms, the LC state appeared in the subsequent pulsed voltage immediately after stopping the photoirradiation.

A minimum voltage amplitude (ΔH_T) to produce the HC state without further photoirradiation was also identified (data not shown), and it was found that ΔH_T decreased with increasing ΔW. These observations indicate that the photoinduced HC state cannot be sustained without photoirradiation unless ΔW and ΔH exceed threshold values. It should be reiterated here that ΔW_T and ΔH_T are defined as the parameters required to recover the HC state without photoirradiation and differ from the critical values for the initial LC-to-HC switching. At small ΔW, a bistability region is observed in the $I-I_{irr}$ curves (Figure 1d), indicating that reversible photoswitching is possible between the HC and LC states. The behavior of the LC−HC switching can thus be controlled by a combination of I_{irr}, ΔW, and ΔH.

The memory effect in α-(BEDT-TTF)$_2$I$_3$ may be due to the presence of metastable states after the application of a pulsed voltage.[6] In general, high-current filaments running along the field direction are formed in the HC states.[3,7] It is likely that a high-current filament is formed in the HC state of α-(BEDT-TTF)$_2$I$_3$, giving rise to metastable states that cause the memory effect. This effect is thus intrinsically related to relaxation of the high-current filament. In such a scenario, the high-current filament might swell with increasing ΔW and ΔH and shrink during relaxation following the end of the pulsed voltage. The thickness of the remnant filament just before the application of a subsequent voltage pulse may then depend on the growth exhibited by the filament in the preceding voltage pulse, and the threshold-like behavior with respect to ΔW and ΔH may be related to the critical thickness of filament remaining immediately before the application of a subsequent voltage pulse. The filament in the HC state may be metallic in nature since the resistivity of the HC state, 0.01−0.04 Ω cm, calculated based on the optical depth (ca. 1 μm) of the crystal, is close to that of the metallic phase.[5] At the wavelength of the laser light (532 nm), there are two absorption bands ascribed to the intramolecular transitions of both BEDT-TTF and I_3^-.[8] The photoirradiation may enhance the field-induced swelling of the filament thickness via the photoinduced M−I phase transition.[1]

The current produced by the LC-to-HC switching may dissipate via a heating process in the sample, and such a thermal effect should be considered as a cause for the HC switching memory effect. However, as the repetition rate was low (8.3 Hz), the pulses of both voltage and photoirradiation were short (<10 ms), and the sample was maintained at low temperature (115 K); the temperature rise due to application of each voltage pulse is considered to have been completely quenched within the period of pulse repetition. Besides, the memory effect was also observed at a temperature as low as 79 K (data not shown), though ΔW_T and ΔH_T at this temperature were greater than those at 115 K. Such a heating effect is, therefore, not expected to be an essential factor in the present experiments. Electronic excitation plays an absolute role in the appearance of the photoinduced HC state that is sustainable and controllable by pulsed voltage.

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Supporting Information Available: The circuit diagram, the description of the experimental methods, and the real-time movie of the current switching. This material is available free of charge via the Internet at http://pubs.acs.org.

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