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Stable and reversible optoelectrical dual-mode data storage based on a ferrocenylspiropyran molecule

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A spiropyran molecule bonded with ferrocene (SPFc) was synthesized as data storage medium. Optical recording pattern was obtained through the reversible modulation of UV and visible light on the SPFc film, which exhibited good reversibility compared with the spiropyran without ferrocene moiety. In addition, the SPFc thin film also possessed reversible electrical switching property with high ON/OFF ratio, low threshold voltage, and long retention time. Accordingly, reliable, stable, and reversible nanoscale data storage was achieved on the SPFc thin film by scanning tunneling microscopy. The results will be significant to develop multifunctional molecule and reversible multimode data storage. © 2009 American Institute of Physics. [doi:10.1063/1.3259647]

Data storage is based on the ability to control and resume changes in a particular physical property of a material, such as, optical, electrical, or magnetic response. In recent years, single-mode data storage (e.g., optical and electrical storage) based on one of the physical channel has been widely investigated.¹⁻⁸ When two different physical channels of the material are simultaneously involved, multimode data storage could be expected, which would not only greatly increase the information density to satisfy future large-capacity storage, but also be promising to develop multifunctionality on a single device.⁹⁻¹¹ So far, however, there have been few reports on multimode data storage simultaneously in a single stable material. In 2002, Haddon and co-workers reported the magneto-opto-electronic bistability in a phenalenyl-based neutral radical by thermal control.¹⁰ However, the realization of practical information storage was not achieved.

Our initial study on multimode data storage began with a dual-responsive organic molecule, 1,1'-dicyano-2,2-(4-dimethylaminophenyl) ethylene (DDME), in which nanoscale electrical data memory and three-dimensional optical information storage were realized in the DDME thin film.⁹ However, the reversibility, an important factor for data storage, was not further studied. For this reason, and considering the enormous perspectives of the multimode data storage, the design and exploration of multifunctional molecules that can undergo different reversible transformation depending on the type of external stimulus has become an objective of current interest.

Photochromic spiropyran (SP) molecules have been attracting much attention because of their potential technological application in molecular switches and memories. The photochromism of SP molecules is due to the photocleavage of the spirobond under UV irradiation, creating a deeply col-

ored ring-opened merocyanine form, and can be converted back to the closed-ring form by visible light irradiation.¹² However, application of SP is hindered by the spontaneous thermal reversion process and photodegradation that destroys switchability of the molecule. Chemical modification has been proved an effective method to improve the fatigue resistance and thermal stability of the spiropyran molecule.¹³

With these considerations, herein, a spiropyran molecule bonded with ferrocene (SPFc) was designed and synthesized for data storage medium. Ferrocene (Fc), a kind of robust system with remarkable chemical as well as thermal stability,² can be expected to improve the reversibility and fatigue resistance of the spiropyran. More importantly, Fc has been widely accepted as a moderate electron donor and represented a target of opportunity in a context of conductance switching due to its sensitive redox activity.^{14,15} In this letter, optical recording pattern was obtained through the reversible modulation of UV and visible light on the SPFc film, which exhibited good reversibility compared with the spiropyran molecule without ferrocene moiety. In addition, the SPFc thin film also possessed reversible electrical switching behavior with high ON/OFF current ratio, low threshold voltage, and long retention time. Accordingly, reliable, stable, and reversible nanoscale data storage was achieved on the SPFc thin film by scanning tunneling microscopy (STM). This work represents a further step on developing multifunctional molecule and reversible multimode data storage.

Figure 1 represents the structure and photochemical

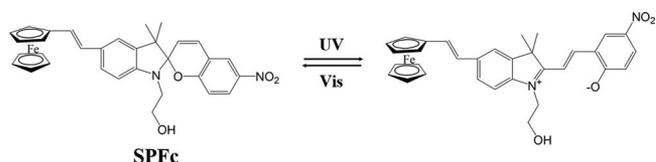


FIG. 1. The structure and photochemical isomerization of SPFc. Right: Photomerocyanine form.

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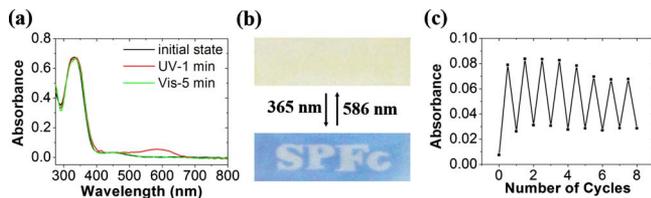


FIG. 2. (Color online) (a) Sequential spectral changes of SPFc in dichloromethane (10^{-5} M): initial state (black line), after irradiation with 365 nm light for 1 min (red line), and followed by irradiation with 586 nm light for 5 min (green line). (b) Optical recording pattern on SPFc-doped PMMA film (1:20 by weight). (c) Fatigue resistance of SPFc-PMMA film under the recording-erasing conditions. In each cycle, the film was irradiated for 5 min with UV light (365 nm) and the 10 min with visible light (586 nm). The absorbance at $\lambda=590$ nm was monitored.

isomerization of the SPFc molecule. It was synthesized by covalently bonding the parent spiropyran with a ferrocene moiety through ethylene. Like other SP molecules,¹² SPFc undergoes reversible photochromic reaction. Figure 2(a) shows the absorption spectra of SPFc in dichloromethane (10^{-5} M). Before irradiation, the absorption spectrum exhibits a prominent band with λ_{\max} at 334 nm assigned to π - π^* transition. Another weaker band at higher wavelength (about 456 nm) is attributed to a metal-to-ligand charge-transfer (MLCT) band.¹⁴ Irradiation of the weak-orange solution of SPFc with UV light ($\lambda=365$ nm) gives a blue solution. This process results in the formation of an extended π -conjugation system and the appearance of an absorption band ($\lambda_{\max}=590$ nm) in the visible region. The spectrum can come back to the initial state by irradiation with 586 nm light and the blue solution reversed to the initial color. Similar isomerization process of the present spiropyran also can occur on the SPFc-poly(methyl methacrylate) (PMMA) film (Fig. S1).²² Accordingly, optical recording pattern is obtained in SPFc-doped PMMA film (1:20 by weight). As shown in Fig. 2(b), the letters “SPFc” are formed with a photomask after irradiation with 365 nm UV light. The color can be reversed by irradiation with 586 nm visible light. For practical application, high fatigue resistance is indispensable to achieve the repeated “recording and erasing” of optical information. The robustness of the present SPFc in neat film is further examined by repeatedly performing the cycles. It can be seen from Fig. 2(c) that the reversible changes in the recorded image can be repeated at least eight times. As a comparison, the reversibility of a similar spiropyran molecule without ferrocene moiety is also investigated. However, it shows a poor fatigue resistance with a great attenuation in absorption intensity (570 nm) just after four cycles (Fig. S2).²² It can be concluded that the incorporation of the ferrocene moiety improves the reversibility of the spiropyran effectively. The increased fatigue resistance of the SPFc may be a result of the electronic interaction between SP and ferrocene moiety.²

The macroscopic I - V characteristics of the SPFc thin film deposited on indium tin oxide-coated glass are also investigated. As can be seen from Fig. 3(a), when a forward voltage is applied, the thin film exhibits its high-resistance state (OFF state, curve I). As the voltage approaches +1.25 V, a sharp increase in the current takes place, indicating the thin film switches on to its low-resistance state (ON state). After the transition, the thin film remains in the ON-state during the second sweep from 0 to +1.4 V (curve II).

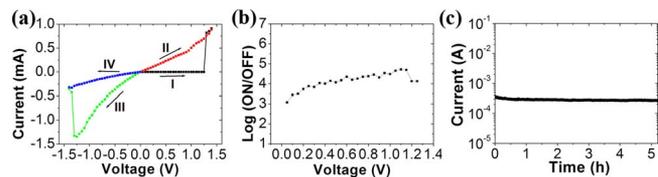


FIG. 3. (Color online) (a) Macroscopic I - V characteristics of the thin film, exhibiting the conductance transition from the high-(OFF) state to low-resistance state in curve I, the memory effect of the low-resistance state (ON state) in curve II, and the recovery of the high-resistance state with the application of a reverse voltage scan in curves III and IV, respectively. (b) The logarithm of the ON and OFF state current ratio as a function of the applied voltage. (c) Long-term response of the ON state under an electric field of 0.5 V.

The low-resistance state can be returned to the high-resistance state as the voltage approaches -1.25 V when sweeping from 0 to -1.4 V (curve III). Then it shows a high-resistance state, as indicated by a followed reverse scan (curve IV). The OFF state can be switched back to the high-conductivity state by applying a positive bias higher than the threshold, resulting in an OFF-ON-OFF-ON reversible trait. The maximum ON/OFF ratio is about 10^5 , and that for all measured devices are typically greater than 10^3 [Fig. 3(b)]. Such a high ON/OFF current ratio is crucial for the memory device to realize high-resolution and low error rate data storage.^{16,17} We also measure the retention time of the ON state. The SPFc thin film is found to retain the ON state without degradation under 0.5 V bias during more than 5 h continuous operation [Fig. 3(c)], which indicates the non-volatile switching ability of the devices. Furthermore, it is worthwhile to emphasize that the absolute value of threshold voltages for both ON and OFF states are lower than 2 V for all devices we have measured. The low operating voltage is desirable for low-power memory devices.^{5,15}

Based on the electrical bistability of the SPFc molecule, nanoscale electrical information storage experiments using STM are performed. In the experiments, the SPFc thin film is deposited on highly ordered pyrolytic graphite. To write data, suitable voltage pulses are applied between STM tip and substrate. Figure 4(a) shows a typical recording pattern on the film by STM and the average size of the marks is about 4 nm in diameter. Studies show that when the voltage pulse applied is above +3.2 V, the recorded dots can be easily

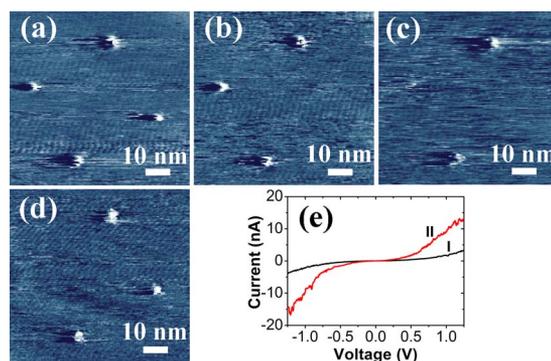


FIG. 4. (Color online) STM images of typical information dots pattern and the corresponding I - V curves. (a) Recording pattern composed of four information dots: pulsed voltage, +3.2 V; 4 ms. [(b) and (c)] Erasing one and two dots, respectively: pulsed voltage, -2.96 V; 4 ms. (d) Rewriting one information dot: pulsed voltage, +3.2 V; 4 ms. (e) Typical STM I - V curves in the unrecorded (curve I) and recorded region (curve II).

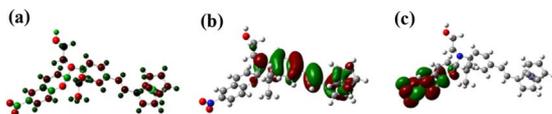


FIG. 5. (Color online) (a) Charge density distribution of SPFc. (b) HOMO and (c) LUMO of the SPFc molecule.

formed. Furthermore, the formed marks are very stable and no obvious changes could be observed during 8 h continuous scanning process. Further studies show that when a reverse polar voltage pulse higher than an absolute value of 2.96 V is applied to the recorded region, the marks could be erased. The images in Figs. 4(b) and 4(c) indicate, respectively, the situation after one and two information dots are erased. By applying a positive pulsed voltage on the same area of thin film again, a dot can be rewritten on it [Fig. 4(d)]. With alternating exposure of the film to positive and negative voltages beyond the threshold value, write–read–erase cycles are demonstrated in the same region. Typical current–voltage (*I*-*V*) characteristics of the SPFc thin film before and after recording [Fig. 4(e)] reveal that the electrical resistance of the recorded region is much lower than that of the unrecorded region, which means that a conductance transition occurs after the voltage pulse and leads to bright dots observed by STM on the recorded region.

To elucidate the electrical switching mechanism, UV-vis spectra of a SPFc thin film in two different electrically stable states are then compared (Fig. S3).²² The results show clearly that a slight redshift and intensification of the MLCT absorption band of the SPFc thin film have occurred owing to the electronic transition. The redshift suggests an increase in the polarity of the SPFc molecule as a result of the intensive interaction among molecules, especially intermolecular charge-transfer.^{18,19}

For further understanding the electrical recording mechanism, quantum chemical calculations are carried out by using the hybrid Hartree–Fock/density functional theory at B3LYP/6-31G* level.^{20,21} Figure 5 shows the charge-density distributions, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) of the SPFc molecule, respectively. The calculations demonstrate that the HOMO is almost entirely located on the ferrocene moiety, while the LUMO is almost entirely located on the nitryl moiety (NO₂). The HOMO-LUMO gap is 2.7 eV. These results indicate that the HOMO of the molecule might interact with the LUMO of its neighboring molecule for charge-transfer. When the right voltage pulse is applied on the thin film, the external electric field can give the molecule enough energy to make the charge-transfer from the donor (Fc) to the acceptor (NO₂) between the adjacent molecules. This would lead to an increased number of the carriers and a delocalized state, resulting in a higher conductivity. Meantime, the delocalized state can be stably retained due to the unique stable redox property of ferrocene, where ferrocenium can maintain its oxidized state.¹⁵ Ferrocenium can reduce back to ferrocene moiety only when a sufficiently large reverse voltage was applied. This could be further supported by X-ray photoelectron spectroscopy (XPS), in which ferrocenium was detected by XPS after the

application of an electric field with a voltage of 3 V on a ferrocene-containing SPFc thin film (Fig. S4).²²

In summary, a multiresponsive ferrocenylspiropyran molecule was designed and synthesized to achieve reversible multimode data storage. The incorporation of ferrocene into the spiropyran framework not only can improve the reversibility and fatigue resistance of optical data storage, but also contribute stable, rewritable nanoscale electrical data storage. This work would be useful in designing multifunctional switchable molecular systems that can be used as multimode information storage devices.

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