High-Density Data Recording in an Optoelectrical Dual-Responsive Thin Film

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High-density data storage has been receiving much attention with the ever-increasing amount of stored data and the continuous miniaturization of optoelectronic devices.[1–3] To increase the storage density, various recording schemes have been explored;[4–7] these include scanning tunneling microscopy (STM) for achieving maximal area density[2] and two-photon excitation (TPE) for recording information in multiple layers; these techniques are considered as two of the most attractive.[1] Meanwhile, the development of novel recording media is also a critical factor to achieve high-density storage. Organic materials, due to their good stimuli-responsive properties, versatility in molecular design, and low cost, have been proved to be promising candidates.[8–10]

In past decades, great progress has been made using different organic media both in nanoscale electrical data recording and in high-density optical information storage, which utilize their electrical bistability[3, 11–14] and light characteristics such as refractive index,[15] fluorescence properties,[16] and absorption spectrum.[17] However, most of these achievements were based on the single-mode (photon or charge) modulation of the recording materials. For practical application in high-density data storage and also to enhance the multifunctionality of optoelectronic devices, media that would permit the manipulation of optical and electrical signals with alternative operating modes such as multimode are more desirable.[18, 19] Although it has been proposed that multiple physical channels, such as optical, electrical, and magnetic schemes, could be utilized for recording and transmitting information using a multifunctional material,[20] so far there have been few reports on simultaneously achieving optical and electrical recordings in a stable material. The main problems may be the difficulty in finding a suitable multiresponse medium,[21] and amplifying the effects of molecular multiresponse in the solid state.[22]

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Herein, we present optoelectrical dual-responsive recording with a stable organic molecule, 1,1-dicyano-2-(4-dimethylaminophenyl)ethylene (DDME), which is a conjugated system with a strong electron donor group (—N(CH$_3$)$_2$) and two electron acceptor groups (—CN). Its molecular structure is shown in Scheme 1. Based on our previous results,[12,13] this molecule is a
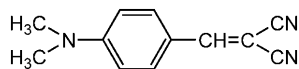
Scheme 1. Molecular structure of DDME.

typical material possessing good electrical bistability, and can be used in nanoscale data recording by STM. Furthermore, this material also shows intense absorption from 400 to 450 nm, which is highly suited to the recording wavelengths of the blue laser (GaN) and femtosecond two-photon recording at 800 nm to increase the data density and readout resolution.[1,23] Accordingly, nanoscale electrical data recording by STM and three-dimensional optical information storage based on two-photon excitation were achieved in the DDME thin films. Charge transfer and the conformational change induced by an electric field or light were attributed to the recording mechanism. The ability to achieve information storage in the dual mode suggests that the recording medium is not only a promising candidate for data storage, but also of important potential in electro-optical modulation, image processing, two-photon microfabrication, and other nonlinear optical applications.[24]

DDME was synthesized according to the literature.[24a,25] Its thin films used in electrical information storage were deposited on a freshly cleaved, highly oriented pyrolytic graphite (HOPG) substrate by the vacuum deposition method. By applying suitable pulsed voltages between the STM tip and the HOPG substrate, a 2×2 matrix pattern (Figure 1a) was obtained; the average size of the recording dots was about 6 nm in diameter, which corresponds to a potential storage density of about 10^{12} bit cm^{-2}. Typical current–voltage (I–V) characteristics of the DDME thin film before and after recording (Figure 1b) reveal that the electrical resistance of the recorded region is much
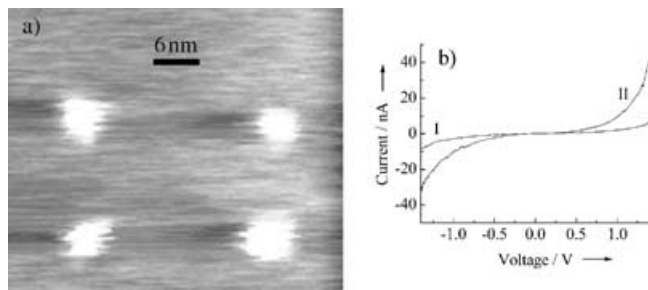
lower than that of the unrecorded region, which means that a conductance transition occurs after the voltage pulse and leads to bright dots observed by STM on the recorded region. In our experiments, the recorded dots could be scanned continuously without discernible changes for several hours, which indicates the high stability of the pattern under ambient conditions.

To elucidate the electrical information recording mechanism, the macroscopic I–V characteristics of the DDME thin film deposited on indium tin oxide (ITO)-coated glass were measured. The voltage was scanned in steps of 0.02 V from 0.0 to 2.5 V. Figure 2a shows the I–V characteristics of the first and second bias scans. It can be seen that before the first bias scan, the I–V curve of the film shows an insulating behavior. When the voltage is increased to 2.02 V, the DDME film is switched to a conducting state with a clear conductance transition judged
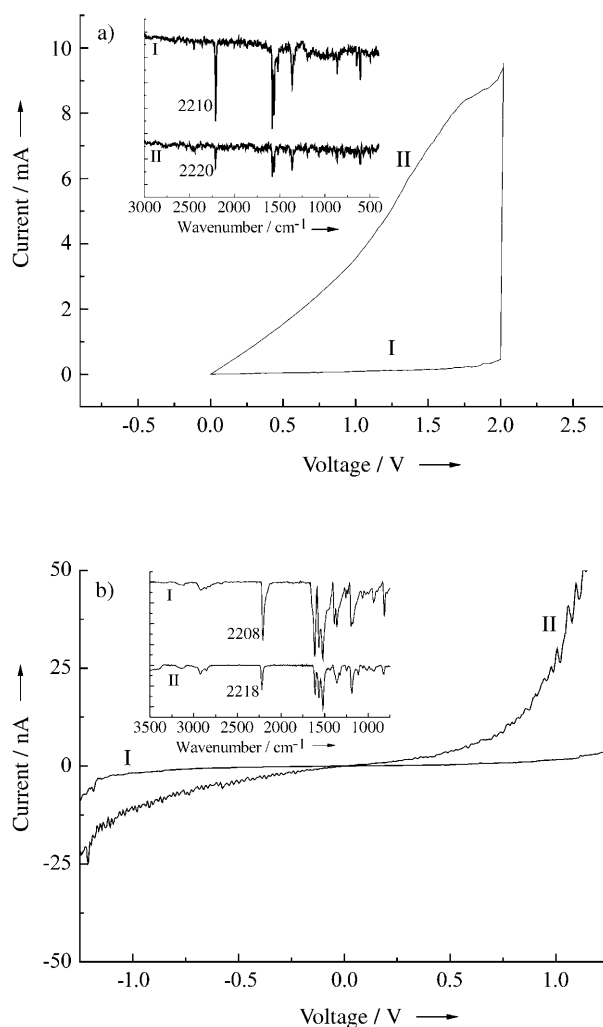
Figure 2. a) Macroscopic I–V characteristics of a DDME thin film. Curve I is related to the high-resistance state by the first bias scan and curve II is related to the low-resistance state by the second bias scan after transition. The threshold voltage is 2.02 V. The inset shows the corresponding Raman spectra. b) Typical local I–V curves of the DDME thin film before (I) and after (II) exposure to UV light at 400 nm. The curves were obtained by scanning tunneling spectroscopy (STS). The inset shows the FTIR spectra of a DDME thin film before (I) and after (II) exposure to UV light.

Figure 1. a) STM image of a 2×2 recording pattern in a DDME thin film. The average size of the mark is 6 nm. The scanning conditions are: $V_{bias} = 0.404$ V, $I_{ref} = 0.04$ nA; voltage pulse 3.1 V for 10 ms. b) Local I–V curves of the regions before and after recording. Curves I and II are related to the unrecorded and recorded regions, respectively.

from the *I–V* curve, which indicates that the material has electrical bistability. It was confirmed that the state transition from high to low resistance corresponds to a 10 cm^{-1} shift of the —C≡N absorption peak in the Raman spectrum,[13] which could be ascribed to the enhanced polarization of DDME molecules induced by the applied pulse voltage (Figure 2a). The —C≡N group has a higher vibration frequency when the DDME is in its low-resistance state. Interestingly, upon irradiation, the same 10 cm^{-1} blue shift of the —C≡N absorption band is also observed without discernible change in the absorption peaks of other groups of the DDME molecule, as evidenced from the FTIR spectra (Figure 2b). This finding indicates that the same structural change occurred as that induced by an electric field, and thus optoelectrical dual-responsive recording becomes possible. This could be further proved from a change of local *I–V* properties induced by irradiation (Figure 2b). It can be seen that the film has been switched from the original high-resistance state to a low-resistance state upon illumination at 400 nm; the same transition behavior can also be induced by an electric field as mentioned above (Figure 2a).

Figure 3 shows the absorption spectra of DDME in chloroform (10^{-5} M) and the fluorescence spectra of DDME dispersed in poly(methyl methacrylate) (PMMA) films (1:20 by weight). Before irradiation, the absorption spectrum exhibits two bands with λ_{max} at 269 and 430 nm, which correspond to the π–π* transition of the phenyl ring and the whole conjugated system of the molecule, respectively. Upon irradiation at 400 nm, the absorption band at 430 nm disappears, which indicates that a structural change has occurred. It is also shown in Figure 3a that there is no absorption at 800 nm, as the molecule absorbed synchronously two 800-nm laser photons (confirmed by the data in the Supporting Information). A large reduction of the fluorescence intensity was observed after 15 min of two-photon illumination at 800 nm (Figure 3b). The change in the fluorescence intensity could be explored to write and read data for optical information storage.

To demonstrate the possibility of using DDME for three-dimensional optical recording, an experiment was performed by two-photon excitation utilizing DDME-doped PMMA film (DDME/PMMA = 1:20 by weight). The film was coated with a thickness of about 100 μm onto a glass microscope slide under ambient conditions. When the written areas in the film were exposed to a "reading" laser beam, the fluorescence became much weaker. Compared with the nonwritten areas, the low-fluorescence signals could be easily distinguished as bits "0" or "1". To view the recording images clearly, we processed the pattern as dark background and bright spots, where the bright spots represent the decreased fluorescence signal. Figure 4a shows typical patterns for data recording in a DDME-doped PMMA thin film. The letters "I, C, C, A, S" are in five layers of the same film at different depths. A vertical section across the top of the letters is shown in Figure 4b. The diameter of each dot is about 1.2 μm. The separation between two adjacent layers is about 10 μm, and the distance between two adjacent dots in each layer is about 4.5 μm. Each dot was written within 35 ms at an average irradiation intensity of about 110 kW cm^{-2} with an 800-nm, 80-MHz, 80-fs laser. The data were read with a
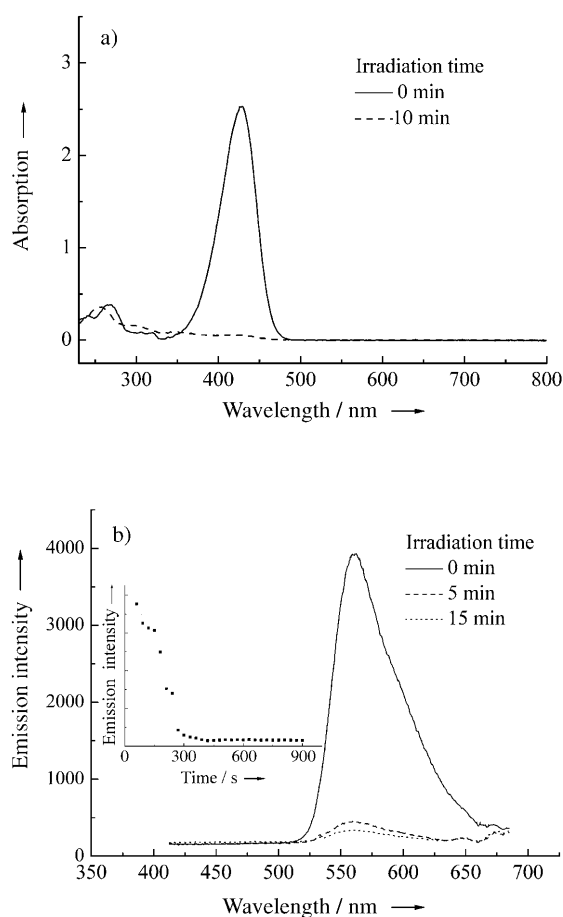

Figure 3. a) Absorption spectra of DDME in chloroform (10^{-5} M) before (——) and after (-----) irradiation with UV light for 10 min. b) Fluorescence spectra as a function of time for the two-photon-induced change of the DDME (dispersed in PMMA thin film, 1:20 by weight) using an 800-nm femtosecond pump beam at an irradiation intensity of 560 W cm^{-2}; the inset shows the change in the intensity of the fluorescence peak with time under the same conditions.
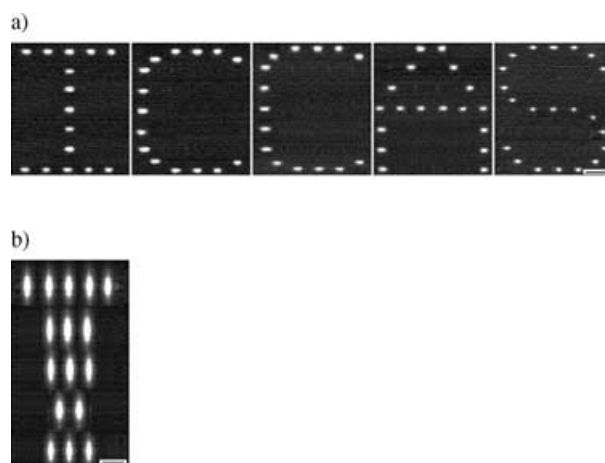

Figure 4. a) Letters "I, C, C, A, S" written by two-photon excitation in five layers of a DDME-doped PMMA thin film. b) A vertical cross-section across the top of the letters. The separation between two adjacent layers is about 10 μm, the diameter of each dot is about 1.2 μm, and the interval between two neighboring dots is about 4.5 μm. Scale bars are 5 μm. To view the recording images clearly, the pattern was processed with reversal contrast, where the bright spots represent the decreased fluorescence signal (recording).

reading intensity of about 8 µW cm^{-2} from a 400-nm laser with an average signal-to-noise ratio (the intensity ratio of the fluorescence to background) up to 24.5. The reading power is far lower than the threshold, and the pattern was illuminated continuously at this power longer than 3 h with no discernible change in fluorescence (see the Supporting Information).

Based on the above experimental facts, the following mechanism for the optoelectrical dual-responsive recording was proposed. As described in Scheme 2, the DDME molecule is initial-
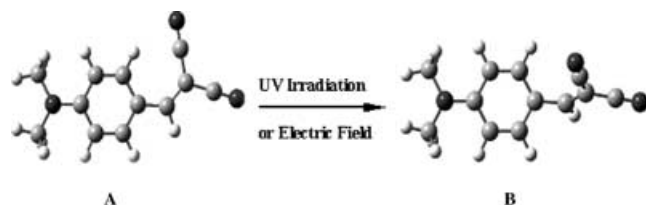
Scheme 2. The recording mechanism of the DDME molecule by conformational change.

ly in its coplanar form (conformation **A**). Once the molecule is excited by an external field (light or electric field), charge transfer could efficiently happen and result in twisting of the initial coplanar molecule structure.[26] As regards the stability of the recording pattern and the contributions of the groups to the whole conjugated system, it is suggested that the twisting of the dicyanoethylene part rather than the −N(CH$_3$)$_2$ group of the DDME molecule is responsible for the disappearance of the 430-nm absorption band after irradiation, which corresponds to conformation **B**. Consequently, the overall conjugated structure of the molecule is distorted, and such structural change accompanies the charge separation between the donor and the acceptor groups of the molecule,[26] which enhances the polarity of the molecule. In detail, during electrical recording, a conformation change with a complete charge separation induced by an electric field could reduce the resistance of the DDME thin film, and the data can be recorded by STM based on the difference of the conducting behaviors.[12] As for optical recording, the photoinduced change of the conjugated structure of the molecule causes the disappearance of the band at 430 nm in the absorption spectra and the large decrease of the fluorescence intensity, and thus the data can be read based on such contrasting variance between the original high-fluorescence state and the decreased fluorescence state. It can be concluded that charge transfer and the conformational change enable the molecule to simultaneously possess optical and electrical responses, which means that the data can be recorded and read optically and/or electrically.

In summary, optoelectrical dual-responsive recording within a DDME thin film has been investigated, in which nanometer-scale electrical information recording and three-dimensional optical data storage are successfully achieved by STM and TPE, respectively. An analysis of the recording mechanism suggests that both the conductance transition and the optical property variance arise from charge transfer and the conformational change induced by an electric field and/or light. The fact that the same conformational change can be induced by different stimuli is particularly important for intelligent molecule design, and such dual-responsive thin films may have significant applications in novel recording technology and multifunctional optoelectronic devices.

Experimental Section

DDME thin films (thickness ca. 100 nm) for electrical information storage were obtained on HOPG substrates by the vacuum deposition method. The base vacuum of the deposition system was about 7×10^{-4} Pa, and the organic material was heated to 80 °C in a crucible in the vacuum chamber. STM experiments were performed with a Solver P47 instrument (NT-MDT Co.) in constant high mode, using tips made of tungsten wires by electrochemical etching. The recording marks were obtained by applying voltage pulses of 3.1 V for 10 ms between the STM tip and HOPG substrate, and the local I–V curves were obtained by scanning tunneling spectroscopy (STS). The scanning conditions were $V_{bias} = 0.404$ V and $I_{ref} = 0.04$ nA. The macroscopic I–V characteristics were measured by scanning the voltage from 0 to 2.5 V using a Keithley 4200 semiconductor system.

To achieve three-dimensional data storage by two-photon excitation, the excitation beam was generated by a homemade mode-locked Ti:sapphire laser oscillator pumped from a Nd:YVO$_4$ laser (Verdi-5, Coherent) at 532 nm. This system produced a train of femtosecond laser pulses (800 nm, 80 fs) at a repetition rate of 80 MHz. For data writing, the femtosecond laser was focused into a DDME-doped PMMA film (Acros Organics) through a beam expender and an objective. To prepare the DDME-doped PMMA film for data storage, the DDME and PMMA were mixed together with a weight ratio of about 1:20 in chloroform, and a thin film was coated with a thickness of about 100 µm onto a microscope slide under ambient conditions. A three-dimensional stage driven by a piezoelectric lead zirconate titanate (PZT) actuator and a mechanical shutter were controlled by computer. A confocal laser scanning fluorescence microscope consisting of an objective, dichroic mirror, pinhole, photomultiplier tube (PMT), and scanning stage was used for reading the data. An appropriate dichroic mirror was switched, and a 400-nm laser was introduced instead of the 800-nm femtosecond laser. A 40× objective (NA 0.65) was used for recording and reading. A suitable bandpass filter was placed in front of the PMT to select the fluorescence and block the laser scattering and other stray light from the detector during reading. The optical characteristics of DDME dispersed in PMMA films were measured using a Hitachi U-4100 UV/Vis spectrometer and a Hitachi F-4500 fluorescence spectrophotometer.

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