

A Triphenylamine-Containing Donor–Acceptor Molecule for Stable, Reversible, Ultrahigh Density Data Storage

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In the past few years, there has been increasing interest in the application of organic functional molecules for next generation information storage and future optoelectronic devices.¹ With the development of the scanning probe microscopy (SPM), ultrahigh density data storage based on SPM technology has made great progress in recent years.² Among these studies, organic functional materials have been reported extensively.^{2b–c}

Despite the remarkable research achievement on SPM-based storage, there are important limitations that need to be overcome. From the practical view, future developments will aim at decreasing the error rate, improving the stability, etc.³ With these motivations, scientists are trying to develop SPM-based storage from both technical and material aspects, of which the improvement of stability and ON/OFF ratio between the two states of the thin film would be one of the most important routes. Among the organic recording materials being extensively studied, donor–acceptor (D–A) type charge-transfer complex and compounds are considered to be very promising materials for future information storage because of the electronic switching property induced by reversible intermolecular charge transfer.⁴

In the previous studies, we realized nanometer scale data storage on thin films using scanning tunneling microscopy (STM), where stable storage was achieved by improving of the quality of film.⁵ In this work, a new D–A molecule, 2-((Z)-2-(4-diphenylamino)benzylidene)-1,2-dihydro-1-oxoindene-3-ylidene) malononitrile (BDOYM, Figure 1a), with a triphenylamine unit as the electron donor and two cyanovinyl groups as the electron acceptor, has been designed and synthesized. The triphenylamine unit, a large conjugated tertiary amine system, can not only act as a strong electron donor in its initial state but also stabilize the charge-transferred state. Furthermore, because of the good hole-transporting ability of the triphenylamine group,⁶ it can be expected to modify the electrical conductivity of the material effectively. In our studies, two distinctive conductivity states have been observed on BDOYM films, and the ON/OFF current ratio was determined to attain 10⁴. Stable, reliable, reversible data storage has been demonstrated using STM. Thus, with this new molecule, we have further developed STM-based storage by improving the stability and ON/OFF ratio of the thin film. Furthermore, because of the difference of spectra before and after the action of an electric field, the information written on BDOYM thin film with an electrical method can be read out using an optical one. This will be a substantial step forward toward the development of multimode data storage.

The typical UV–vis spectrum of BDOYM (10^{−5} M solution in cyclohexane) displays an intramolecular charge transfer (CT) transition at 548 nm, as shown in Figure 1b. In the UV–vis spectra of the film on ITO substrate prepared by vacuum vapor deposition method, the CT transition shows an obvious red-shift compared with that of the solution state. This red-shift between the λ_{max} (at 573 nm) of thin film and the λ_{max} (at 548 nm) of solution might be

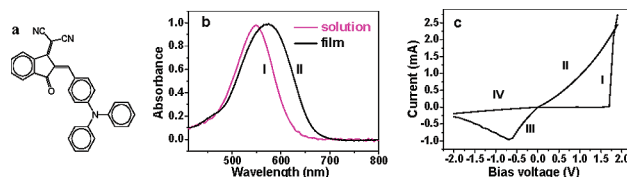


Figure 1. (a) Structure of BDOYM; (b) UV–vis spectra of BDOYM (I, in cyclohexane solution; II, film on ITO substrate); and (c) macroscopic I – V characteristics of the film.

related with the formation of molecular aggregates and/or increased polarizability of the film.⁷

A thin film (with the thickness about 50 nm) was prepared on ITO coated glass for measurement of electrical properties. The sweep directions and typical current–voltage (I – V) characteristics are shown in Figure 1c. When a forward voltage was applied, the thin film exhibited its low conducting state (OFF-state, curve I). As the voltage approached +1.7 V, a sharp increase in the current took place, indicating the thin film switches on to its high conducting state (ON-state). After the transition, the thin film remained in the ON-state during the second sweep from 0 to +2.0 V (curve II), where the current arrived at 4 orders higher than that of the thin film before switching. Such a high ON/OFF current ratio is crucial for the memory device to realize high-resolution and low error rate data storage.⁸ As known, the charge mobility of organic materials is often determined by an electron or hole transport process, in which an electron or hole is transferred from one molecule to the neighboring one.⁹ Triphenylamine groups may have played an important role in this case.⁶ The thin film switched off to its low conducting OFF-state as the voltage approached −0.7 V when sweeping from 0 to −2.0 V (curve III). Then it showed a low conducting state, as indicated by a followed reverse scan (curve IV). In our studies, the ON-state had been proven to remain stable for more than two weeks after the external electric field was removed. The electrical switching behavior exhibited by the thin film made it a promising candidate for application in electric-based erasable data storage.

Molecules with D–A structure are a kind of important materials for data storage owing to existing two stable conducting states. At the initial state, the thin film shows low conductivity. Upon application of an external field, the intermolecular CT state would be easily accessible and the conductivity of the thin film could be greatly enhanced, which could be proved through the analyses of the two states.¹⁰ In our electrical investigations of the thin film, a color transition from purple to orange was observed when the applied voltage was higher than the threshold value, and the relevant changes in UV–vis (Figure 2) and IR (Figure S1) spectra occurred. As can be seen from Figure 2, after the action of an electric field, the UV–vis spectra exhibits a peak centered at 448 nm (Figure 2b, Peak 2), which indicates the intense interaction among molecules, especially intermolecular charge transfer.^{4c,10,11} This would lead to an increased number of the carriers and a delocalized

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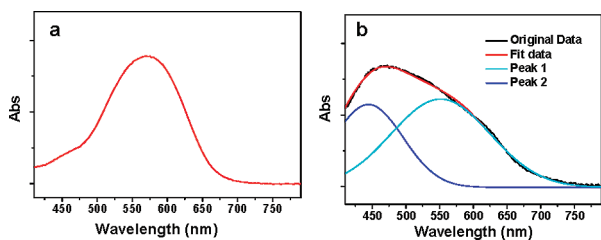


Figure 2. The UV-vis spectra of BDOYM thin film before (a) and after (b) application an electrical field.

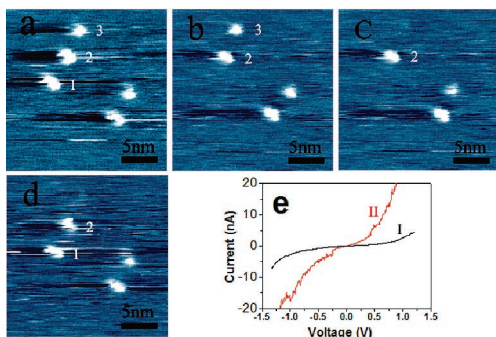


Figure 3. STM images of typical information dots pattern and the corresponding $I-V$ curves. (a) Recording pattern composed of five information dots: pulsed voltage, +2.3 V; 3.0 ms. (b, c) Erasing the first and the second dots at position 1 and 3, respectively: pulsed voltage, -1.4 V; 3.0 ms. (d) Rewriting one information dot at position 1: pulsed voltage, +2.3 V; 3.0 ms. (e) Typical STM $I-V$ curves in the unrecorded (curve I) and recorded region (curve II).

state, resulting in a higher conductivity. The spectrum can come back to the initial state after the application of a negative bias (Figure S3). The UV-vis and IR spectral changes of the BDOYM thin film before and after application of an electrical field not only indicated that the charge-transfer had happened, but also implied that the information written by the electrical method might be readout by the optical method.

Electrical bistability is an essential prerequisite for STM-based information storage. To write data, suitable voltage pulses were applied between the STM tip and substrate. In our experiments, the BDOYM film was deposited on highly ordered pyrolytic graphite (HOPG), and the amplitude and width of voltage pulses were varied to study the dependence of the information dots on these parameters. Studies showed that when the voltage pulse applied was above the threshold (2.3 V), the error rate was very low, and the probability of the dot formation was almost 100%. Figure 3a shows a typical recording pattern on the thin film by STM and the average size of the marks is about 2.5 nm in diameter. In our experiment, the recorded marks were very stable and no obvious changes could be observed during a 24 h continuous scanning process. Further experiments indicated that when a reverse-polarity voltage pulse above 1.4 V was applied to the recorded region, the recorded marks could be substantially erased (Figure 3b,c), and a new data mark can be rewritten on the erased region of the thin film by applying another positive pulsed voltage (Figure 3d). With alternating electric field treatments with positive and negative voltages beyond the threshold value, write-read-erase cycles have been demonstrated in the same area.

The local $I-V$ characteristics of the thin film were compared between the recorded and the unrecorded regions to obtain an insight into the mechanism for the formation of the information dots. As

can be seen in Figure 3e, the conductivity of unrecorded regions on the film is in a high resistance state (curve I), while it is in a low resistance state at the recorded regions (curve II). The comparisons presented herein indicated that the applied voltage pulse induced a conversion of the conductance of the thin film from a high resistance to a low one, which is in accordance with the macroscopic $I-V$ characteristics. That is to say, the applied voltage pulses have induced charge transfer among the adjacent molecules, leading to the switching of conductivity of the thin film. This could be further supported by theoretical studies (Figure S2).

In summary, a triphenylamine-containing donor-acceptor molecule was designed and synthesized to improve the intrinsic storage performance. The thin film showed excellent bistable electronic switching behavior with a high ON/OFF current ratio. Reversible data storage was successfully demonstrated on the thin film by STM. Mechanism analysis indicated that the recording dot was due to the intermolecular charge transfer induced by electric field. This research has made a further step toward realizing stable, reliable, and reversible electric data storage.

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Supporting Information Available: Experimental details, theoretical calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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