

Optoelectric Charge Trapping/Detrapping in Thin Solid Films of Organic Azo Dyes: Application of Scanning Tunneling Microscopic Tip Contact to Photoconductive Films for Data Storage

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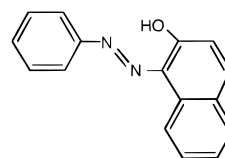
Received August 21, 1997. Revised Manuscript Received January 12, 1998

Charge trapping/detrapping within thin solid films of the organic photoconductive materials Sudan I and Disperse Red I was investigated. Charge trapping took place under an external bias upon irradiation. Trapped charges could be stored for long times in the dark under open-circuit or short-circuit conditions and could be removed (detrapped) with irradiation at short-circuit. These substances show good photoconductivity and high dark resistance and are promising for electrooptical information storage. A sharp tip of a scanning tunneling microscope was used as a liftable electrode for the optoelectric characterization. Such a point contact with the tip/organic thin film/ITO configuration provided for more reproducible measurements, since they were essentially unaffected by factors such as structural defects, isolated impurity domains (e.g., dust), nonuniform thickness, and point electrical shorts that frequently perturb measurements with sandwich thin-film cells of larger area. Moreover, the tip can easily penetrate into the film to obtain thickness-dependent information, which is often time-consuming to obtain with conventional thin-layer cells. The fact that charge can be trapped and detrapped in a highly localized area under a sharp tip within the organic thin films demonstrates their potential application as an alternative memory media for high-density data storage (as charge). Information could be written, read, and erased by controlling irradiation and electrical bias as previously reported for zinc octakis(doceoxyethyl)-porphyrin thin solid films.

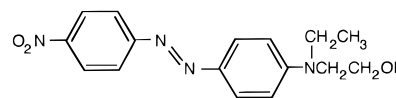
Introduction

We describe here charge trapping and detrapping in organic photoconductive insulators under irradiation as studied with a sharp tip contact in a scanning tunneling microscope (STM). These results extend our earlier reports^{1–4} of similar phenomena in a solid film of zinc octakis(doceoxyethyl)porphyrin (ZnODEP), which forms a liquid crystal phase at high temperature.⁵ We have suggested a possible application of this effect to high-resolution information storage in a rewritable electro-optical medium. The compounds employed here were the azo dyes: 1-phenylazo-2-naphthol (Sudan I) and 2-[ethyl[4-[(4-nitrophenyl)azo]phenyl]amino]ethanol (Disperse Red I). Although these compounds differ considerably in their chemical structure, we show here that they have similar electrooptical characteristics, i.e., good photoconductivity, high dark resistance, and the capability of trapping electrical charge. Upon irradiation,

information can be stored as trapped charge, read, and erased in the thin layers of photoconductive materials under an appropriate bias.



Sudan I



Disperse Red 1

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Organic molecular crystals are one of the most important and challenging subjects in contemporary chemistry of materials.^{6–8} Their physical and chemical properties are substantially different from those of other solid-state substances and therefore find many new

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applications, especially in high-technology areas.⁹ There are also wide possibilities for manipulating these properties by varying the electronic and geometric structure of the constituent molecules using synthetic skills^{6,7} to control rationally molecular structure and packing for specific properties. Significant progress has been made recently in many interesting areas related to organic molecular crystals. For example, the stacking of pre-designed flat molecules of porphyrins,¹² phthalocyanines,¹³ and triphenylene¹⁴ to form quasi one-dimensional molecular crystals allows a degree of rational control of their bulk electric and optoelectric properties. Large area (up to several square millimeters) organic single-crystal thin films (\sim micrometer) of porphyrin,¹⁵ 1-phenylazo-2-naphthol (Sudan I),¹⁶ and 1,4-di-*p*-toluidinoanthraquinone (Solvent Green 3)¹⁷ have been successfully grown, making it possible to characterize optically and electrically a molecular crystal at the same spot at the same time. Large orientation-dependent photo/dark conductivity and optical absorption effects, including orientation effects of color, have been observed.^{15–17} High-resolution nanosecond charge trapping, which is promising for ultrahigh-density information storage, has been discovered in porphyrin photoconductive thin films.^{1–4} This paper extends these studies to reversible charge trapping and detrapping in two different dye molecular crystals using the sharp tip of an STM as one electrical contact.

The basic principle of charge trapping as a means for information storage within photoconductive media, described in earlier papers,^{1–4} is briefly illustrated in Figure 1. Upon irradiation, electron–hole pairs are generated within the medium (Figure 1a) and are subsequently separated by the electric field applied to the photoconductive layer (Figure 1b). Since the dark resistivity of the medium is high, these separated charges are frozen by switching off the light. The trapped charge remains stored in the dark under open-circuit or short-circuit conditions (Figure 1c,d). In the latter case, a few electrons and holes at the surface may recombine through the external wire. Most charges, however, remain trapped and represent the information stored within the photoconductive film. The written data (charge) can then be read out, for example, as a photodischarge current by irradiation of the sandwich cell with a read beam under short-circuit conditions (Figure 1e).

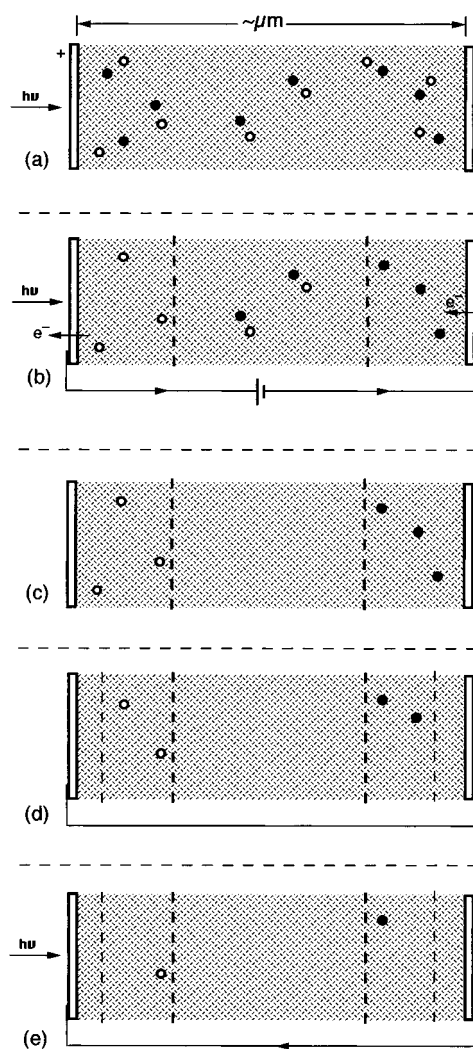


Figure 1. Schematic illustration of charge trapping within photoconductive insulators. (a) Charge generation with irradiation. (b) Charge separation with applied electric field. (c) Charge trapping in the dark. (d) Data stored as charge under open- or short-circuit conditions in the dark. (e) Data read out as a photodischarge current at short-circuit.

Experimental Section

Sudan I (97%) and Disperse Red 1 (95%) were used as purchased (Aldrich) without further purification. Their absorption maxima are at 476 and 502 nm, respectively. Powders of these photoconductive substances were placed on indium–tin oxide (ITO)-coated glass (Delta Technologies, Stillwater, MN), which were subsequently heated to the melting points of the compounds. The molten material spread out and formed a liquid film on the ITO surface. These films were not very smooth, and the thickness (\sim 1–4 μ m) varied considerably from spot to spot. However, this was not a problem, since only a tiny area of the film (a few tenths of a micrometer) was contacted by the tip in any measurement. Relatively uniform films were prepared by squeezing the molten photoconductive material between two ITO plates to make a sandwich cell and then cooling slowly to form a solid phase at room temperature. The cell was then mechanically separated to produce a single surface of the photoconductive layer.

A sharp Pt–Ir tip of the STM was prepared by electrochemical etching^{18,19} and was used as a liftable electrode to make a point contact to the film and to confine the electric field to a

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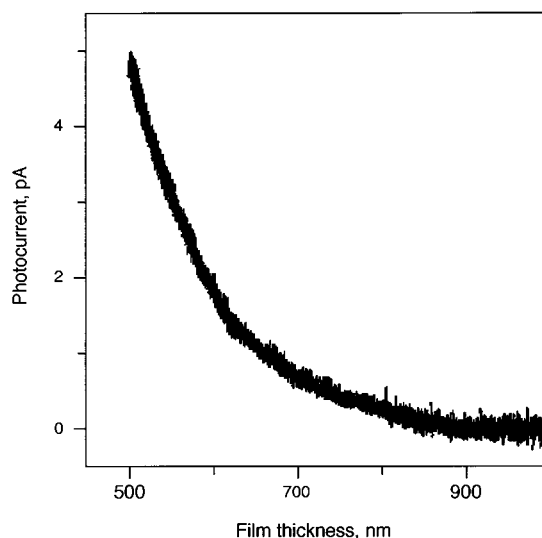


Figure 2. Effect of film thickness of Sudan I on photocurrent under a bias of 5 V with the tip positive. Tip was moved through the layer at a rate of 5 nm/s.

very small spot on the active medium. The movement of the tip was precisely controlled by a combined inchworm motor and PZT pusher (Burleigh) for rough and fine approaches, respectively. A 650-W tungsten halogen lamp was used as a light source, and output power was controlled by adjustment of the applied voltage with a transformer. A 420-nm cutoff filter and a 14-cm long circulating water bath were used to eliminate UV and IR radiation. An optical fiber was employed to irradiate the sample. Experiments were carried out in a dark room. Since the contact area of the Pt–Ir tip with the active layer was extremely small, the measured current was generally at subpicoampere levels. Therefore, a highly sensitive home-built amplifier and Faraday cage were employed. All results presented here were obtained from samples with a configuration of tip/organic layer/ITO, although large-area symmetrical sandwich cells, e.g., ITO/organic layer/ITO, were also fabricated according to a previously reported method^{11,15,16} for comparison and verification of the tip data.

Results and Discussion

Effect of Bias on Dark Current and Photocurrent of Sudan I. The general procedure for measurement was as follows. The Pt–Ir tip was first moved far from the thin film and then was made to approach the surface (in the *Z*-direction) slowly (~ 30 nm/s) with an applied bias voltage of 10 V between the tip and the ITO back-contact (tip either positive or negative) and with the active layer irradiated by an optical fiber through the ITO side of the film. No photocurrent was observed until the tip touched and penetrated the film. The photocurrent increased as the tip slowly moved into the photoconductive layer. The tip was finally fixed at a position where photocurrent of the desired magnitude (~ 0.5 pA) was produced. With the same tip, the key factor determining the photocurrent was the separation between the Pt–Ir tip and the ITO, i.e., the thickness of the photoconductive medium. When a sample with a relatively thick layer was used, the tip was moved deeper into the film to produce about the same tip–ITO separation and therefore to generate the same photocurrent. The photocurrent tracked the tip movement when the tip was moved up and down within the photoconductive layer to a certain extent. Therefore, the total film thickness and uniformity were not crucial

for these measurements. Since the results taken at different vertical positions of the tip (different tip–ITO separations) might vary in magnitude, a series of measurements were made first and were used to determine the most desirable tip position. Once the tip position was fixed at a given point, measurements such as current vs voltage, current vs time, and charge/discharge vs time could be performed. When the tip was too close to the ITO surface (when the tip–ITO separation became too small), a tunneling current with a magnitude several orders greater than the picoampere level was observed. Such a large current arose suddenly and increased exponentially with the distance of tip displacement before physical contact between the tip and the ITO, which gave rise to an even greater current (\sim microampere). Note that the tunneling current was of nanoampere level with a tip–ITO separation of a few nanometers and could easily be distinguished from picoampere-level photocurrents obtained with a gap of about a micrometer between tip and ITO, which is the range of interest for the charge storage experiments.

The optoelectric properties of a single-layer sandwich cell generally depend on the thickness of the photoactive layer, as discussed in detail previously.¹¹ Studies of the thickness dependence of photocurrent in thin-layer cells require a large number of samples of different thickness, which have an accompanying statistical uncertainty because of problems of reproducibility in cell fabrication. For example, in the earlier studies of symmetrical cells consisting of ZnOOEP between two pieces of ITO glass,¹¹ 29 samples were used to determine the dependence of the short-circuit photocurrent on cell thickness. The variations in photocurrent in cells with nominally the same thickness (as determined by absorbance measurements) were as large as 100% (see Figure 6 in ref 11). However, this kind of comparison could be made more easily with a single layer and a sharp tip that is moved through the film. Figure 2 shows the relationship between photocurrent as a function of film thickness (tip position) at a bias of 5 V. In this experiment, the tip was moved at a rate of 5 nm/s within a film of Sudan I. Measurements made with the tip moving continuously in the *Z*-direction or by stopping at different positions within the photoconductive layer were essentially the same. Generally, *I* vs *V* and *I* vs *t* data were collected at several locations across the surface of the film. Comparison of the results obtained at different positions was much more accurate, since the data were taken with exactly the same sample under the same conditions for the measurements. Moreover, the major failure in the fabrication of sandwich cells is often caused by a single impurity site, dust, or a structural defect leading to an electric short, even when most of the area of the cell appears perfect. Since a single short can ruin the behavior of a cell, the yield in the preparation of good sandwich cells is generally low ($<10\%$) especially for thin films less than 1 μm thick. Such a problem does not arise with a tip/organic layer/ITO configuration where only a tiny area of the thin film is involved in the measurement and the tip position can be easily moved to study many different sites on the same organic layer. In addition, the uniformity of a film thickness is of less concern. A difficulty with tip measurements, however, is that the contact area between tip and film

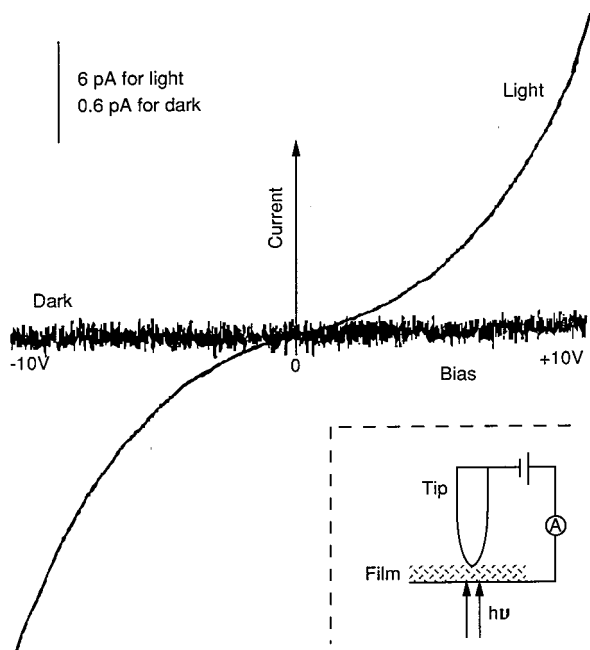


Figure 3. Current–voltage characteristics of Sudan I thin films at a point contact of an STM tip. Scan rate 0.2 V/s. The insert is a schematic diagram of the experimental setup.

is unknown and changes as the tip penetrates the film. This makes quantitative intercomparison of measurements made with different tips difficult.

A typical plot of steady-state photocurrent and dark current as functions of voltage for a Sudan I film is shown in Figure 3. Note that a rather blunt tip was deliberately used for this measurement to maximize the background level (i.e., the dark current), which was below 50 fA. The photocurrent was much larger and increased with potential. No saturation of photocurrent was found under our conditions. When the light was chopped, the photocurrent dropped to essentially zero in the dark and recovered to the same level once the light was turned on again. No hysteresis was observed. The photocurrent level at a given bias was very stable, and no changes were evident after several tens of potential scans, indicating that Sudan I was both chemically and electrooptically stable under our test conditions.

Charge Trapping and Detrapping in Sudan I.

High dark resistivity and good photoconductivity are highly desirable properties for charge storage, which is the basis of the proposed electrooptical memory as discussed previously.^{1–4} Indeed, previous experimental results showed that charges could be readily trapped within such photoconductive thin films upon irradiation under the proper bias, and charges could be stored and later released by the irradiation of the sample producing a photodischarge current similar to that seen with ZnODEP.^{1–4} Figure 4a shows the short-circuit photocurrent (I_{sc}) of an initially uncharged film upon irradiation. In this case, the current from electrons generated directly by photoexcitation of Sudan I molecules or indirectly from the dissociation of excitons ejected into the ITO electrode and holes into the organic layer rapidly attains a steady-state level. Such an interfacial photoinjection is primarily responsible for the production of I_{sc} , which has also been seen in previous reports from our laboratory at ITO symmetrical sandwich cells

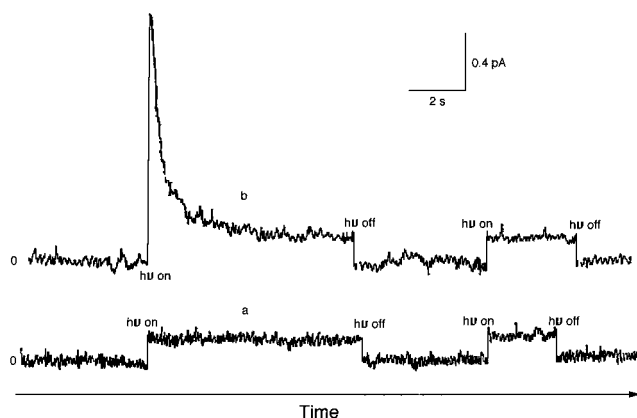


Figure 4. Short-circuit photocurrent at a contact tip as a function of time for Sudan I thin films on ITO where the sample (a) was not previously charged and (b) was previously photocharged at an ITO bias of -10 V.

with a number of different organic crystal thin films, such as porphyrins,^{1,4,11,15} Sudan I,¹⁶ and Solvent Green 3.¹⁷ I_{sc} was stable and dropped to zero when irradiation ceased. By contrast, when the same sample was previously irradiated first for about 10 s under a negative bias to the ITO and was then short-circuited in dark for another 10 s, an anodic I_{sc} spike was seen that decayed in a few seconds to a steady-state level, as shown in Figure 4b. This I_{sc} spike was seen only with the very first irradiation and was not observed with subsequent irradiation unless the sample was recharged again (Figure 4b) once a steady state was reached. This represents the trapping and detrapping process as observed with ZnODEP, which may be useful for high-density information storage.^{1–4} When the sample was irradiated under a negative bias, electrons were injected into the Sudan I layer and trapped there. These trapped electrons were later released during irradiation under short-circuit conditions leading to the I_{sc} spike. Once the trapped electrons were totally depleted, I_{sc} reached a steady-state level, as seen in an initially uncharged sample. Note that such trapping/detrapping processes were inherently different from charge/discharge operations with a conventional capacitor, since the sample was short-circuited in the dark for 10 s, discharging all electrons from the ITO surface before photodetrapping. Similarly, when the sample was positively biased with irradiation and then short-circuited in the dark, a cathodic I_{sc} spike was observed (Figure 5). In this case, the initial photodischarge current overwhelmed the anodic I_{sc} , giving rise to a cathodic I_{sc} spike that was also observed only once with the first irradiation. A steady-state anodic I_{sc} was seen after trapped charges were completely released (Figure 5). Such trapping and detrapping phenomena were identical to what was observed with ZnODEP as discussed previously.^{1–4}

Figure 6 shows a series of short-circuit photodischarge currents as a function of time from Sudan I, which was previously charged under a different applied bias with the same level of irradiation. In these results, a photodischarge current spike appeared when the charged sample was exposed to light under short-circuit conditions. No current spike was observed with uncharged or fully discharged samples under the same conditions. Again, the current spike in Figure 6 appeared once and

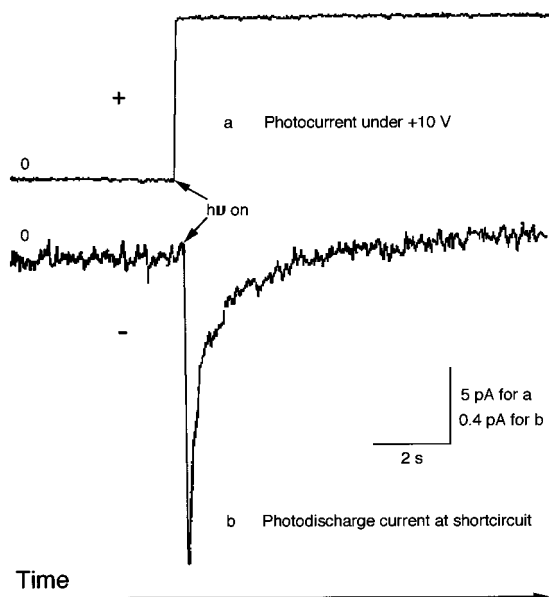


Figure 5. (a) Photocurrent as a function of time for a Sudan I thin film under an ITO bias of +10 V. (b) Short-circuit discharge photocurrent as a function of time for a Sudan I thin film that was previously photocharged at an ITO bias of +10 V.

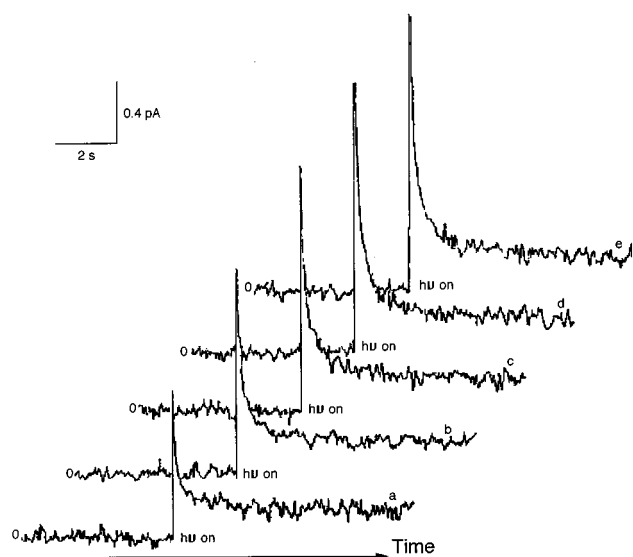


Figure 6. Photodischarge current as a function of time with a Sudan I thin film under short-circuit conditions. Charges were previously stored under potentials of (a) 2, (b) 4, (c) 6, (d) 8, and (e) 10 V.

only once with the first irradiation pulse and did not appear with successive light pulses unless the sample was recharged again. All these charge and discharge results were further confirmed with large-area symmetrical sandwich cells of ITO/Sudan I/ITO, indicating that the charge-trapping and -detrapping processes observed were independent of the physical size of the contact electrode and resulted from the intrinsic property of the Sudan I molecular crystal. When the light pulse for reading (discharging) was weak or of very short duration (10 ns), many readings could be made before the charges were depleted.¹ The magnitude of the discharge current increased with the precharge bias; more charge was stored under a higher bias. The total amount of charge stored electrooptically also depended on the intensity and wavelength of light.

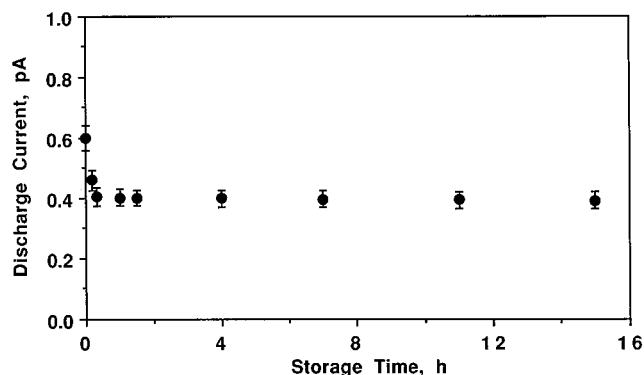


Figure 7. Photodischarge current as a function of charge storage time with a Sudan I film under short-circuit conditions. Charges were initially stored with a tip bias of 10 V for all readings.

Stability and Spatial Resolution. A number of experiments were carried out to test the mechanical stability of the point contact with the STM tip and the retention time of stored charge within Sudan I. In this case, the sample was charged at 10 V (tip positive), stored in the dark for a given period, and then fully discharged under short-circuit conditions with irradiation. The sample was then recharged under the same conditions, stored for another period of time, and discharged again. After a number of charge/discharge cycles, the photodischarge current of each reading was plotted as a function of storage time (Figure 7). The photodischarge current was essentially constant with dark storage time after an initial decay in the first 20 min. This decay was probably caused by a back flow of charges stored near surfaces through external wire under short-circuit conditions and by some thermal detrapping of charge at shallow levels. For those measurements, the Pt-Ir tip of STM was always in point contact with the Sudan I film. The photodischarge current was about the same if the tip was lifted off the film after charging and then retouched at the same position on the surface for discharging. In this case, the tip was moved up and down the same distance, which was precisely controlled by the external voltage applied to the PZT pusher. Normally, after each discharge of the sample shown in Figure 7, a steady-state photocurrent under a given bias was recorded, and a discharge current was collected after the charged sample was stored for only about 15 s in the dark. Both the steady-state photocurrent and photodischarge current taken after each measurement in Figure 7 showed negligible differences from one measurement to another, suggesting that the mechanical stability of the point contact system was very good; thus these data accurately reflect the long-time retention of stored charge by Sudan I.

Attempts to test retention of stored charge for an even longer period were unsuccessful, however. The point contact system could not maintain its positional stability overnight, probably because of temperature fluctuations and mechanical drifts. In a number of tests, the tip penetrated completely through the active medium and came very close to or even contacted the ITO substrate on standing, as indicated by a very large current on recording. In such cases, the system showed the usual behavior after the tip was moved back and some

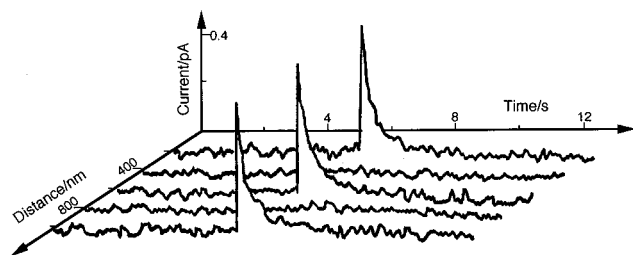


Figure 8. Photodischarge current as a function of time and distance for three adjacent pixels on a Sudan I thin film. Data were stored under a tip bias of 10 V and were read out under short-circuit conditions both with irradiation. Scans are spaced 200 nm apart. Note the absence of photodischarge on alternate scans.

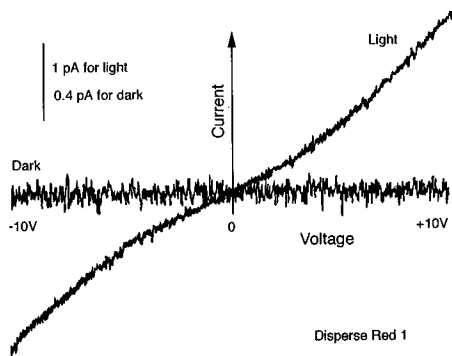


Figure 9. Current-voltage characteristics of a Disperse Red I thin film at a point contact of an STM tip. Scan rate 0.2 V/s.

photodischarge current was still observed. This indicated that charge storage within photoconductive film remained, although the magnitude of the discharge current was much smaller. No efforts were made to improve the long-term stability, since point contact could not be used to test stability for very long periods (weeks to months). Studies of single-layer sandwich cells, however, have shown that charge can be stored for thousands of hours within the ZnODEP medium.¹⁻⁴

The tip was also used to estimate the spatial resolution of the charge trapping by the method described in detail earlier.⁴ The sample was initially charged with the tip at one point and then the discharge current was measured as the tip was moved to nearby locations to determine the distance beyond which no discharge current was observed. This yields an estimate of the maximum size of an individual memory element (pixel) and thus the possible data storage density under given conditions.⁴ The size of a pixel was below 0.3 μm , corresponding to 1 billion pixels per square centimeter, as seen in Figure 8, which shows discharge current from three independent storage sites. Charge localization is an intrinsic property for many organic crystals that are composed of discrete molecules with poor orbital overlap and delocalization. Thus, in the dark, these materials are excellent candidates for isolated charge trapping and are potentially useful for high-density information storage as discussed in our previous papers.^{1,2,4}

Measurements with Disperse Red I Films. The bias dependence of photocurrent and dark current of a thin film of Disperse Red I shows similar behavior to that of Sudan I (Figure 9). It similarly shows charge-trapping and -detrapping processes (Figure 10). The discharge current spike as a function of bias applied in the photocharging process is shown in Figure 11. In

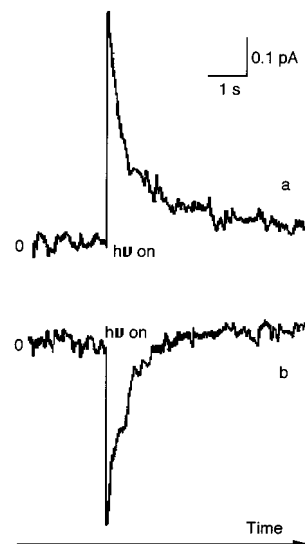


Figure 10. Short-circuit photocurrent of a tip/Disperse Red I/ITO cell as a function of time with constant irradiation after the samples were irradiated under a bias of (a) -6 and (b) $+6$ V followed by a dark period of 10 s under short-circuit conditions.

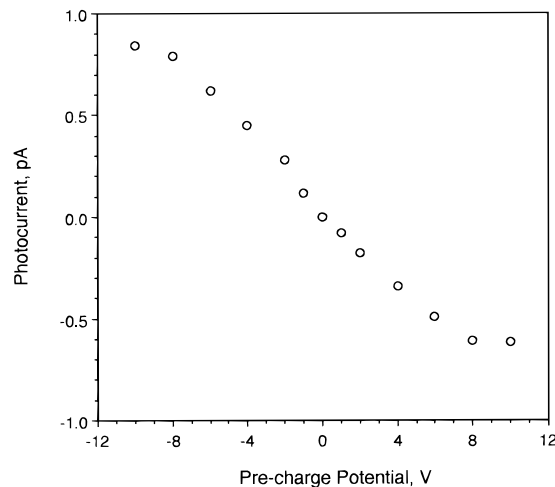


Figure 11. Short-circuit photodischarge current maximum as a function of bias applied during previous charging with irradiation on a Disperse Red I film.

all of these measurements, the cell was short-circuited for 10 s in the dark before photodischarging. Note that the discharge current tended to level off at about ± 9 V. A relatively sharp tip was employed for the characterization of Disperse Red I, but a quantitative comparison of this compound with Sudan I is difficult because it is not possible to measure the tip size. Preliminary measurements with other compounds, such as Methyl Red, showed similar behavior to Sudan I and Disperse Red I.

Conclusions

The unique characteristics of many organic molecular crystals originate from rather weak van der Waals forces between the molecules, promoting charge localization at a molecular level. These organic molecular crystals are therefore promising for high-density information storage based on charge trapping and detrapping.

Acknowledgment. We thank Dr. F.-R. F. Fan for technical assistance. The support of this work by the National Science Foundation (CHE-9423874), Hewlett-

Packard, and the Robert A. Welch Foundation is gratefully acknowledged.
CM970583K