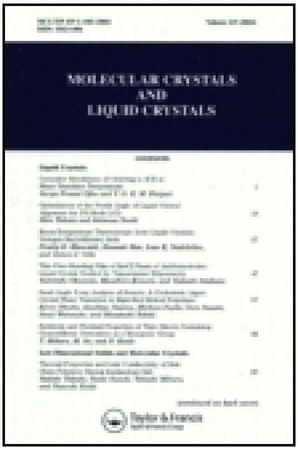

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Photochromism of Diarylethene Single Crystals and Single Molecules

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Photochromism of Diarylethene Single Crystals and Single Molecules

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Diarylethenes undergo thermally irreversible and fatigue resistant photochromic reactions. In this lecture photochromic performance of the diarylethenes under two extreme conditions will be presented. One is the photochromism in the single-crystalline phase, and the other is at the single-molecule level. The diarylethene single crystals undergo very efficient photochromic reactions and exhibit physical property changes, such as surface morphology changes. One of the dreams of organic photochemists is to directly follow photochemical reactions at the single-molecule level. This was demonstrated using a diarylethene derivative linked with a fluorescent unit. The digital fluorescence switching of the single molecules is the first step to achieve the ultimate ultra-high density "Single-Molecule Optical Memory".

Keywords: diarylethene; optical memory; photochromism; single crystal; single molecule

INTRODUCTION

A new class of photochromic compounds named diarylethenes has been developed and the properties have been continuously improved [1]. The diarylethene derivatives undergo fatigue resistant photochromic reactions and both isomers are thermally stable. In addition the response time of the photoreactions is less than 10 ps. Because of the excellent photochromic performance the diarylethene derivatives are the most promising candidates for the applications to photonics devices.

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For the practical applications the photochromic reactions should take place efficiently in a solid state. Although so far polymer matrices are used to prepare solid systems, the polymer systems have drawbacks, such as limited reactivity and low contrast. When the reactions take place in the crystalline state, the system is ideal, because in the crystalline state highly efficient reactivity is anticipated if the molecules are packed in a favorable conformation.

Single crystals contain the highest concentration of molecules. An extremely low concentration system is single molecules. We have tried to detect the single molecule photochromism by fluorescence. Although uncontrollable fluorescence switching of single molecules has been studied, on/off digital switching of synthetic molecules by photoirradiation in a controllable manner has not yet been accomplished for the lack of sufficiently durable photochromic molecules.

Here we report on photochromic performance of diarylethene derivatives in the single-crystalline phase and at the single-molecule level.

SINGLE CRYSTALLINE PHOTOCHROMISM [2]

Single crystals of diarylethne derivatives shown in Figure 1 exhibited reversible color changes upon irradiation with UV and visible light [2–10]. Compound **1** changed the color from colorless to yellow upon irradiation with UV light and the yellow color disappeared upon irradiation with >450 nm light. When the substitution position of the thiophene rings to ethene moiety was changed from 2- to

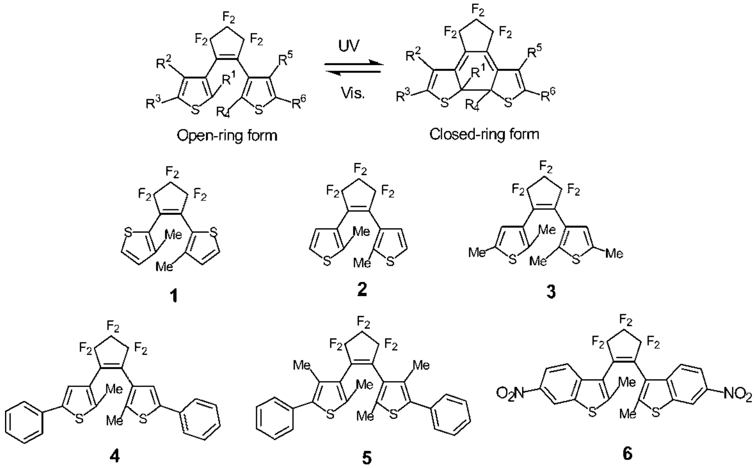


FIGURE 1 Photochromic reactions of single-crystalline diarylethenes.

3-positions, the color of the closed-ring form changed to red, as observed for compounds **2** and **3**. By the substitution of phenyl groups at 5-positions of the thiophene rings the color changed to blue, as observed for compounds **4** and **5**. The π-conjugation length of the closed-ring isomers controlled the color of the photogenerated isomers.

QUANTUM YIELDS IN CRYSTALS [7,8]

In solution dithienylethene derivatives have two conformations, anti-parallel and parallel, in almost equal amounts, and they interconvert each other, as shown in Figure 2. The conrotatory photocyclization reaction can proceed only from the anti-parallel conformation. In order to increase the photocyclization quantum yield it is required to increase the population of the anti-parallel conformers.

The most effective approach to increase the anti-parallel population is to include the molecules in crystal lattice, in which only anti-parallel conformers can exist. X-ray crystallographic analysis revealed that all molecules shown in Figure 3 are packed in the crystalline phase in the photoactive anti-parallel conformation. We measured the photocyclization quantum yields and the distance between the reactive carbons of these 10 derivatives [8]. As can be seen from Figure 3 the photocyclization quantum yields are almost 1 (100%) so far the distance is less than 4.0 Å. This means that in these crystals all absorbed photons are fully used for the photochemical reaction. In other words, perfect photochromic reactions take place in these diarylethene crystals.

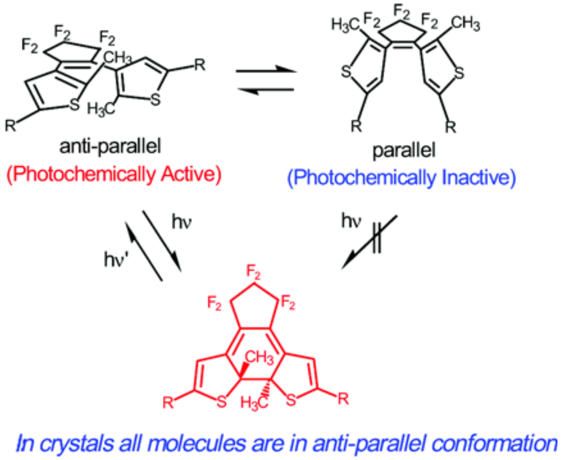


FIGURE 2 Conformations of dithienylethene derivatives.

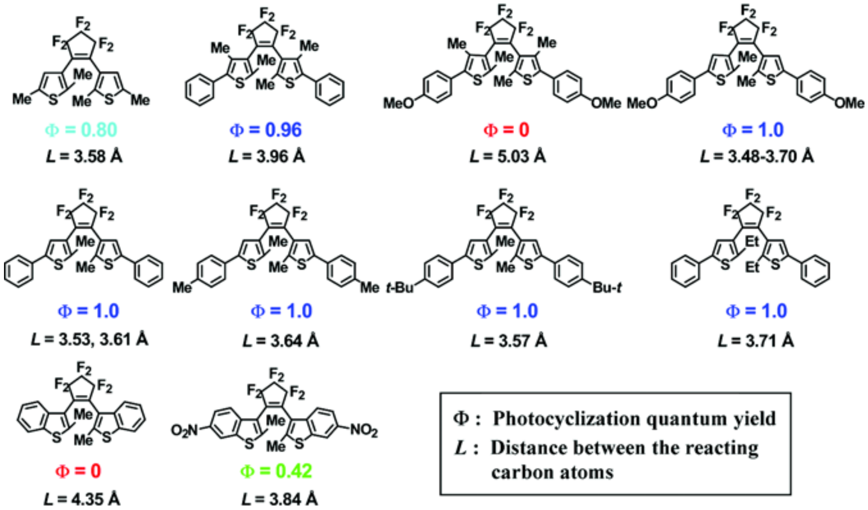


FIGURE 3 Photocyclization quantum yields and the distances between reactive carbons of diarylethene derivatives.

REVERSIBLE SURFACE MORPHOLOGY CHANGES [11]

X-ray crystallographic analysis of single crystal **3** revealed that each molecule shrinks during the photocyclization reaction and expands in the reverse photocycloreversion process [5]. The unit cell volume was found to shrink as much as 0.3%. This suggests possible shape changes of bulk single crystals upon alternate irradiation with UV and visible light. We examined the surface morphology change of single crystal **5** using atomic force microscope (AFM) [11].

The colorless single crystal of **5** turned blue upon irradiation with 366 nm light. The surface of the crystal before photoirradiation was flat. Upon irradiation for more than 10 sec with 366 nm light (12 mW/cm^2) a step appeared on the surface as shown in Figure 4. Any step formation was not discerned during the initial 10 sec. The step height was 1.0 ± 0.1 nm. The step disappeared by bleaching upon irradiation with visible light. When the irradiation time was prolonged the number of steps increased and steps with height of 2.0 ± 0.2 nm and 3.0 ± 0.3 nm appeared. The height was always a multiple of the minimum height (1.0 ± 0.1 nm). The morphological change was reversible and correlated with the color change of the crystal.

To determine the relation between the reversible formation of steps and photoisomerization of the molecules, we carried out X-ray crystallographic analysis of the crystal. The X-ray analysis data indicated

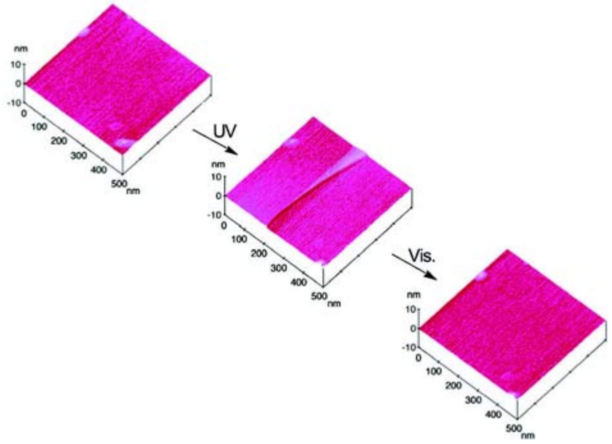
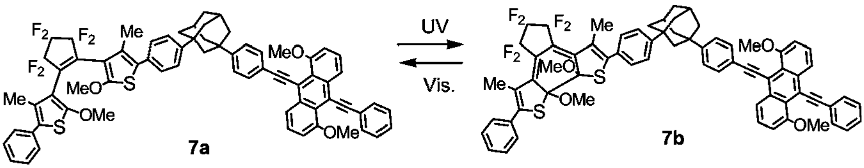


FIGURE 4 Reversible surface morphology changes of single crystal **5** upon irradiation with UV and visible light.

that the end to end distance of each molecule is shortened as much as 0.02 nm during the photoisomerization, and the single molecular layer is around 1.0 nm. This means that photoisomerization of at least 50 molecular layers is required to cause the sink of one molecular layer of 1.0 nm. 10 sec irradiation corresponds to the reactions of 600 molecular layers. The reaction of 600 layers is considered to produces one layer vacancy in the crystal bulk.

PHOTOCHROMISM AT THE SINGLE-MOLECULE LEVEL [12]

Diarylethene derivatives with heterocyclic aryl groups are the most promising candidates for single-molecule optical memory media because of their excellent photochromic performance. After several trials, we have designed and synthesized fluorescent photochromic molecule **7** as shown below.



7a converts to **7b** upon irradiation with UV light and **7b** returns to **7a** with visible light. The relative energy levels of component chromophores are shown in Figure 5. The bis(phenylethynyl)anthracene unit

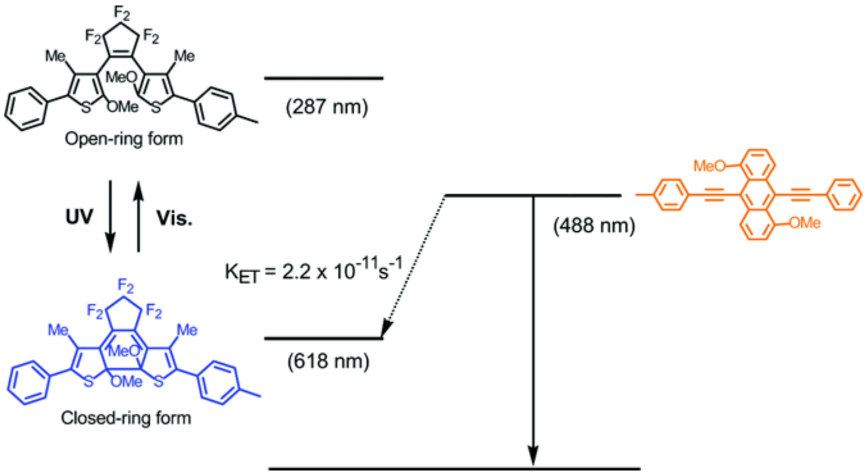


FIGURE 5 Relative energy levels of the component chromophors of compound **7**.

has characteristic absorption and fluorescence bands at 488-nm and 503-nm, respectively. The fluorescence spectrum well matches the absorption spectrum of the closed-ring form of the diarylethene unit and, therefore, the fluorescence is efficiently quenched when the diarylethene unit converts from the open- to the closed-ring form.

Although in a toluene solution (an ensemble system) the fluorescence intensity gradually changed upon alternate irradiation with UV (313 nm) and visible ($\lambda > 450$ nm) light, the switching behavior of **7** dramatically changed at the single-molecule level. Figure 6

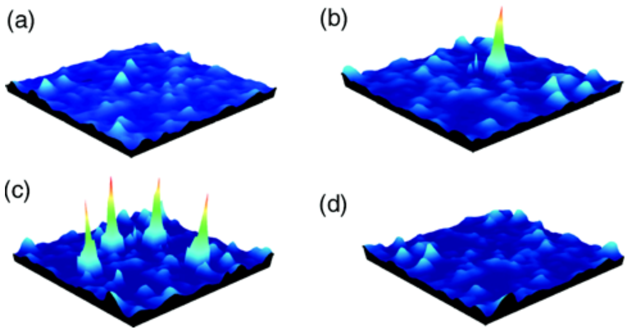


FIGURE 6 Fluorescence images of single photochromic molecules **7**. (a) Before irradiation. After irradiation with visible light for (b) 5 sec, (c) additional 15 sec. (d) After irradiation with UV light.

demonstrates the fluorescence images and switching behavior of the single molecules on a polymer film Initially all **7b** molecules were in the dark state. Upon irradiation with visible light (488-nm, 100 W/cm^2) for 5 sec, one of the molecules was switched to the fluorescent on state. Additional 15 sec irradiation converted three more molecules into the fluorescent on-state. Upon irradiation with weak UV light (325-nm, 0.27 mW/cm^2) for 3 sec the four fluorescent on-state molecules were switched to the non-fluorescent off-state. The on/off fluorescence switching of the single molecules is ascribable to the photoisomerization of **7**.

On/off digital switching of the fluorescence of diarylethene molecules was controlled by irradiation with UV and visible light at the single-molecule level. The fluorescent diarylethene derivative can be potentially utilized for ultrahigh-density erasable optical data-storage media (1 bit per molecule, ~peta bit/in^2).

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