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# Photochromic diarylethene molecules and crystals\*

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*Abstract*: Some of the diarylethene derivatives were found to undergo photoisomerization reactions between two isomers even in the single-crystalline phase. The two isomers have different electronic as well as geometrical structures. The electronic structure change induces the reversible color change of the crystal. Single crystals composed of three different kinds of diarylethenes having similar geometrical structures, bisoxazolylethene, bisthiazolylethene, and bisthienylethene have been prepared. The crystals exhibited multicolor photochromism. The colorless crystals turned yellow, red, and blue upon irradiation with the appropriate wavelength of light. The geometrical structure change of component diarylethene molecules in crystals induces reversible surface morphology as well as shape and size changes of the crystals. The photoinduced geometrical structure changes of the molecules in the densely packed crystals were successfully linked to the macro-scale mechanical motion of the solid crystals and resulted in the net task of launching a tiny silica particle.

*Keywords*: diarylethenes; photochromism; photomechanical effects; single crystals; X-ray crystallographic analysis.

## INTRODUCTION

Photochromism is defined as a reversible transformation of a chemical species between two isomers upon irradiation with the appropriate wavelength of light [1,2]. The two isomers have different electronic as well as geometrical structures. The reversible and quick structure changes between them upon photoirradiation can be potentially applied to various photoactive devices [3–7]. The electronic structure change causes the absorption spectrum (or color), refractive index, and oxidation/reduction potential changes. Figure 1a shows the absorption spectrum change of 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene (1) in hexane solution. The spectrum change is ascribed to the electronic structure change of the molecule. In the left-side isomer (open-ring isomer)  $\pi$ -conjugation is localized to each benzothiophene ring. On the other hand, in the right-side isomer (closed-ring isomer)  $\pi$ -conjugation delocalizes throughout the molecule. Therefore, the absorption spectrum exhibits a bathochromic shift. At the same time, the molecule changes the geometrical structure, as shown in Fig. 1b. In the open-ring isomer, two benzothiophene rings tilt or twist, but in the closed-ring isomer, both benzothiophene rings become coplanar and the closed-ring isomer has a planar structure.

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Fig. 1 Absorption spectrum (a) and geometrical structure (b) changes of 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene.

Although the photoinduced electronic as well as geometrical structure changes have potential to be applied to memory media, switching devices, light-driven actuators, and others, for practical applications the photochromic materials should fulfil the following requirements:

- thermal stability of both isomers
- fatigue-resistant character
- high sensitivity
- rapid response
- reactivity in the solid state

We have developed a new class of photochromic molecules named "diarylethenes", which are derivatives of stilbene. Phenyl rings of stilbene are replaced with five-membered heterocyclic rings, such as thiophene, benzothiophene, or furan rings. The diarylethene derivatives show excellent photochromic performance, as summarized in Fig. 2 [8,9]. Both isomers are thermally stable, and the molecules undergo fatigue-resistant photochromic reactions. Rapid and efficient photochromic reactions are observed in both solution and crystalline phase [10]. In this article, we focused on single-crystalline photochromism of diarylethene derivatives and their applications [11].



Fig. 2 Photochromic performance of diarylethene derivatives.

#### SINGLE-CRYSTALLINE PHOTOCHROMISM

Photochromic molecules, which show photochromism in the single-crystalline phase, are very rare, because in crystals large geometrical structure change is prohibited. For example, azobenzene and most of the spirobenzopyran derivatives cannot undergo photochromism in crystals. The reason is that they require large geometrical structure changes during the photochromic reactions. Fortunately, the geometrical structure change of diarylethene derivatives is very small [12,13]. Therefore, many of the diarylethene derivatives can undergo photochromism even in the single-crystalline phase.

Figure 3 shows typical color changes of several diarylethene single crystals. Upon irradiation with ultraviolet light, colorless crystals turn yellow, red, blue, or green, depending on the molecular structure of the diarylethenes. The color change is ascribed to the electronic structure change of the component diarylethene molecules in crystals upon photoirradiation. The colored forms are stable even at 100 °C and never return to the initial colorless forms in the dark. The colors disappeared by irradiation with visible light. The photoinduced coloration/decoloration cycle can be repeated more than  $10^4$  times without any destruction of the crystals.

In usual one-component systems, they interconvert between only two states, "colorless" and "colored". On the other hand, in multicomponent systems composed of different kinds of diarylethenes, reversible multimode or multicolor switching can be realized by the combination of two states of each component. In a two-component system, for example, four states  $(2^2 = 4)$  can be produced, and eight states  $(2^3 = 8)$  in a three-component system. Although several multicomponent systems have been reported, such as multicomponent mixtures in solution as well as in silica plates [14] and fused diarylethene dimers [15], the photocoloration/decoloration cycles, coloration efficiency, resolution of the color images, and stability of the colored state are limited. Ideal multicomponent systems are multicolor single crystals, because of their high durability, high efficiency of photocoloration, and molecular scale resolution.



Fig. 3 Color changes of several diarylethene single crystals.

As a consequence of examining a great number of combinations of single-crystalline photochromic diarylethenes, we found following diarylethenes form three-component single crystals, of which the closed-ring isomers exhibit different colors, yellow, red and blue, respectively [16].



Figure 4 shows the color change of the three-component crystal upon irradiation with the appropriate wavelength of light. The crystal turns yellow, red, and blue upon irradiation with 405 and 578 nm; 405, 458, and 692 nm; and 405 and 492 nm light.





Although clear full-color change was observed upon photoirradiation, the content of the blue component was very low (<0.5 %). In order to prepare three-component crystals which exhibit full color and contain almost equal amounts of the three-color component diarylethenes, we prepared mixed crystals composed of the following three diarylethene derivatives [17,18].



These three diarylethene derivatives have very similar geometrical structures, but the colors of the closed-ring isomers are different. Colorless bisoxazolylethene (5a), bisthiazolylethene (6a), and bisthienylethene (7a) turn yellow, red, and blue upon ultraviolet irradiation in solution. The three derivatives could be readily mixed in almost any ratios into single crystals. The color change of the three-component crystal upon irradiation with the appropriate wavelength of light is shown in Fig. 5. The crystal color changed from colorless to yellow, red, and blue upon photoirradiation. The multicolor change was also observed for a single-component crystal under polarized light. The dichroism is another characteristic property of photochromic single crystal [19,20].

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Fig. 5 Color changes of a three-component crystal containing diarylethene 5, 6, and 7 upon irradiation with the appropriate wavelength of light.

Next, we examined the geometrical structure changes of component diarylethene molecules in single crystals. The geometrical structure changes in crystals can be directly observed by X-ray crystallographic analysis. The diarylethene crystal of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**8a**) was irradiated for 24 h with polarized 360-nm light and analyzed by single-crystal X-ray diffraction [12,13]. The difference Fourier electron density map of the crystal indicates the existence of two quite high electron density peaks corresponding to the sulfur atoms of the photogenerated closed-ring isomer. High electron density peaks corresponding to two carbons at the reacting points also appeared. Figure 6 shows the ORTEP drawings of the molecular structures that are a mixture of open- and closed-ring isomers. The occupancy factor for the photogenerated closed-ring isomer is 0.084 (2), which indicates that ca. 8 % of the component molecules in the crystal undergo the photocyclization reaction upon 360-nm light irradiation.

As can be seen in Fig. 6, almost all atoms remain in the same positions even after photocyclization. Only sulfur and reactive carbon atoms change the positions. The small geometrical structure change is favorable for the photochromic reaction to take place in crystal. It is worthwhile to note small but significant geometrical structure changes of the two isomers. The end-to-end distance of the photogenerated closed-ring isomer is short in comparison with that of the initial open-ring isomer and the molecular thickness becomes thin upon photocyclization. The result indicates that the diarylethene molecule shrinks upon ultraviolet irradiation. The shrink of component diarylethene molecules upon ultraviolet irradiation suggests the change of the bulk shape of the crystal. The most convenient way to measure the crystal shape change is to measure the surface morphology by using atomic force microscopy (AFM). Figures 7A, 7B, and 7C show the morphology changes of the (100) and (010) surfaces of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocycopentene (9) upon irradiation with ultraviolet (366 nm) and visible (>500 nm) light measured with AFM [21]. Upon irradiation for more than 10 s with ultraviolet light, steps appeared on the (100) surface. No step formation was discerned during the irradiation for the initial 10 s but appeared after the induction period. The step height was 1.0 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 and 3.0 nm appeared. The height was always a multiple of the minimum step height in 1.0 nm, and any step with a height lower than the unit height of 1.0 nm was not observed. Each step of 1.0 nm requires the reactions to depth to ca. 600 molecular layers. On (010) surface, ultraviolet irradiation-induced valley formation, as shown in Figs. 7D, 7E, and 7F. The valley almost disappeared by bleaching upon irradiation with visible light.

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Fig. 6 ORTEP drawing of diarylethene (8) upon irradiation with 360 nm light. The open-ring isomer and the photogenerated closed-ring isomer are shown in blue and red, respectively.



**Fig. 7** AFM images of the (100) crystal surface (A–C) and the (010) crystal surface (D–F) of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (9): before photoirradiation (A and D), after irradiation with 366-nm light for 10 s (B) and 15 s (E), and after irradiation with visible light ( $\lambda > 500$  nm) (C and F).

The morphological change was reversible and correlated with the color change. This result indicates that the small shape changes of component molecules are directly linked to the shape change of the crystal surface.

### PHOTOMECHANICAL EFFECTS

It is of particular interest from both scientific as well as technological points of view to have synthetic molecules make mechanical motion by photoirradiation and link the motion to large macro-scale mechanical work of bulk materials [22,23]. When azobenzene is isomerized from the *trans*- to the *cis*-form, the length of the molecule is shortened from 0.90 to 0.55 nm. The size change of the molecule by photoirradiation is anticipated to alter the shape of the polymer films or gels which contain the azobenzene molecules. However, it is not the case in the polymer systems. The large free volume of the polymer films and gels relaxes the strain energy generated by the geometrical structure change of the molecules is required for the photoinduced deformation of bulk materials [24–26].

Molecular crystals are densely packed organized systems. In the dense systems, the strain energy is considered to directly influence the shape of the bulk crystal. In order to modulate the shape of bulk crystals upon photoirradiation without breaking, the following conditions should be fulfilled:

- homogeneous illumination
- no phase separation between the photogenerated isomers and unreacted isomers
- random and noncooperative reaction
- high conversion efficiency

The most convenient way to fulfil the above conditions is to use small-size crystals. When the crystal size is 10–100  $\mu$ m and the thickness is less than 1  $\mu$ m, the crystal can be homogeneously illuminated. Figure 8 shows the color and shape changes of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**10**) and 1,2-bis(5-ethyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**11**) crystals upon irradiation with ultraviolet (365 nm) and visible (>500 nm) light [27]. The color of crystals **10** and **11** turned to blue and red, respectively. The colors are stable in the dark, but disappeared on irradiation with visible light.



Fig. 8 Photoinduced shape changes of single crystals 10 and 11 upon irradiation with ultraviolet and visible light.

The crystal shape changes during the photochromic reactions were directly followed with a microscope. Ultraviolet irradiation changed the corner angle of single crystal **10** from 88 and 92 to 82 and 98°, and hence the shape from a square to a lozenge. Figure 9 shows the time dependence of the color and shape changes upon alternate irradiation with ultraviolet and visible light by showing the relation between the absorption intensity of the crystal at 600 nm and its corner angle. As can be seen from the figure, the angle initially remains unchanged and then decreases by as much as 5 to 6°. Any evidence of hysteresis between the forward and reverse processes is not observed. Although the color



Fig. 9 Relationship between the corner angle of the single crystal **10** and the absorption intensity of the crystal measure at 600 nm upon irradiation with ultraviolet and visible light.

change of the crystal **11** is different from the crystal **10**, both showed very similar shape changes from a square to a lozenge.

A rod-like crystal was prepared from 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (12) by sublimation. The rod-like crystal mounted at one end on a glass surface bent upon irradiation with ultraviolet light. As shown in Fig. 10, the rod bent toward the direction of the incident light. This effect is due to the gradient in the extent of photoisomerization caused by the high absorbance of the crystal, so that the shrinkage of the irradiated part of the crystal causes bending just as in a bimetal. The bent rod-like crystal became straight again upon irradiation with visible light. Such reversible bending could be repeated over 80 cycles.



Fig. 10 Bending of rod-like crystal 12 upon irradiation with UV and visible light.

The crystal rod (about 200  $\mu$ m long and 5  $\mu$ m diameter) was used to launch a tiny silica particle (diameter 80  $\mu$ m), as shown in Fig. 11. The rapid response and relatively large elastic modulus of the crystal rod enabled us to hit the silica particle as if it were a tennis ball.

The shape change of component molecules in crystal upon photoirradiation is directly linked to the macro-scale shape change of the crystal. The suitable packing of component molecules in the crystal induces a kind of cooperative motion of the crystal lattice and results in the mechanical motion of the crystal. The specific organization of molecules in crystal is, therefore, considered to play an important role in the macro-scale motion of the bulk materials. The photoinduced change of molecular shape

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Fig. 11 Shot of a silica microparticle by rod-like crystal 12 upon irradiation with 365-nm light pulse.

at the molecular level was successfully linked to the macro-scale mechanical motion of the solid crystal and resulted in a net task to launch a tiny silica particle.

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