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Photosalient Effect of a Diarylethene Having Perfluorocyclohexene Ring

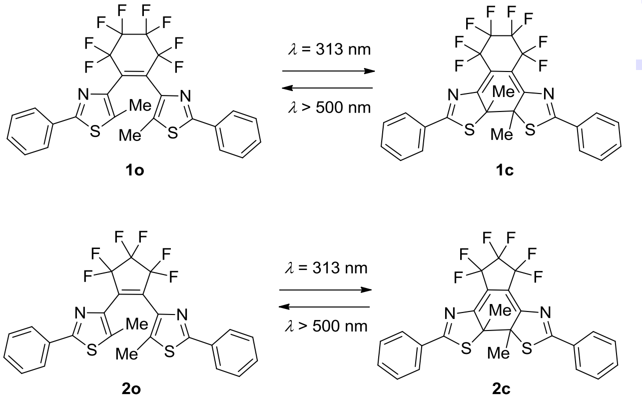
Eri Hatano,[a] Masakazu Morimoto,*[b] Kengo Hyodo,[a] Nobuhiro Yasuda,[c] Satoshi Yokojima,[d] Shinichiro Nakamura,[e] and Kingo Uchida*[a]

Abstract: Crystals of a diarylethene having perfluorocyclohexene ring exhibit a remarkable photosalient effect upon UV light irradiation, which is attributed to the larger structural changes from open- to closed-ring isomers in the crystalline state together with the existance of two conformers with different photo-conversion compared with those of a perfluorocyclopentene derivative. Current results will give a design principle for molecular structures to achieve photosalient effect by the photochromic crystals.

It is well known that plants have a unique strategy to increase their chances of successful reproduction. The lightweight seeds move with the wind and spread out to far distances, especially if they get caught on a bird or insect moving about the region. Impatiens and squirting cucumber have specific mechanism to scatter their seeds explosively.[1] The first organic photosalient effect was reported by Trommsdorff in 1834 on the “burst” of crystals of α-santonin after the color turning yellow by exposing it to the sunlight.[2] The photosalient effect was recently reinvestigated.[3] Recently, Naumov *et al*. intensively studied the crystal jump and breaking due to a strong light stimulus and named it the photosalient effect.[4-8] They reported the following processes for photoirradiated crystals of $[Co(NH_3)_5(NO_2)]Cl(NO_3)$: (1) splitting of a crystal into two pieces of nearly equal size, (2) separation of a small piece off the crystal, which propels the remaining part into a spinning or linear motion, (3) crystal explosion, (4) minor repositioning without lifting off the base and apparent splitting or separation of debris, and (5) rolling or flipping of the crystal.[4]

The crystals of diarylethene derivatives were also reported to undergo crystal shape changes (elongation and shrinkage) as well as photoinduced bending.[9] Irie *et al.* reported the photoinduced crystal jump of diarylethene microcrystals upon UV irradiation.[10] The diarylethenes that have mainly been synthesized previously have a five-membered perfluorocyclopentene ring.[11] On the other hand, a derivative having perfluorocyclohexene ring with two benzothiophene aryl groups was reported in an effort to improve fatigue resistance and physical properties, although no systematic study was performed.[12]

Herein, we have newly synthesized a derivative having phenylthiazole rings as aryl groups on both sides of the perfluorocyclohexene ring **1o**, based on previous papers describing the synthesis of 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclohexene and 1,2-bis(5-methyl-2-phenylthiazo-4-yl)perfluorocyclopentene.[12,13] The photochromism in the crystalline state and the observed photosalient effect of **1o** were compared with those of **2o** with perfluorocyclopentene ring.



Scheme 1. Molecular structures of the two isomers of diarylethene **1** and **2**.

The absorption spectral changes of **1o** in hexane solution are shown in Figure 1. Open-ring isomer **1o** shows the absorption maximum at 298 nm (ε: 3.1 × 10^4 M^{-1} cm^{-1}). Upon 313 nm irradiation, the solution turned to purple, and a band attributed to the closed-ring isomer **1c** appeared at 518 nm (ε: 1.1 × 10^4 M^{-1} cm^{-1}). Upon visible light (λ > 500 nm) irradiation, the solution turned to colorless and the spectrum of **1o** was regenerated. Consequently, photochromism was observed. The quantum yields of cyclization and cycloreversion reactions in hexane were obtained to be 0.29 (Φ_{oc} at 313 nm) and 0.015 (Φ_{co} at 492 nm), respectively. These values were very similar to those of perfluorocyclopentene derivatives **2o** and **2c** (**2o**: λ_{max}: 300 nm (ε: 3.4 × 10^4 M^{-1} cm^{-1}), **2c**: λ_{max}: 525 nm (ε: 1.0 × 10^4 M^{-1} cm^{-1}), 0.32 (Φ_{oc} at 313 nm) and 0.02 (Φ_{co} at 492 nm)) in the

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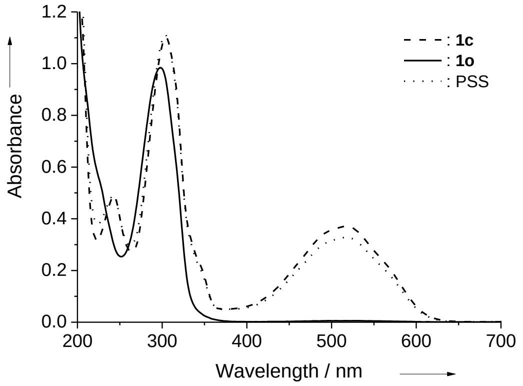

Figure 1. Absorption spectral changes of **1o** in hexane solution (3.27 × 10-5 M); Absorption spectrum of **1o** (solid line), Absorption spectrum of **1c** (broken line), and photostationary state upon 313 nm light irradiation (**1o**: **1c**=12:88) (dotted line).

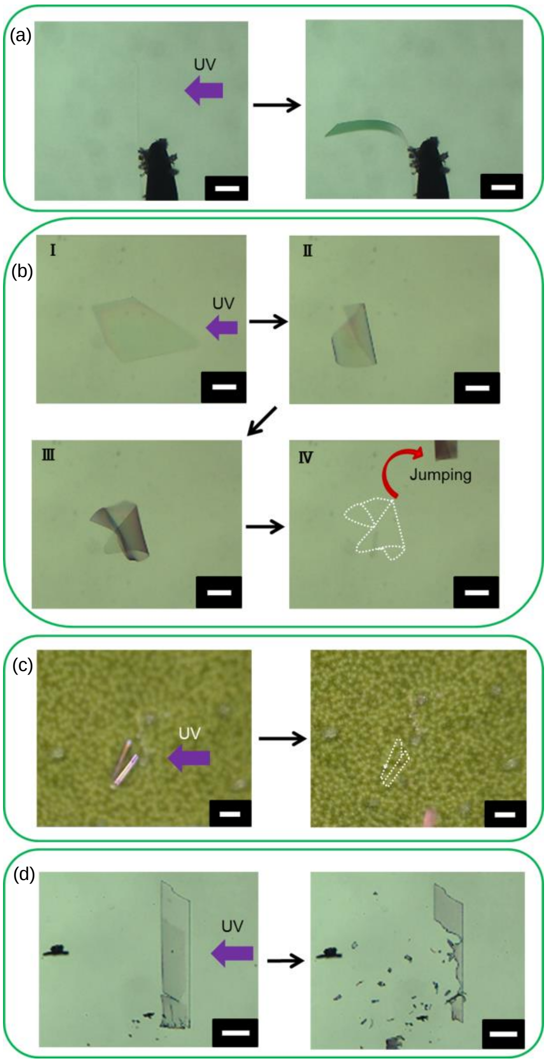

Figure 2. Photoresponsive phenomena of the thin film of **1o**. (a) bending (scale bar: 100 μm), (b) bending (I to II) followed by jumping (III to IV) (scale bar: 50 μm), (c) photoinduced jumping on a lotus leaf (scale bar: 100 μm), (d) photoinduced scattering (scale bar: 50 μm).

same hexane solution. Additionally, **1c** showed much better thermal stability compared with that of **2c**.[14] The thermal stability of **2c** is reported to be reached at the half-life time of 30 h at 180 °C in degassed decalin. In contrast, the half-life time of **1c** was almost 80 h at the same temperature in decalin under the same condition (Figure S1 in the Supporting Information).

Compound **1o** also showed the photochromism, even in the crystalline state. In the single crystal, the two conformers of **1o** are located in a unit cell, and the distances between the reactive carbon atoms were 3.476 Å (conformer A) and 3.582 Å (conformer B), respectively (Figure S2 in the Supporting Information). These values are shorter than 4.2 Å, which satisfies the condition for photo-reactivity in the crystalline state.[15]

Upon UV irradiation to the thin crystals of **1o**, the crystals changed colour to purple, indicating the formation of **1c**. Then the crystals showed ***bending*** (Figure 2a), ***jumping*** (Figures 2b, c (Movie I)), and ***explosive scattering*** into small pieces (Figure 2d (Movie II)), i.e. the photosalient effect appeared. As for the photoinduced jumping, the use of lotus leaf is effective to observe the event, because the adhesion force between the thin crystals and the surface of lotus leaf is small compared to that between the thin crystals and the glass surface.[16] Their ratio was nearly 6: 3: 1 for bending, jumping, and scattering. Comparing to single crystals of **2o**, which showed very fatigue-

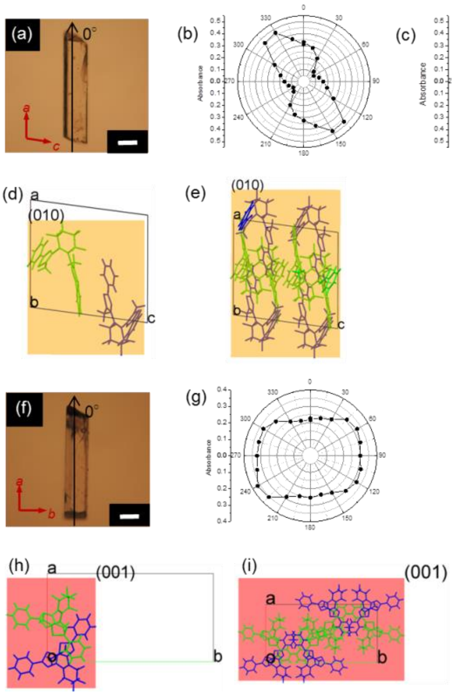

Figure 3. Single crystal of **1o** prepared by recrystallization from ethanol-dichloromethane mixture and the polar plot figures. (a) (010) surface of single crystal of **1o** (scale bar: 200 μm), (b) polar plot of (010) surface monitored at λ_{max} of 540 nm after irradiation with UV light of 313 nm, (c) two separated components of polar plots of (b) by waveform analysis, (d) unit cell consisting of two conformers of **1o** from (010) surface, (e) molecular packing of (d), (f) side view of (a) surface indicating (001) surface (scale bar: 200 μm), (g) polar plot of (001) surface monitored at λ_{max} of 537 nm after irradiation with UV light of 313 nm, (h) unit cell consists of two conformers of **1o** from the (001) surface, and (i) molecular packing of (h), (j) bending direction to the incident light.

resistant photoinduced bending, those of **1o** showed a remarkable photosalient effect (“salient” means leaping).[5]

The largest surface of the thin crystals of **1o** is estimated to be a (010) surface from their XRD pattern (Figure S8 in the Supporting Information). In order to clarify the reason why crystals of **1o** show the remarkable photosalient effect, we carried out the X-ray analysis of the crystal of **1o**,[17] and compared it with that of **2o**. A crystal of **1o** was prepared by recrystallization from an ethanol-dichloromethane mixture, and the polar plots of two faces of the crystals were observed as shown in Figure 3. A CCD image of the (010) surface of a single crystal of **1o** is shown in Figure 3a. The crystal was irradiated with UV light of 313 nm for 1 min, and the polar plot was measured with a polarized microscope. In the measurement, a polarizer and an analyzer were set parallel to each other. Then the asymmetric polar plot (Figure 3b) was divided into two components as an assumption that each polar pot should be symmetric (Figure 3c). The intensity variation by rotation depended on the perfluorocycloalkene rings. The dichroism under polarized light clearly indicates that **1o** underwent photochromic reactions in the crystal lattice, and the existence of two conformers with a tilt angle of about 60°, which is very close to the twisting angle of 64° viewed from (001) face estimated from X-ray analysis (Figure S6 in the Supporting Information). Therefore, the face in Figure 3f is considered to be the (001) surface. This is in good agreement with the XRD results of thin crystals (Figure S8 in the Supporting Information). The distances between two reactive carbons of the two conformers in a unit cell were 3.476 Å (conformer A, blue) and 3.582 Å (conformer B, green). These distances were shorter than 4.2 Å, indicating that both conformers are photoreactive in the crystalline state. Consequently, the crystalline surface shown in Figure 3a can be attributed to the (010) surface.

Irie *et al*. demonstrated that the molecular shape changes from an open- to closed-ring isomer of diarylethene in the crystals are the driving force of photoinduced crystal bending.[9] Therefore, larger shape changes of diarylethene are expected to induce larger crystal deformation. Then the changes in molecular structure from the open-ring isomer to the closed-ring isomer of **1** and **2** are summarized and compared in Figure 4. Upon UV irradiation to the crystals, **2o** converted to **2c** with expansion of the longitudinal axis of the molecules from 5.930 to 6.086 Å. The expansion ratio was 2.6%. For the horizontal axis, it expanded 0.6% from **2o** to **2c,** accompanied with a cyclization reaction. The molecule also showed reduced thickness upon cyclization. In the photoinduced bending of crystals of **2o**, cofacial packing of the photogenerated thinner closed-ring isomers allows the molecules to be stacked one-by-one, resulting in contraction along the long axis of the needle-like crystal and the bending phenomena.[9] In contrast, **1o** has two types of conformers positioned in a twisted configuration to each other as shown in Figure 3 (also in Figure 4a). Upon UV irradiation, both conformers undergo cyclization reaction to form **1c**. The longitudinal axes of the blue- and green-coloured conformers shrunk from 6.736 and 6.742 Å, respectively, to 6.132 Å, at shrinkage ratios of 9.0 and 9.0%. The horizontal axes of the conformers A (blue) and B (green) of **1o** were 13.662 and 13.646 Å. They expanded to 14.456 Å when the molecules were converted to **1c**,[17] and the expansion ratios were 5.8 and 5.9%, respectively. These changes are far larger than those of **2o** to **2c**.

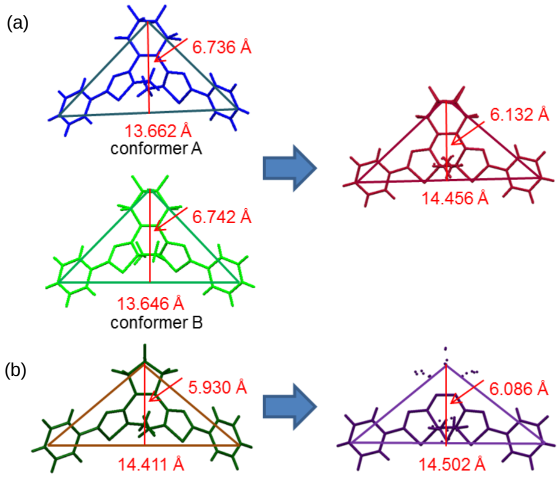

Figure 4. Structural changes in the conformers of open-ring isomer **1o** to the closed-ring isomer **1c** in the crystals (a) compared with **2o** to **2c** (b).

The large molecular shape change in **1o** upon cyclization reaction is the direct consequence of the use of perfluorocyclohexene instead of perfluorocyclopentene. The interior angle of 6 membered-ring (perfluorocyclohexene) is larger than that of 5 membered-ring (perfluorocyclopentene). Thus, the angles (θ) related to the C-C bond between perfluorocyclohexene and thiazole rings changed (Figure S9 in the Supporting Information) and the distance between two thiazole rings becomes shorter in **1o** than in **2o**. This results in the shorter horizontal axis and longer longitudinal axis in **1o** than in **2o**. Similar tendency is observed for the closed-ring isomer as well. However, the strong framework of the closed-ring isomer suppresses the difference in horizontal and longitudinal axes between the **1c** and **2c**.

The large geometrical change of the diarylethene molecule induces the deformation of the crystal lattice as well as the bending and salient phenomena. The photoinduced changes in the cell parameters were directly observed by X-ray analysis on a UV-irradiated crystal of **1o** (**1o-UV** in Table S1 in the Supporting Information).[17] Upon UV irradiation, the *a*- and *b*-axes were elongated from 13.3855(4) to 13.4391(6) Å (+0.40%) and from 25.1206(9) to 25.2408(14) Å (+0.48%), respectively, while the *c*-axis was contracted from 14.7089(5) to 14.6414(8) Å (−0.46%) accompanied with the 0.45% increment of angle β. The expansion of the horizontal axes of the diarylethene molecule upon photocyclization contributes to the elongation of the *a*-axis, which is parallel to the long axes of the thin plate crystals of **1o**. Therefore, the crystals bent in the direction away from the UV light source (Figures 2a, b). The large shape changes from **1o** to **1c** in the crystals, and the orientation of the two conformers also gives rise to the effective photosalient effect. By performing the crystographic analysis on the electron density peaks of the sulfur atoms for a UV-irradiated crystal as has been done previously,[18] we obtained the ratio of photocyclization for two conformers (Figure S5 in the Supporting Information). After UV irradiation, the conformer A converted to the closed-ring isomer of 6.9%, while the conformer B converted to that of 4.4%. The different conversion of open-ring isomers with different orientation in the crystal will also work for photosalient effect (Figure S5 in the Supporting Information). The photosalient phenomena were observed mainly after bending. To induce photosalient effect, much more conversion and difference of the conversions to their closed-ring isomers of the two conformers of open-ring isomers are necessary. The explosive scattering (Figure 2d) can be attributed to the significant deformation in the *ac*-plane, which corresponds to the large (010) face of the thin plate crystal. The diarylethene molecules are stacked along the *c*-axis. The shrinkage of the thickness of the diarylethene molecule upon photocyclization results in contraction along the *c*-axis. The accumulated strain produced by the elongating and contracting deformation in the *ac*-plane induces the scattering phenomenon. The photoinduced jump of the **1o** crystal on the surface of a lotus leaf (Figure 2c) and the photoinduced breaking of the crystal **1o** are included in the Supporting Information as movies.

A diarylethene having perfluorocyclohexene **1o** undergoes a cyclization reaction to form **1c** even in the crystalline state. Due to the large geometrical changes in the molecules during the reaction, the thin crystals broke into their pieces explosively. This is in very clear contrast to changes in the corresponding thiazole-based diarylethene having perfluorocyclopentene **2o**, which shows reversible bending upon UV irradiation. The diarylethene **1o**, having the size of a six-membered ethene moiety, showed larger changes in the size of the molecule during a cyclization reaction in the crystalline state and induced remarkable photosalient phenomena. In general terms, modification of the molecular structure of diarylethenes will induce the more remarkable photosalient effect and will be the candidates to represent a direct and visually impressive demonstration of the conversion of light into mechanical motion through a photochemical reaction on a macroscopic scale, which will be a foundation for the new design of fast biomimetic and techno-mimetic actuating materials that can mimic impatiens and squirting cucumber.

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Keywords: Photosalient effect • Photochromism • Diarylethene • Perfluorocyclohexene

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Layout 1:

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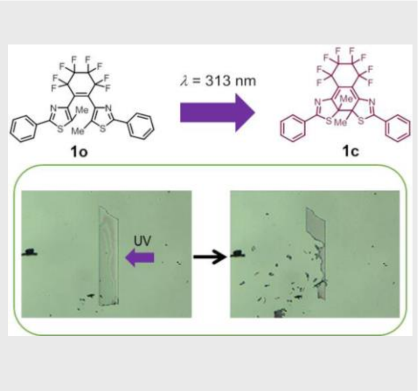

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