CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Title: Photosalient effect of diarylethene crystals of thiazoyl and thienyl derivatives

Authors: Kingo Uchida, Yuma Nakagawa, Masakazu Morimoto, Nobuhiro Yasuda, Kengo Hyodo, Satoshi Yokojima, and Shinichiro Nakamura

To be cited as: *Chem. Eur. J.* 10.1002/chem.201900811

Link to VoR: http://dx.doi.org/10.1002/chem.201900811

Supported by ACES

WILEY-VCH

Photosalient effect of diarylethene crystals of thiazoyl and thienyl derivatives

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

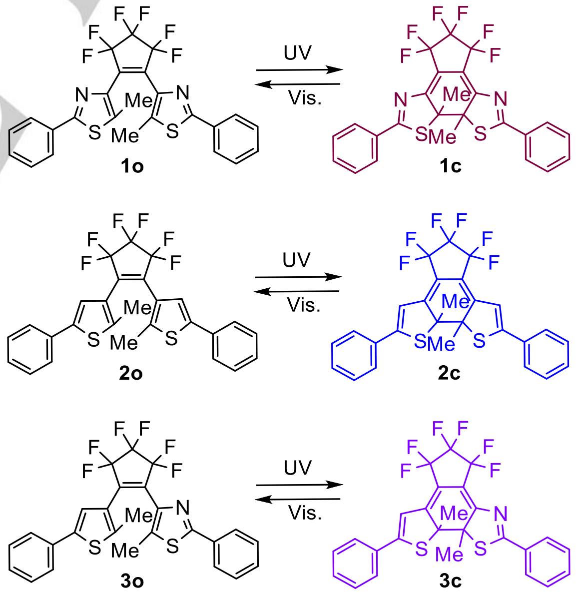
Abstract: The photo-response of diarylethene crystals is found to depend on the intensity of UV light, i.e., photoinduced bending is switched to photosalient phenomena by increasing the light intensity. The size change in crystal unit cell upon UV irradiation is larger for asymmetric diarylethenes having thiazole and thiophene rings than for corresponding symmetric diarylethenes. As a result, the crystals of an asymmetric diarylethene show much more drastic photosalient effects than do the corresponding symmetric diarylethene crystals upon UV irradiation. We also discover that the crystals of diarylethene, which had no previous report of a photosalient effect, show photosalient phenomena upon irradiation with strong UV light. We further report the dependence of photosalient phenomena on the size and shape of the crystals.

Introduction

The scattering phenomenon of artificial crystals by light stimuli is called the photosalient effect.[1–11] The first organic photosalient effect was reported by Trommsdorff in 1834 on the bursting of crystals of α-santonin after they turned yellow by exposure to sunlight.[1] The photosalient effect has recently been the subject of further investigations.[4] Naumov *et al.* intensively studied the crystal jumping and breaking that resulted from strong light stimuli. Consequently, they named this the photosalient effect.[5-10]

Diarylethenes are thermally stable photochromic compounds that undergo cyclization and cycloreversion reactions upon alternate irradiation with UV and visible light.[11] Photoinduced bending and twisting phenomena are commonly observed in diarylethene crystals.[12,13] Recently, we synthesized a diarylethene having a perfluorocyclohexene ring with two thiazole rings. The thin crystals of this diarylethene prepared by sublimation showed photochromism as well as the photosalient effect.[14] Specifically, they showed bending, jumping, and scattering upon UV irradiation.[14]

In this work, symmetric diarylethenes **1o** and **2o** were synthesized, where **1o**[15] has thiazole rings and **2o**[16] has thiophene rings at both ends of the molecule (Scheme 1). Photochromism in these solutions has already been reported.[15,16] Photoinduced bending behavior of the crystals has also been reported, whereas no photosalient phenomena has been reported.[12,17] We prepared an asymmetric diarylethene **3o** (Scheme 1) according to a previous paper.[18] We prepared the crystals of **1o**, **2o**, and **3o** by recrystallization from hexane solutions as well as by sublimation. As a result, photo-induced phenomena were observed in all three of these crystals.



Scheme 1. Molecular structures of diarylethenes **1**, **2**, and **3**.

Results and Discussion

Although, synthesis of **3** was carried out by a microflow system, the photochromic properties were not considered in that earlier work.[18] We first investigated the absorption spectral changes of **3** in hexane solution (Figure S1). Open-ring isomer **3o** has an

---

[a] Y. Nakagawa, Dr. K. Hyodo, Prof. K. Uchida*
Department of Materials Chemistry
Faculty of Science and Technology, Ryukoku University, Seta
Otsu, Shiga 520-2194, Japan
E-mail: uchida@rins.ryukoku.ac.jp

[b] Prof. M. Morimoto*
Department of Chemistry and Research Center for Smart Molecules
Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima-ku
Tokyo 171-8501, Japan
E-mail: m-morimoto@rikkyo.ac.jp

[c] Dr. N. Yasuda
Japan Synchrotron Radiation Research Institute
1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

[d] Prof. S. Yokojima
School of Pharmacy, Tokyo University of Pharmacy and Life Sciences
1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan.

[e] Prof. S. Yokojima, Dr. S. Nakamura, Prof. K. Uchida*
RIKEN, Cluster for Science, Technology and Innovation Hub
Nakamura Laboratory, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.

Supporting information and the ORCID identification number for the author of this article can be found under

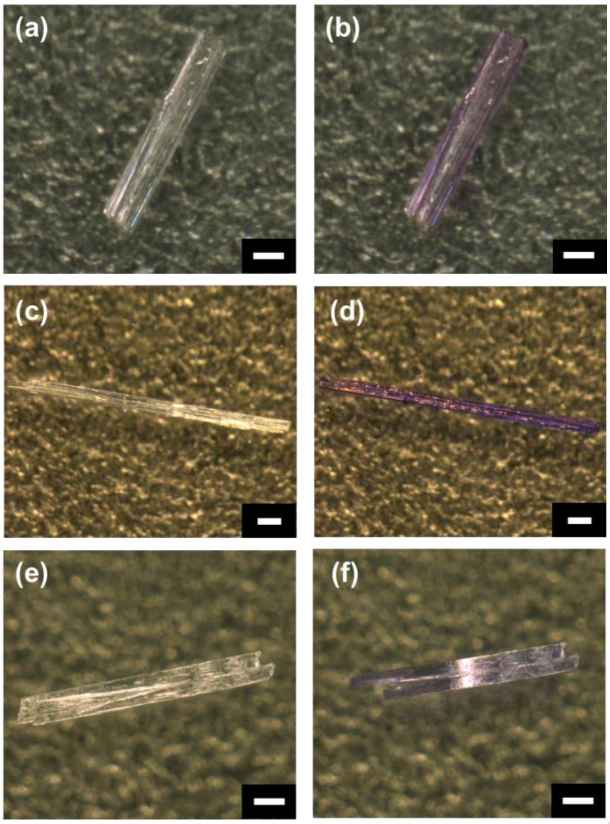


Figure 1. Photochromism of single crystals of diarylethenes (**1o**): (a) and (b), (**2o**): (c) and (d), and (**3o**): (e) and (f). Before UV irradiation: (a, c, e) and after UV irradiation: (b, d, f). Scale bars: 200 μm for (a, b, e, f), and 100 μm for (c, d).

absorption band at 295 nm in hexane. Upon UV irradiation, the colour of the solution turned purple and a new band appeared at 550 nm, which is attributed to **3c**. Upon visible light irradiation, the colour disappeared and the band of **3o** was regenerated. Absorption coefficients and quantum yields are summarized in Table 1, together with those of **1** and **2**. The absorption maxima of open- and closed-ring isomers and the quantum yields of photochromic reactions (cyclization ($\Phi_{o\rightarrow c}$) and cycloreversion ($\Phi_{c\rightarrow o}$)) closely approximate the values averaged between the corresponding symmetric derivatives **1** and **2**. This has often been observed in other asymmetric diarylethene derivatives.[18,19]

The photochromism of **1o** and **2o** in crystalline states has already been reported. A single crystal of newly prepared **3o** also showed photochromism upon alternate irradiation with UV and visible lights. Upon UV irradiation at weak intensity (λ = 365 nm, 810 μW cm^{-2}) for 30 min, crystals of **1o** and **2o** showed coloration without any photosalient phenomenon (Figure 1a-d). These results are consistent with previous reports.[15,16] Upon irradiation by the same weak intensity of UV light (λ = 365 nm, 810 μW cm^{-2}), the crystal **3o** displayed both coloration and photosalient phenomena when irradiation was prolonged (80 s) (Figure 1e and f, Movie S1).

Upon strong UV irradiation (λ = 365 nm, 277 mW cm^{-2}) to the crystals prepared by recrystallization from hexane solutions, all crystals of **1o**, **2o**, and **3o** showed remarkable photosalient phenomena on their surfaces accompanied with coloration (Figure 2, Figure S2-4). A schematic illustration showing the differences is also given in Figure 2g-i. To compare the crystals' reactivity and deformation, we conducted X-ray analysis of these crystals of open- and closed-ring isomers upon 400-nm light irradiation for 1 min under the same conditions (results summarized in Table S1). Graphical images of the deformations for each crystal are depicted in Figure 3.

Under UV irradiation (λ = 365 nm, 277 mW cm^{-2}), cracks appeared on the surface of **1o** crystals perpendicular to the long axis, followed by the crystal surface being cast off. Moreover, flipping[5] of the peeled[20] crystalline surface was also observed (Figure 2a and b, Figure S2). This is due to shrinkage of 0.50% along the a-axis, which is parallel to the crystal's long axis (Figure 2a, Table S1). When the crystals are thin, the crystal showed reversible shrinkage and elongation by alternate irradiation with UV and visible light. When the aspect ratio of **1o** crystal is high, the crystal showed bending concave to the incidence of UV light.[12] In our case, the crystal is thick enough not to bend, and only the surface was photo-converted to **1c** and shrank along the long axis of the crystal (a-axis). Then cracks were generated perpendicular to the a-axis. Each fragmented crystal showed bending and dispersion on the surface (Figure 2g, Movie S2). At the same time, flipping of the crystals was also observed (Figure S2, Movie S3).

For the crystals of **2o**, cracks in the vertical and horizontal directions appeared on the surface. Upon UV irradiation (λ = 365 nm, 277 mW cm^{-2}), the crystalline surface collapsed (Figure 2c and d, Figure S3). Diarylethene **2o** also changed its molecular size in the crystal, and ribbon shaped crystals have been reported to show complicated helical deformation, depending on the direction of the incident light.[17] This is due to the herringbone orientation of **2o** molecules in the crystals, where two conformers exist in a unit cell. The size changes of the unit cell of **2o** were the smallest among those of the three derivatives, so only a modest photosalient phenomenon was observed for **2o**. Nevertheless, it is significant that small-fragment scattering was observed on the surface during UV irradiation (Figure 2h, Movie S4). The cracking pattern may be attributed to the release of photo-induced shrinkage of the a- and c-axes (indicating shrinkage of the crystal's surface area) with the expansion caused by elongation of the a-axis (vertical direction of the

Table 1. Photochromic properties of diarylethene **1**, **2**, and **3** in hexane solution.

Compound	λ_{max} / nm (ε / 10^4 M^{-1} cm^{-1})		$\Phi_{o\rightarrow c}$ (313 nm)	$\Phi_{c\rightarrow o}$ (492 nm)
	Open-ring isomer	Closed-ring isomer		
1[15]	300 (3.4)	525 (1.0)	0.32	0.020
2[16]	280 (3.6)	575 (1.6)	0.59	0.013
3	295 (3.5)	550 (1.5)	0.25	0.013

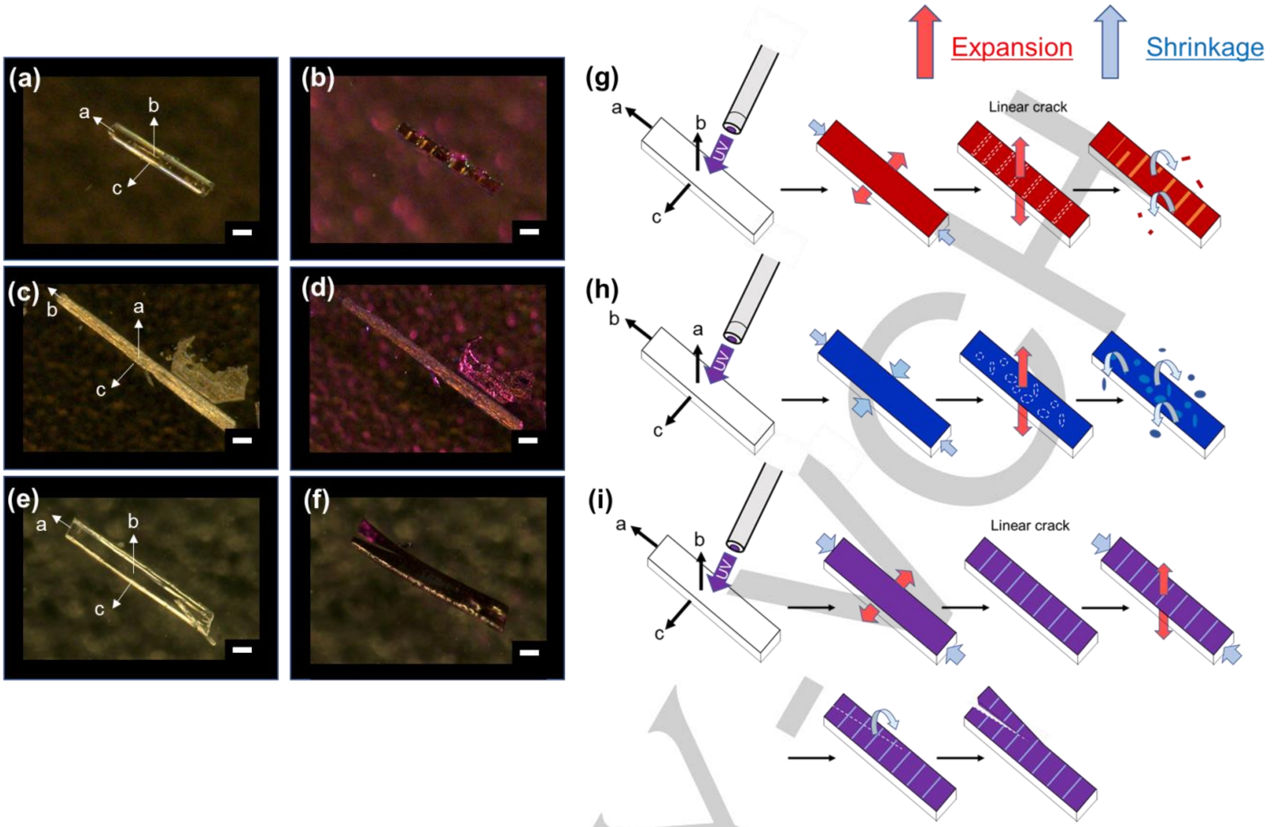


Figure 2. Photosalient effect of single crystals of diarylethenes (**1o**): (a) and (b), (**2o**): (c) and (d), and (**3o**): (e) and (f). Before UV irradiation (λ = 365 nm, 277 mW cm^{-2}): (a), (c) and (e) and after UV irradiation: (b), (d) and (f). Scale bars: 100 µm. Schematic illustration of the differences in photosalient phenomena of **1o**: (g), **2o**: (h), and **3o**: (i).

surface). The direction of photoinduced size changes is different from those found in other crystals (Figure 2c, Table S1). Therefore, cracking perpendicular to the long axis of the crystal such as **1o** was not observed for **2o**; instead, irregular breakage of the crystal surface was observed. From the recrystallization of **2o** in a hexane solution, not only rod-shaped but also cubic-shaped crystals were obtained. In spite of the difference in the crystal habit, both types of crystals have the same crystal structures. Peeling phenomena were observed for both of them (Figure S3, Movie S5).

Upon UV irradiation to the single crystal of **3o**, a drastic collapse of the crystal surface was observed. Small cracks were initially generated perpendicular to the long axis on the surface, then drastically larger cracks were generated along the long axis and the whole crystal was scattered (Figure 2e, f and i, Movie S6). The initial cracks on the surface are attributed to the shrinkage of the a-axis of the unit cell, and as a result only cracks appeared while no breaking of the crystal followed in this direction. On the other hand, the b-axis of the unit cell expanded at the maximum ratio in these crystals (Table S1). The direction corresponds to the increase in the widths of **3o** crystals. Therefore, this induced tearing along the long axis of the **3o** crystals.

In this study, we examined the correlation of area, thickness, and volume of crystals, with respect to the latent periods until the development of the photosalient effect, for three types of diarylethene bulk crystals. There was no such correlation in the latent periods until the appearance of crystal surface cracks commonly found in the three types of diarylethene crystals as

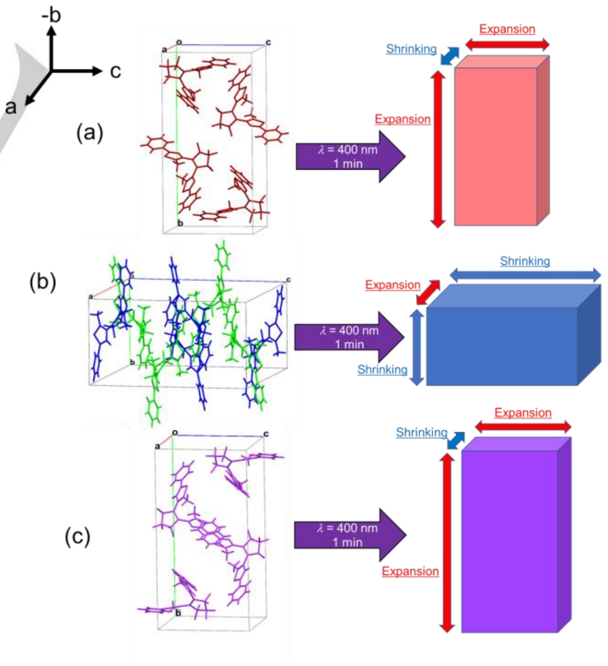


Figure 3. Crystal lattice fluctuation of **1o** (a), **2o** (b), and **3o** (c) upon 400-nm light irradiation.

shown in the supplement (**1o**: Figure S6, **2o**: Figure S7, and **3o**: Figure S8). This is because UV light (λ= 365 nm) is absorbed on the crystal surface and light does not reach the backside of the crystal. That is, in a crystal the dye highly concentrates, and thus the entire molecules in the crystal do not isomerize.[12] The photosalient phenomenon originates in the tension between non-reacted interior and the reacted surface. Therefore, the photosalient phenomenon on the crystal surface has no correlation with the area, thickness and volume of the crystals. In contrast, for the phenomena occurring in the whole crystal, the latent periods for each crystal and the corresponding phenomena are different from each other. Therefore, it is necessary to examine a correlation between crystal area, thickness and volume as mentioned by Naumov.[5] Actually, the tearing of **3o** crystals has dependence on the thickness of the crystal, and a thicker crystal takes more time to tear. In fact, in crystals with a certain minimum thickness, cracks were observed only on the surface, but such crystals never split (Figure 4).

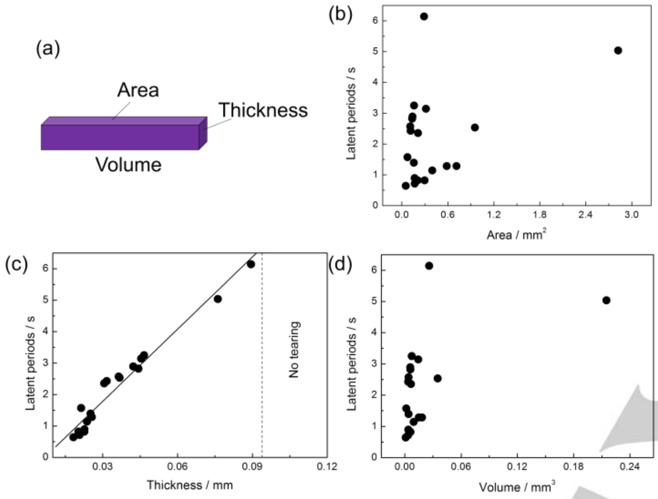


Figure 4. Illustration of crystal (a) and the latent periods of photosalient effect (tearing) by area (b), thickness (c), and volume (d) for crystal **3o** under UV irradiation (λ = 365 nm, 277 mW cm^{-2}).

X-ray crystallographic analysis of **3o** was carried out, and the results were compared with those of **1o** and **2o**. The 400-nm light was irradiated for 1 min for all crystals, and the deviation of the crystal axis was monitored. The data are summarized in Table S1. Upon 400-nm light irradiation for 1 min to a crystal of **1o**, the a-axis shrank by 0.50%, while the b- and c-axes expanded by 0.50, and 0.19%, respectively. As a result of these changes, the volume of a unit cell expanded by 0.20%. For a **2o** crystal, the a-axis expanded by 0.41%, while the b- and c-axes shrank by 0.24, and 0.04%, respectively. As a result of these changes, the volume of a unit cell expanded by 0.26% under the same irradiation.

For a **3o** crystal, the a-axis shrank by 0.73%, while the b- and c-axes expanded by 0.89, and 0.13%, respectively. The large shrinkage along the a-axis induced cracking, and the expansion along the b-axis induced tearing. Then the unit cell volume of the **3o** crystals expanded by 0.35%, which was the largest change among the three crystals. Furthermore, the largest changes among all axes were observed for the crystal of **3o**; such changes in **1o** were moderate, and those in **2o** were the smallest. As a result of having the largest overall changes, the crystal of **3o** has shown the most dramatic photosalient phenomena among the three derivatives. Such dramatic phenomena were observed in Naumov's system.[5,21] Here, each fragmented surface crystal also jumped or scattered, and in fact the most dramatically impressive photosalient phenomena were again observed for **3o** crystals.

We next attempted to confirm whether the photosalient phenomena observed here were due to the strain caused by the photoisomerization, i.e., we investigated the thermal effect due to the strong UV irradiation. During the strong UV irradiation, the temperature of each surface was monitored by thermography (testo 882). Even upon strong UV irradiation, the temperature on the crystals remained nearly unchanged (at room temperature (24-26 °C): temperature increase due to UV irradiation; 0.9 ± 0.3 °C, under cooling (at 3-5 °C): it was 0.6 ± 0.5 °C). Accordingly, we conclude that the contribution of temperature rising was negligible (Figure S10-S18).

Large changes in the unit cell of the crystals induced rapid responses of the photosalient effect. The relationships of latent periods to light intensities for these crystals are summarized in Figure 5. Naturally, irradiation with stronger light shortens the latent periods. With relatively weak intensities of light (below 300 mW cm^{-2}), the responsiveness of the salient phenomena (i.e. shorter latent periods) was **3o** > **1o** > **2o**. This order is in agreement with the order of the relative axis changes of the unit cells.

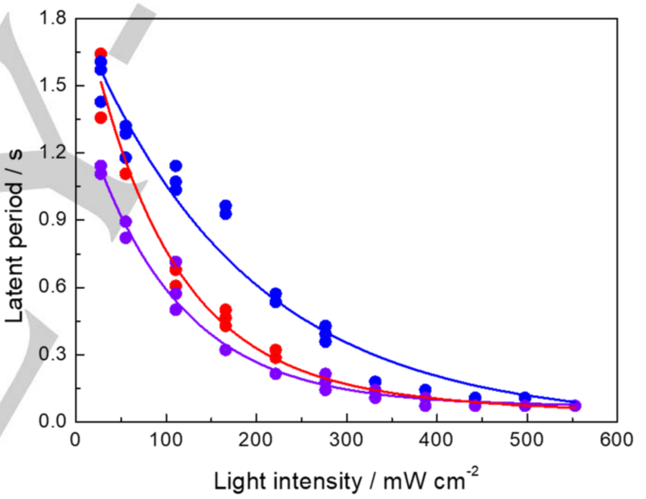


Figure 5. Relationship between UV light intensity (λ = 365 nm) and latent periods for single crystals of **1o** (red circles), **2o** (blue triangles), and **3o** (violet squares). Focusing on the peeling phenomenon, the latent periods were calculated for the photosalient effect.

The results mentioned above indicate that the photosalient phenomena on the crystalline surface of bulk crystals obtained by recrystallization are independent on crystal size. However, the photosalient (tearing) phenomena of the thin crystals prepared by sublimation showed dependence on the thickness of crystals. For the thin crystals of **1o** and **2o**, photoinduced bending phenomena were already been reported, but there has been no report on photosalient phenomena.[12,17] The crystal structures of thin crystals have been reported to be the same as those of bulk crystals of **1o** and **2o** prepared by recrystallization.[12,17] Moreover, the structure of the thin crystals of **3o** was the same as that of bulk crystals from recrystallization. (Table S2, Figure S19). We prepared thin crystals of **1o**, **2o**, and **3o** by sublimation and observed their photoreactive motions upon weak (λ = 365 nm, 810 μW cm^{-2}) and strong (λ = 365 nm, 277 mW cm^{-2}) UV light irradiation. Initially, weak UV light was irradiated to the crystals. Consequently, they showed

10.1002/chem.201900811

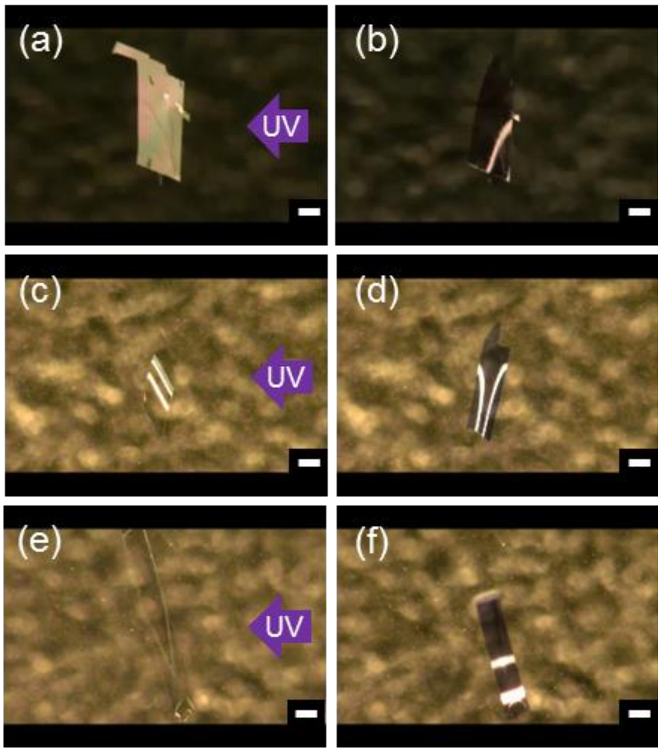


Figure 6. Photoinduced bending of thin crystals of diarylethenes (**1o**): (a) and (b), (**2o**): (c) and (d), and (**3o**): (e) and (f). Before UV irradiation (λ = 365 nm, 810 μW cm-2): (a, c, e) and after UV irradiation: (b, d, f). Scale bars: 100 μm.

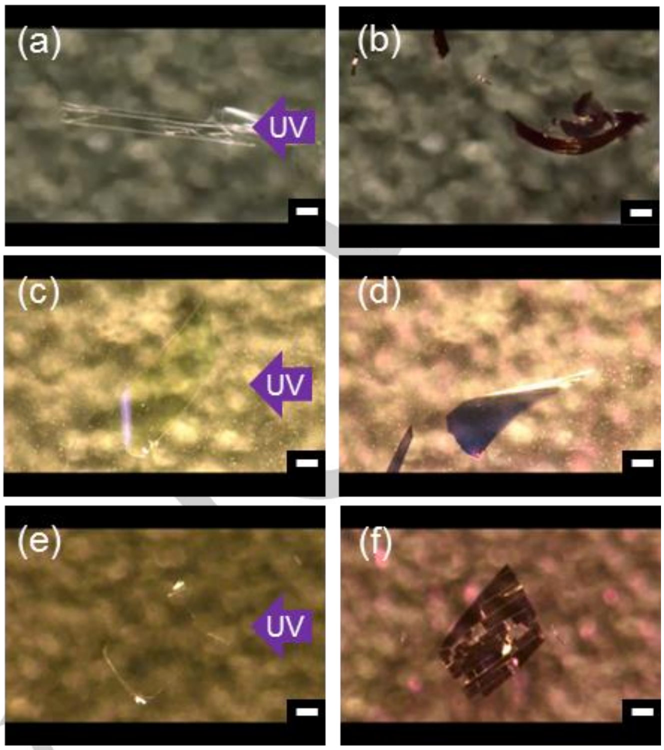


Figure 7. Photosalient effect of thin crystals of diarylethenes (**1o**): (a) and (b), (**2o**): (c) and (d), and (**3o**): (e) and (f). Before UV irradiation (λ = 365 nm, 277 mW cm^{-2}): (a), (c) and (e), and after UV irradiation: (b), (d) and (f). Scale bars: 100 μm.

photoinduced bending as reported,[12,17] where no photosalient phenomena occurred (Figure 6).

The strong UV light was then irradiated to the same thin crystals (Figure 7). Now, instead of bending, the thin crystals of **3o**, among the three types, showed distinct photosalient phenomena. The thin crystal of **1o** showed bending followed by scattering into small pieces. The thin crystals of **2o** also showed bending with strong UV light. Some thin crystals of **2o** showed cracking without bending (Figure S20). As soon as the UV light was irradiated to the thin crystals of **3o**, they immediately and explosively broke down (Figure 7e and f, Movie S7); they also showed jumping, which is a much more dramatic photosalient phenomenon compared to the phenomena of **1o** and **2o** (Figure S21, Movie S8). This is attributed to the large size changes from **3o** to **3c** compared with those of the other crystals (Figure 3).

Moreover, when irradiating UV light to **3o** rod crystals, photoinduced bending was observed with weak UV light and a photosalient effect was observed with strong UV light, as with the thin crystals (Figure 8). Specifically, the **3o** rod crystal showed bending when irradiated with weak UV light but reversibly changed back to its original shape with irradiation by visible light (observation of digital microscope: white light). The reversible bending was successively controlled upon alternate irradiation with the weak UV and visible lights (Figure S23). In comparing the curvature on the crystal with weak and strong UV light, the strong UV light produces bending in a short time than does the weak UV light. With strong UV light, the crystal cracked when it bent to about half of the maximum curvature value reached by weak UV light (Movie S9). Therefore, photoinduced bending and photosalient phenomena of the thin crystals of **3o** were certainly switched as a function of the intensity of UV light (810 μW cm^{-2} or 277 mW cm^{-2}). Recently, Chizhik and co-workers proposed an elaborated model to describe the photoinduced bending motion of molecular crystals.[22] Although their model is quite general, the light intensity considered in their study is much weaker than that in our study. It will be interesting to investigate the threshold between the bending and salient but it is beyond the scope of this paper.

Conclusions

The photosalient phenomena of crystals found in three diarylethenes were examined while focusing on the effect of crystal size and UV intensity. Although the diarylethenes of **1o** and **2o** have been previously investigated in detail, there has been no report on the photosalient effect of their crystals.[12,17] This is due to the fact that the photosalient effect was observed only when strong UV light was irradiated. Consequently, it is likely that a much wider class of crystals of diarylethenes may show the photosalient effect upon irradiation with strong UV light. This possibility should be carefully investigated not only for application of the photosalient effect but also for our understanding of the limitations of using the intensity of UV/visible light in applying the bending phenomena.

For the bulk crystals prepared by recrystallization, UV-induced peeling of the surfaces was observed. The peeling phenomena appeared on the crystalline surfaces, so they were independent of crystal sizes. On the other hand, the photosalient phenomena

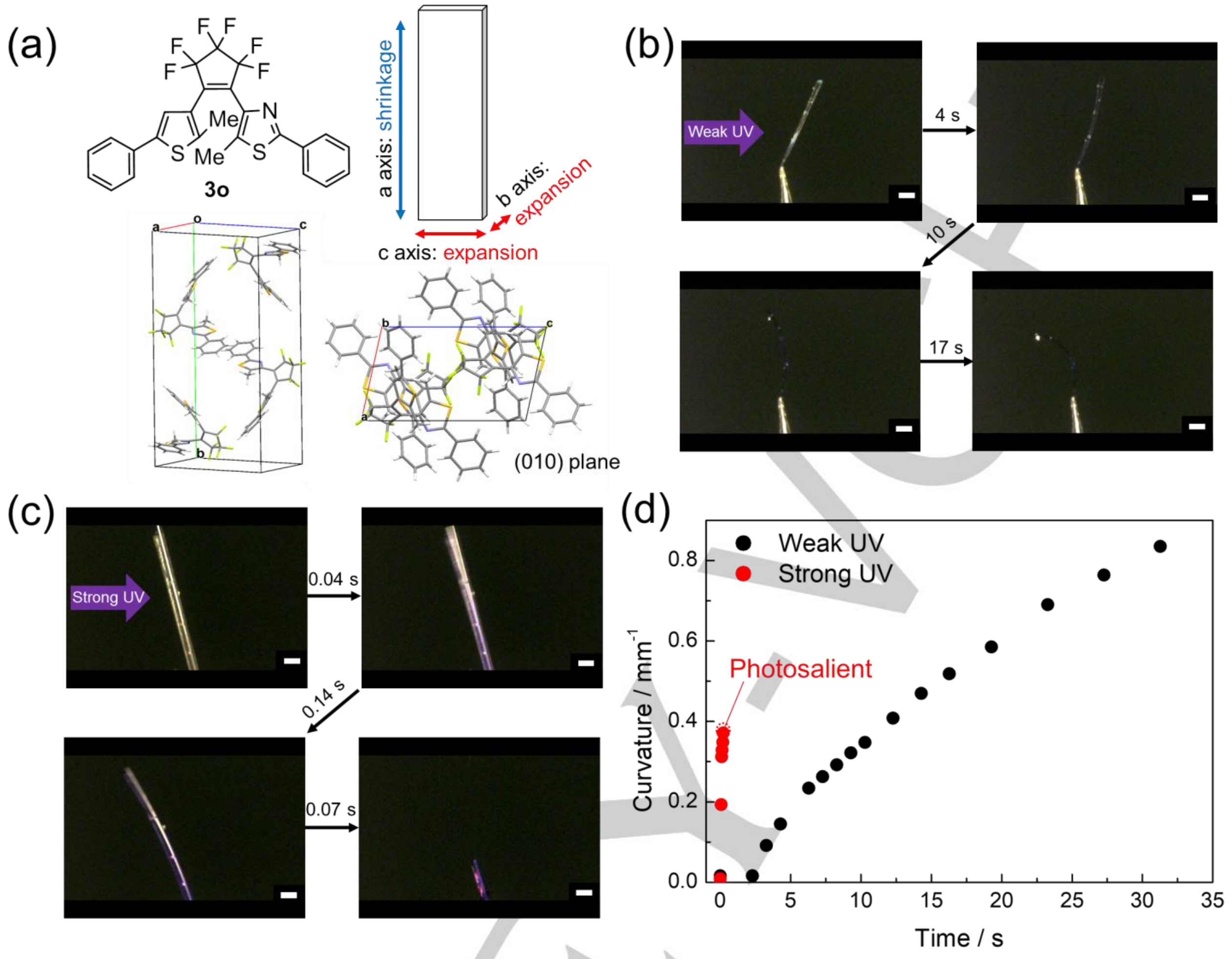


Figure 8. (a) Molecular packing of **3o**. (b) Photoinduced bending of **3o** rod crystal due to weak UV light (**3o** rod crystal: 2.29 × 0.132 × 0.0325 mm (length × width × thickness), λ = 365 nm, 810 μW cm^{-2}). (c) Photosalient effect of **3o** rod crystal due to strong UV light (**3o** rod crystal: 1.01 × 0.154 × 0.0351 mm (length × width × thickness), λ = 365 nm, 277 mW cm^{-2}). (d) Change in the curvature with irradiation time: photoinduced bending of (b) (black circles) and photosalient effect of (c) (red circles). Scale bars: 0.4 mm for (b), and 100 μm for (c). Both (b) and (c) were irradiated from the b-axis direction.

of thin crystals prepared by sublimation did show the size dependency. In particular, the photosalient phenomena of the crystal of **3o** showed dependence on thickness, i.e., thinner crystals of **3o** showed more remarkable photosalient phenomena. As soon as UV light was irradiated, breaking and jumping phenomena occurred. This finding is in contrast to the observation that the thin crystal of **3o** only showed bending with coloration upon weak UV light irradiation. For a bulk crystal of **3o**, the crystal showed coloration upon weak UV irradiation, while breaking occurred throughout the entire crystal. The crystal of **3o** showed the most remarkable photosalient phenomena in its ability to switch the photoresponse depending on the UV light intensity. Recently, the application of the photosalient phenomena has been reported for the hybrid material of an electrical fuse link,[23] and for hollow-crystal scattering inclusions.[24] In the near future, photosalient phenomena will be given much more attention, and related applications could be developed by effectively controlling these phenomena by light intensity. We believe the current results provide an important clue toward achieving this goal.

Acknowledgements

The authors express thanks to A. Fujimoto, R. Nishimura, R. Kono, and A. Nagai for their help for measurements of thin crystals of **3o** at a synchrotron radiation facility Spring-8, and are grateful to Zeon Co., Ltd., for providing the octafluorocyclopentene to synthesize the diarylethene derivatives having perfluorocyclopentene moiety. This work was supported by JSPS KAKENHI Grant Number JP26107012, JP15H01096, and JP17H05272 in Scientific Research on Innovative Areas “Photosynergetics” and the CREST program (JPMJCR17N2) of the Japan Science and Technology Agency, the Core-to-Core Program A. The synchrotron radiation experiments were performed using the BL02B1, BL40B2 and BL40XU beamlines of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2014B1213, 2015A1240, 2015B1215, 2018A1104, 2018A1208, 2018B1091, 2018B1092 and 2018B1674).

10.1002/chem.201900811

Conflicts of interest

There are no conflicts of interest to declare.

Keywords: photochromism • diarylethene • crystal • photosalient effect • asymmetric structure

References

[1] H. Trommsdorff, *Ann. Chem. Pharm.*, **1834**, *11*, 190-207.

[2] H. D. Roth, *Angew. Chem. Int. Ed. Engl.*, **1989**, *28*, 1193-1207.

[3] M. A. Garcia-Garibay, *Acc. Chem. Res.*, **2003**, *36*, 491-498.

[4] P. Commins, A. Natarajan, C.-K. Tsai, S. I. Khan, N. K. Nath, P. Naumov, M. A. Garcia-Garibay, *Cryst. Growth Des.*, **2015**, *15*, 1983-1990.

[5] P. Naumov, S. C. Sahoo, B. A. Zakharov, E. V. Boldyreva, *Angew. Chem. Int. Ed.*, **2013**, *52*, 9990-9995.

[6] P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath, E. Boldyreva, *Chem. Rev.*, **2015**, *115*, 12440-12490.

[7] N. K. Nath, M. K. Panda, S. C. Sahoo, P. Naumov, *CrystEngComm*, **2014**, *16*, 1850-1858.

[8] R. Medishetty, A. Husain, Z. Bai, T. Runčevski, R. E. Dinnebier, P. Naumov, J. J. Vittal, *Angew. Chem. Int. Ed.*, **2014**, *53*, 5907-5911.

[9] M. K. Panda, T. Runčevski, A. Husain, R. E. Dinnebier, P. Naumov, *J. Am. Chem. Soc.*, **2015**, *137*, 1895-1902.

[10] N. K. Nath, T. Runčevski, C.-Y. Lai, M. Chiesa, R. E. Dinnebier, P. Naumov, *J. Am. Chem. Soc.*, **2015**, *137*, 13866-13875.

[11] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.*, **2014**, *114*, 12174-12277.

[12] S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature*, **2007**, *446*, 778-781.

[13] K. Uchida, S. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y. Kojima, S. Nakamura, J. Areephong, A. Meetsma, B. L. Feringa, *Chem. Commun.* **2008**, 326-328.

[14] E. Hatano, M. Morimoto, K. Hyodo, N. Yasuda, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Eur. J.*, **2016**, *22*, 12680-12683.

[15] K. Uchida, T. Ishikawa, M. Takeshita, M. Irie*, Tetrahedron*, **1998**, *54*, 6627-6638.

[16] M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.*, **2000**, *122*, 4871-4876.

[17] D. Kitagawa, H. Tsujioka, F. Tong, X. Dong, C. J. Bardeen, S. Kobatake, *J. Am. Chem. Soc.*, **2018**, *140*, 4208-4212.

[18] Y. Ushiogi, T. Hase, Y. Iinuma, A. Takata, J. Yoshida, *Chem. Commun.*, **2007**, 2947-2949.

[19] K. Uchida, M. Irie, *Chem. Lett.*, **1995**, 969-970.

[20] F. Terao, M. Morimoto, M. Irie, *Angew. Chem. Int. Ed.*, **2012**, *51*, 901-904.

[21] R. Medishetty, S. C. Sahoo, C. E. Mulijanto, P. Naumov, J. J. Vittal, *Chem. Mater.*, **2015**, *27*, 1821-1829.

[22] S. Chizhik, A. Sidelnikov, B. Zakharov, P. Naumov, E. Boldyreva, *Chem. Sci.*, **2018**, *9*, 2319-2335

[23] A. Khalil, E. Ahmed, P. Naumov, *Chem. Commun.*, **2017**, *53*, 8470-8473.

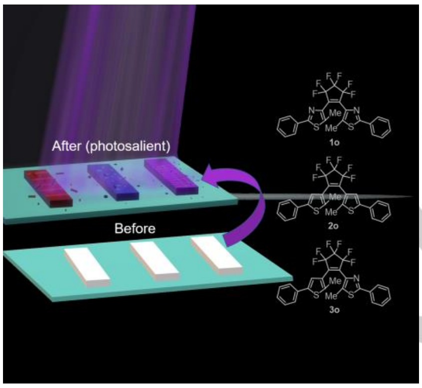
[24] E. Hatano, M. Morimoto, T. Imai, K. Hyodo, A. Fujimoto, R. Nishimura, A. Sekine, N. Yasuda, S. Yokojima, S. Nakamura, K. Uchida, *Angew. Chem. Int. Ed.*, **2017**, *36*, 12576-12580.

.

Entry for the Table of Contents (Please choose one layout)

FULL PAPER

Photosalient phenomena were observed on diarylethene crystals by amplifying the UV incidence. The patterns were dependent on the molecular ordering.



*Y. Nakagawa, M. Morimoto,**
N. Yasuda, K. Hyodo, S. Yokojima,
*S. Nakamura, K. Uchida**

Page No. – Page No.

Photosalient effect of diarylethene crystals of thiazoyl and thienyl derivatives