

Photochromism of diarylethene single crystals: crystal structures and photochromic performance†

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Diarylethenes undergo thermally irreversible and fatigue-resistant photochromic reactions not only in solution but also in the single-crystalline phase. This article describes recent development of the single-crystalline photochromism of diarylethene derivatives. We focused on the relationship between their crystal structures and the photochromic performance. Photocyclization/cycloreversion quantum yields, absorption spectra, the absorption anisotropies, and surface morphology changes are strongly dependent on the conformations and packing structures of the molecules in the crystals.

Introduction

Photochromism is defined as a reversible transformation between two isomers with different absorption spectra upon irradiation with light of appropriate wavelengths.¹ Most photochromic compounds undergo thermally reversible photochromic reactions. The photogenerated coloured isomers are thermally unstable and return to the initial colourless forms even in the dark. In addition, the compounds significantly change their geometrical structures during the photochromic reactions. The molecular shape and size are different between

the two isomers. Therefore, compounds that exhibit photochromic reactions in the crystalline phase are very rare. In general, microcrystalline powders of photochromic compounds don't show any colour change upon photoirradiation.

To date, several photochromic compounds, such as paracyclophanes,² *N*-salicylideneanilines,³ aziridines,⁴ triaryl-imidazole dimers,⁵ diphenylmaleonitrile,⁶ 2-(2,4-dinitrobenzyl)pyridines,⁷ triazines,⁸ and others⁹ have been reported to undergo photochromism in the crystalline phase. Most of the photogenerated coloured states are also thermally unstable at room temperature. These thermally unstable photochromic systems are not suitable for the detailed study of the reaction mechanism in crystals. It is indispensable to develop photochromic compounds which undergo thermally irreversible photochromic reactions to reveal the mechanism in crystals and also for the application to optoelectronic devices. In this article, we describe the photochromism of thermally irreversible diarylethene derivatives in the single-crystalline phase.

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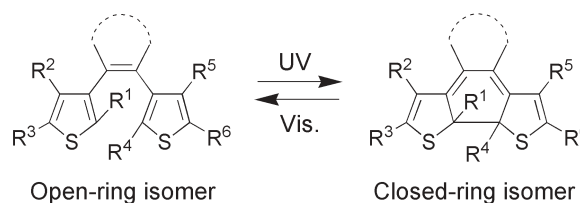
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Professor Masahiro Irie received his BS (1966) and MS (1968) degrees from Kyoto University and his PhD (1973) degree in radiation chemistry from Osaka University. In 1968, he joined the Faculty of Engineering, Hokkaido University, as a research associate and started his research on photochemistry. In 1973, he moved to Osaka University and was promoted to Associate Professor at the Institute of Scientific and Industrial Research in 1978. In 1988, he was appointed Professor in Advanced Material Study, Kyushu University; in 1996, he was reappointed Professor of Chemistry with the Faculty of Engineering (the organization recently changed its name to the Graduate School of Engineering). His research interest concerns the development of photochromic diarylethenes. He received The Chemical Society of Japan Award for 2004.

General features of photochromism of diarylethene single crystals

Diarylethenes with heterocyclic aryl groups are the most promising photochromic compounds for the application to optoelectronic devices because of their outstanding performance (Scheme 1).¹⁰ Diarylethene derivatives in solution undergo thermally irreversible and fatigue resistant photochromic reactions. Both the photogenerated coloured isomers and the initial colourless isomers are stable for more than 1 000 years at room temperature,¹¹ and the colouration/



Scheme 1 Photochromism of diarylethene.

decolouration cycles can be repeated more than 10 000 times.¹² The response times of colouration/decolouration are less than 10 ps.¹³ The cyclization quantum yields in solution are moderate ($\Phi = 0.1 \sim 0.5$).¹⁴ The cycloreversion quantum yield is strongly dependent on the substituents. When methoxy groups are introduced at the central reactive carbons, the cycloreversion quantum yield is strongly suppressed to less than 10^{-4} , while it increases to 0.41 when the substituents are cyano groups.¹⁵

Diarylethene derivatives undergo thermally stable and fatigue resistant photochromic reactions not only in solution but also in the single-crystalline phase (see ESI†).¹⁶ Upon irradiation with ultraviolet (UV) light, the colourless single crystals turn yellow, red, blue, or green depending on their molecular structure, and the colours remain stable in the dark. The coloured crystals return to the initial colourless ones upon irradiation with visible light. In crystals, diarylethene molecules show a very high cyclization quantum yield. When the molecules are packed in antiparallel conformation¹⁷ and the distance between the reactive carbons is less than 0.40 nm, the cyclization quantum yield becomes close to 1 (100%).¹⁸ The large cyclization quantum yield in the crystalline phase is ascribed to three factors. One is the high population of the photoreactive antiparallel conformation in crystals. Other factors are the very low activation energy, almost zero, of the cyclization reaction^{11a} and the rapid cyclization rate, less than 10 ps.¹⁹

X-ray crystallographic analysis was carried out to reveal the reason why the crystalline photochromism can take place in diarylethene single crystals.²⁰ Fig. 1 shows the structures of diarylethene **1** (Chart 1) before and after the photocyclization reaction. As can be seen, almost all atoms remain in the same positions even after the reaction except the sulfur and the reactive carbon atoms. This small structural change allows the molecule to undergo the photochromic reaction in the crystal.

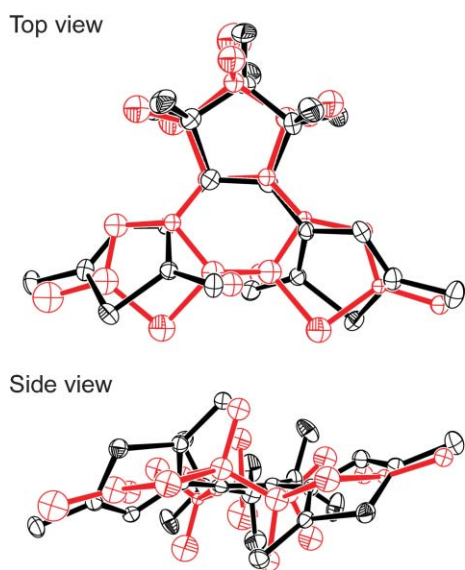


Fig. 1 ORTEP drawings of photoirradiated crystal **1**. Black and red molecules indicate open-ring and photogenerated closed-ring isomers in the crystal, respectively. Hydrogen atoms are omitted for clarity.

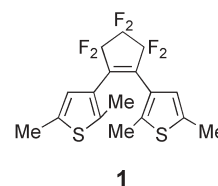


Chart 1 Diarylethene **1**.

The molecular structure of the photogenerated closed-ring isomer was found not to be the same as the structure of the most stable closed-ring isomer.²¹ Fig. 2 shows the structural differences observed in crystal **1** between the photogenerated closed-ring isomer in the crystal of the open-ring isomers and the closed-ring isomer in the crystal of the isolated closed-ring isomers. Although the C1–C10 bond lengths are the same as each other, the distance between S1 and S2 of the photogenerated isomer is larger than this distance in the most stable closed-ring isomer. This means that the structure of the photogenerated isomer is distorted. The distorted structure shifted the absorption spectrum of the closed-ring isomer to longer wavelengths than the spectrum of the most stable closed-ring isomer. The red shift was also confirmed by theoretical calculations.

Multi-colour photochromism of two- and three-component crystals

In usual one-component photochromic systems, they interconvert between only two states, “colourless” and “coloured”. On the other hand, in multi-component systems composed of different kinds of photochromic compounds, reversible multi-state switching between more than two states can be realized by the combination of two states of each component. In a two-component system, for example, four states ($2^2 = 4$) could be produced, and eight states ($2^3 = 8$) in a three-component system. Multi-component or multi-coloured systems of diarylethenes were reported for the first time by Lehn *et al.*²² They demonstrated that the absorption properties of the multi-component diarylethene mixture in solution as well as on silica-gel plates can be modulated by controlling the wavelengths, duration, and slit-width of the irradiation applied. A fused diarylethene dimer which consists of two different photochromic units has also been demonstrated.²³ Although

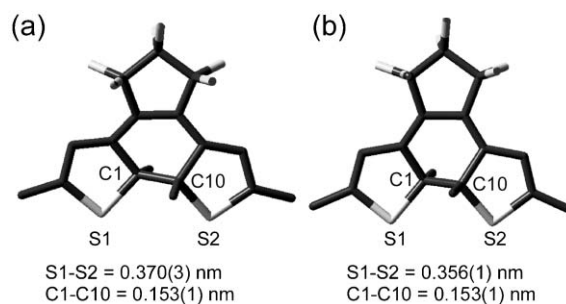


Fig. 2 Molecular structures of closed-ring isomer of **1**: (a) in UV-irradiated single crystal of the open-ring isomers, (b) in the crystal of the isolated closed-ring isomers (Ref. 21).

these systems exhibit multiple colours upon photoirradiation, colouration/decolouration cycles, photocoloration efficiency, resolution of the coloured images, and stability of the coloured state are limited. An ideal system is a multi-component single crystal because of its high durability, high efficiency of photocoloration as described before, and molecular-scale high resolution. If a multi-component photochromic crystal that contains three kinds of compounds which exhibit yellow, red, and blue colours can be prepared, the crystal is expected to show a full range of colours upon photoirradiation. As a result of examining a great variety of combination of photochromic diarylethenes, we found that diarylethenes **1**, **2**, and **3** (Chart 2) formed two- and three-component single crystals.²⁴ Two-component crystal **1**·**3** and three-component crystal **1**·**2**·**3** were prepared and their photochromic performance was examined.

By recrystallization of a mixture of **1** and **3** (molar ratio **1** : **3** = 95 : 5) from ethanol, a colourless single crystal that contains both **1** and **3** in the molar ratio of 99.6 : 0.4 was obtained.^{24a} The shape and crystallographic parameters of the crystal were the same as those of the one-component single crystal of **1**. It is suggested that **3** is substitutionally incorporated into the crystal lattice of **1**. Fig. 3a shows a photograph of partially coloured crystal **1**·**3** by irradiation with light of different wavelengths. The colourless crystal turned red upon irradiation with 370 nm light (left spot in Fig. 3a), and turned blue with 405 nm light (central spot in Fig. 3a). These red and blue colours are due to photogenerated closed-ring isomers of **1** and **3**, respectively. Upon irradiation with both 370 and 405 nm light, the crystal turned purple (right spot in Fig. 3a). These photogenerated colours in the

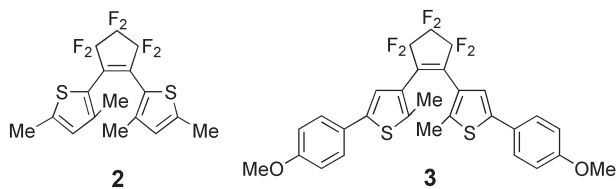


Chart 2 Diarylethenes **2** and **3**.

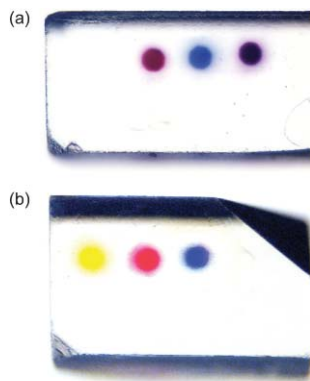


Fig. 3 Photographs of partially coloured crystals **1**·**3** (a) and **1**·**2**·**3** (b); (a) is reproduced by permission of Wiley-VCH (Ref. 24a); (b) is reprinted with permission from Ref. 24b. Copyright 2000 American Chemical Society.

crystal are thermally stable, and completely bleached by irradiation with visible light ($\lambda > 480$ nm). Both **1** and **3** undergo photochromic reactions in the two-component crystal.

A full-colour photochromic crystal that contains three kinds of diarylethenes exhibiting three primary colours, such as yellow, red, and blue, was also prepared.^{24b} Recrystallization of a mixture of **1**, **2**, and **3** (molar ratio **1** : **2** : **3** = 1 : 0.4 : 0.5) from acetonitrile afforded a single crystal composed of **1**, **2**, and **3** in the molar ratio of 97.4 : 2.4 : 0.2. The crystal lattice of **1** provided the sites where **2** and **3** can sit. Fig. 3b shows a photograph of the three-component crystal. Upon irradiation with light of appropriately selected wavelengths, the colourless crystal turned yellow, red, and blue. These colours are due to closed-ring isomers of **1** (red), **2** (yellow), and **3** (blue) generated in the photoirradiated crystal. Although the molecular structures of **2** and **3** were not discerned by X-ray crystallographic analysis because they are only present in small amounts in the crystal, polarized absorption anisotropies of the three colours showed that the three components are packed in a similar manner and undergo photochromic reactions in the single-crystalline phase. In addition, the combination of “ON” and “OFF” states of each primary colour gave eight colours ($2^3 = 8$), such as colourless, yellow, red, blue, orange, purple, green, and black. All the colours are thermally stable and do not fade in the dark. They are completely bleached by irradiation with visible light ($\lambda > 450$ nm). Such multi-coloured photochromic crystals have the potential for application to multi-frequency three-dimensional optical memory media and photo-switchable full-colour displays.

Selective photoreactions with polarized light

Multi-state recoding can also be achieved by using linearly polarized light. When diarylethene molecules are packed into a herringbone-type crystal structure, in which long axes of the molecules are oriented perpendicular to each other, irradiation with linearly polarized light can induce selective photoreactions of the molecules aligned in one direction, because the closed-ring isomer has an electronic transition moment in the direction of the long axis of the molecule.²⁵ The combination of “colourless” and “coloured” states of the molecules oriented to the different directions can give four states ($2^2 = 4$), although the crystal is composed of only one photochromic molecule. Diarylethene **3**^{26a} and diarylethene dimer **4**^{26b} (Chart 3) formed herringbone-type crystal structures suitable for selective photoreactions with linearly polarized light.

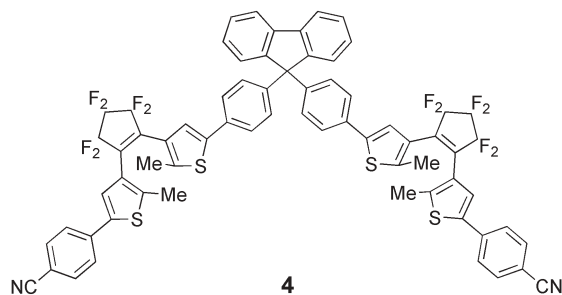


Chart 3 Diarylethene dimer **4** linked via a fluorene spacer.

When **3** was recrystallized from hexane, four kinds of crystals with different shapes were obtained.^{26a} X-ray crystallographic analysis of the crystals revealed that they are polymorphic forms. Three of them had plate-like shapes, while one was a needle. Fig. 4a shows a molecular packing diagram in the needle crystal viewed from the (100) face. In the crystal, the long axes of the diarylethene molecules are oriented into two directions A and B that are perpendicular to each other. The crystal of **3** turned blue upon irradiation with 370 nm light. The photogenerated blue colour is due to the formation of the closed-ring isomers. The blue colour of the crystal disappeared upon irradiation with visible light ($\lambda > 500$ nm). Although in general diarylethene crystals show a clear polarized absorption anisotropy in the coloured states,^{25a-c} crystal **3** did not show any well-defined anisotropy of the blue colour, as shown in Fig. 4b. The shape of the polar plot is ascribed to the herringbone structure. The superposition of the electronic transition moments oriented perpendicularly into two directions gave an almost isotropic polar plot (Fig. 4b, c). This result suggests that linearly polarized light can selectively bleach molecules aligned in one direction. Fig. 5 shows photographs of crystal **3** observed under a polarized microscope with a parallel nicol. The colourless crystal (Fig. 5a) was irradiated with non-polarized 370 nm light to give the blue-coloured crystal (Fig. 5b). When the coloured crystal was irradiated with linearly polarized light ($\lambda > 570$ nm) parallel to the direction A, the coloured closed-ring isomers along the polarized light were preferentially bleached, as shown in Fig. 5c. On the other hand, when the coloured crystal in Fig. 5b was irradiated with linearly polarized light parallel to the direction B, the molecules oriented to the direction B were selectively bleached, as shown in Fig. 5d. The four states of the crystal shown in Fig. 5 can be expressed as follows: directions A/B = 0/0 (Fig. 5a), 1/1 (b), 0/1 (c), and 1/0 (d).

A similar selective photoisomerization induced with linearly polarized light was observed in a single crystal of diarylethene dimer **4** in which two diarylethene chromophores are covalently linked *via* a fluorene spacer.^{26b} Because of the well-defined bond angle at the fluorene moiety, the long axes of the two diarylethene units in the dimer structure are oriented almost perpendicularly and a herringbone-type

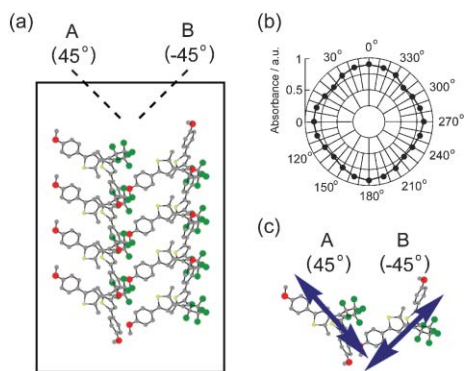


Fig. 4 Molecular packing diagram of crystal **3** (a), polar plots of polarized absorbance of coloured crystal (b), and direction of electronic transition moments of photogenerated closed-ring isomers (c). Reproduced by permission of Wiley-VCH (Ref. 26a).

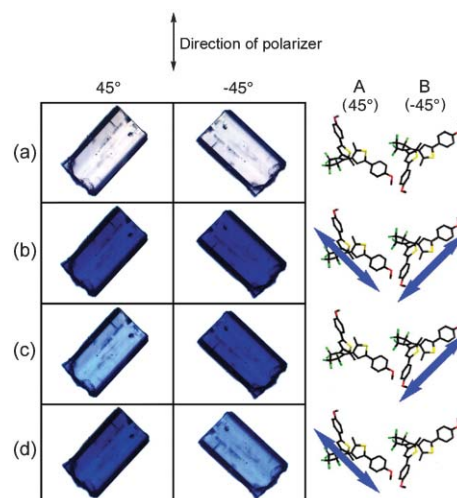


Fig. 5 Photographs of crystal **3** observed under a polarized microscope with parallel nicol: (a) before photoirradiation, (b) after irradiation with non-polarized 370 nm light, (c and d) after partial bleaching by linearly polarized visible ($\lambda > 570$ nm) light parallel to direction A (45°) and direction B (-45°). Reproduced by permission of Wiley-VCH (Ref. 26a).

molecular-packing structure is constructed in the crystal. The crystal underwent photochromism and turned blue by irradiation with non-polarized UV light. Polarized absorption spectra of the blue colour measured on the $(-1\ 1\ 0)$ face of the crystal did not show any specific anisotropy. Upon irradiation with polarized visible ($\lambda > 570$ nm) light parallel to one of the transition moments, the closed-ring isomers along the polarized light were selectively bleached.

Supramolecular architectures formed *via* hydrogen-bonding, metal-coordinating, and aryl-perfluoroaryl interactions

In the field of crystal engineering, non-covalent bonds, such as hydrogen-bonding,²⁷ metal-coordinating,²⁸ and π - π interactions,²⁹ have been widely used for the construction of various types of supramolecular structures of organic or organometallic compounds. In this section, several examples of crystal engineering of photochromic diarylethenes by utilizing these interactions are described.

Hydrogen bonds are the most widely used for the construction of various types of supramolecular architectures of organic compounds because of their robustness, directional-specific character, and diversity.²⁷ Crystal structures and photochromic performance of single crystals of diarylethenes **5–7** having two carboxylic acid groups at *para*-, *meta*-, and *ortho*-positions of the phenyl rings (Chart 4) were studied.³⁰ Fig. 6 shows the supramolecular architectures observed in crystals *para*-**5**, *meta*-**6**, and *ortho*-**7**. The diarylethenes are linked *via* intermolecular hydrogen-bonding interactions between the carboxylic acid groups to form linear-chain structures in the crystals. The chains have a two-fold helical symmetry and the position of the substitution changed the helical pitch. The zigzag chain of *ortho*-**7** has the shortest pitch. All the crystals underwent photochromic reactions. The

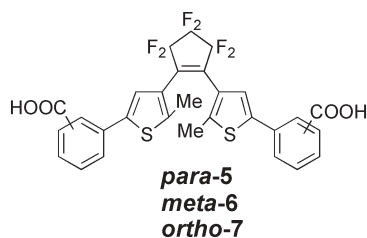


Chart 4 Diarylethenes 5–7 having carboxylic acid groups.

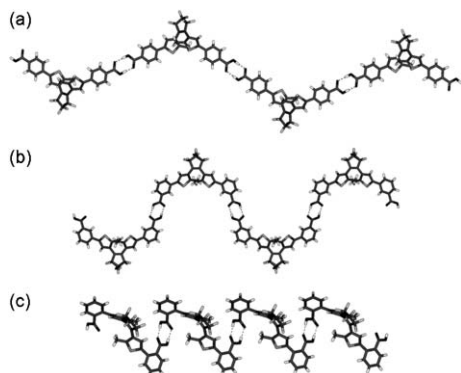


Fig. 6 X-ray structures of one-dimensional linear chains in crystals *para-5* (a), *meta-6* (b), and *ortho-7* (c). Reproduced by permission of Wiley-VCH (Ref. 30).

absorption maxima of the UV-irradiated coloured crystals were 640 nm, 600 nm, and 560 nm for *para-5*, *meta-6*, and *ortho-7*, respectively, as shown in Fig. 7a. Absorption spectra of the coloured crystals showed a significant spectral shift (by as much as 80 nm) depending on the substituted position, although the absorption spectra of the corresponding closed-ring isomers in solution are similar to each other (567 nm ~ 598 nm).

This spectral shift observed in the crystalline state is ascribed to the difference in the molecular conformation, especially the torsion angles between the thienyl and phenyl rings, induced by the intermolecular hydrogen bonds in the crystals. Fig. 7b shows the molecular structures of the diarylethenes in the crystals. The absorption spectra reflect the π -conjugation length of the photogenerated closed-ring isomers in the crystals. As can be seen from Fig. 7b, phenyl rings in the crystal of *para-5* are almost parallel to the molecular plane. This means that in the photogenerated closed-ring isomer π -conjugation extends over the entire molecule. On the other hand, the planes of the phenyl rings are almost perpendicular to the molecular plane in the crystal of *ortho-7*. The twisted phenyl rings do not enter the π -conjugation of the central part of the closed-ring isomer. The molecular structure in the crystal of *meta-6* is in between *para-5* and *ortho-7*. The order of the absorption maxima (*para-5* > *meta-6* > *ortho-7*) corresponds well to the planarity of the molecules in the crystals.

Coordination-driven self-assembly is also an important strategy to construct supramolecular architectures.²⁸ Diarylethene metal–complex systems in which diarylethene ligands having pyridyl groups coordinate to metal centres have been constructed.³¹ Complexes composed of symmetric bidentate and asymmetric monodentate diarylethene ligands **8** and **9**

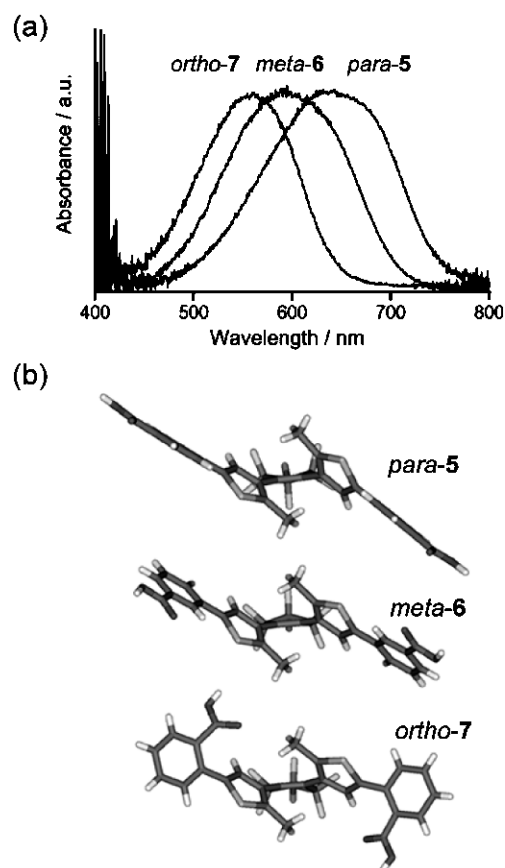


Fig. 7 Absorption spectra of coloured crystals *para-5*, *meta-6*, and *ortho-7* (a) and molecular structures of diarylethenes in the crystals (b). (a) is reproduced by permission of Wiley-VCH (Ref. 30).

having one or two pyridyl groups (Chart 5) and $M(\text{hfac})_2$ ($M = \text{Zn}^{2+}$, Cu^{2+} , and Mn^{2+} ; hfac = hexafluoroacetylacetonate) were synthesized and their crystal structures and photochromic performance in the single-crystalline phase were compared. In the crystals, the bidentate ligand **8** formed linear-chain coordination polymers, while the monodentate ligand **9** formed discrete 1 : 2 complexes. Fig. 8 shows the supramolecular structures of Zn^{2+} complexes with **8** and **9** in the crystals. Although the absorption spectra of the coloured closed-ring isomers are similar in solution, spectra of the UV-irradiated coloured crystals were different among the complexes with Zn^{2+} , Cu^{2+} , and Mn^{2+} , reflecting the molecular conformation of the diarylethene ligands in the crystals.

Stacking between aromatic hydrocarbons and perfluoroaromatics, aryl–perfluoroaryl interaction, is a special class of

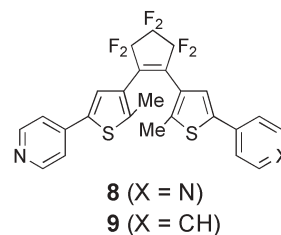


Chart 5 Diarylethene ligands **8** and **9**.

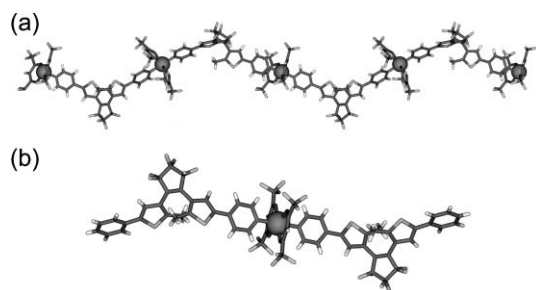


Fig. 8 X-ray structures of a one-dimensional linear coordinating chain in crystal **8**·Zn(hfac)₂ (a) and a 1 : 2 discrete complex in crystal **9**·Zn(hfac)₂ (b).

aromatic–aromatic interaction and has been studied extensively since the first report by Patrick and Prosser in 1960.^{32,33} A diarylethene derivative **10** having two pentafluorophenyl groups (Chart 6) was synthesized, and co-crystals of **10** with aromatic hydrocarbons, such as benzene (**Bz**) and naphthalene (**Np**), were prepared.³⁴ **10** co-crystallized with **Bz** and **Np** in the stoichiometric ratio of 2 : 1 and 1 : 1, respectively, by recrystallization from hexane. Fig. 9 shows assembled structures observed in co-crystals **10**·**Bz** and **10**·**Np**. In crystal **10**·**Bz**, a linear chain structure, which is composed of **10** and **Bz** in the ratio of 2 : 1, is formed as shown in Fig. 9a. On the other hand, in crystal **10**·**Np**, a discrete sandwiched structure composed of **10** and **Np** molecules is formed as shown in Fig. 9b. In both cases, stacking between the pentafluorophenyl groups of **10** and **Bz** or **Np** molecules is clearly observed. The co-crystals of **10**·**Bz** and **10**·**Np** and a single crystal of **10** underwent photochromic reactions. These three crystals exhibited absorption maxima at different wavelengths ($\lambda_{\text{max}} = 630 \text{ nm}$ (**10**), 620 nm (**10**·**Np**), and 555 nm (**10**·**Bz**)), although the coloured species is the same closed-ring isomer of

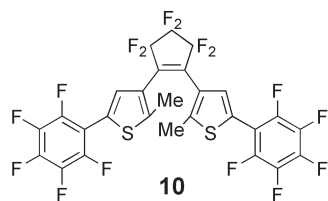


Chart 6 Diarylethene **10** having pentafluorophenyl groups.

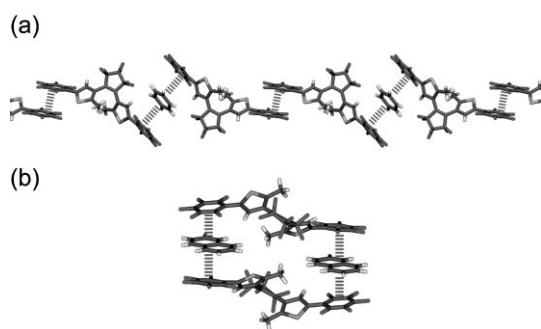


Fig. 9 X-ray structures of a one-dimensional linear chain in co-crystal **10**·**Bz** (a) and a discrete sandwiched structure in co-crystal **10**·**Np** (b).

10. The spectral shift is ascribed to the difference in the conformation of the diarylethene molecules in the crystals induced by the intermolecular aryl–perfluoroaryl interactions.

Nano-layered and nano-mosaic periodic structures

In the full-colour crystal described earlier, diarylethenes **2** and **3** are substitutionally incorporated into the crystal lattice of **1**. Although the crystal showed multi-colour photochromism, the composition ratio of the dopant diarylethenes **2** and **3** in the crystals is very low because of the absence of strong intermolecular interactions. When molecules have substituents which can interact with each other, the composition ratio can be controlled. This section deals with stoichiometric diarylethene co-crystals **10**·**11** and **10**·**12** (Chart 7).³⁵

Recrystallization of a 1 : 1 (molar ratio) mixture of **10** and **11** from hexane gave colourless single crystals. HPLC and X-ray crystallographic analyses indicated that the crystal is composed of both **10** and **11** in the molar ratio of 1 : 1. Fig. 10a shows the molecular packing diagram in co-crystal **10**·**11**. The crystal has a layered structure in which uni-molecular layers of **10** and **11** are alternately stacked. The thickness of each layer is *ca.* 0.65 nm. The phenyl rings of **10** and the pentafluorophenyl rings of **11** are not stacked with each other. This indicates that

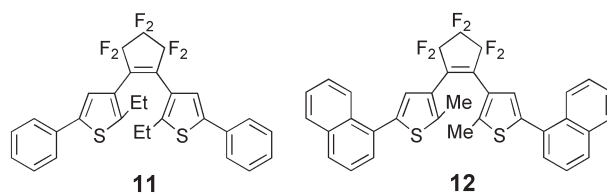


Chart 7 Diarylethenes **11** and **12** having phenyl and naphthyl groups.

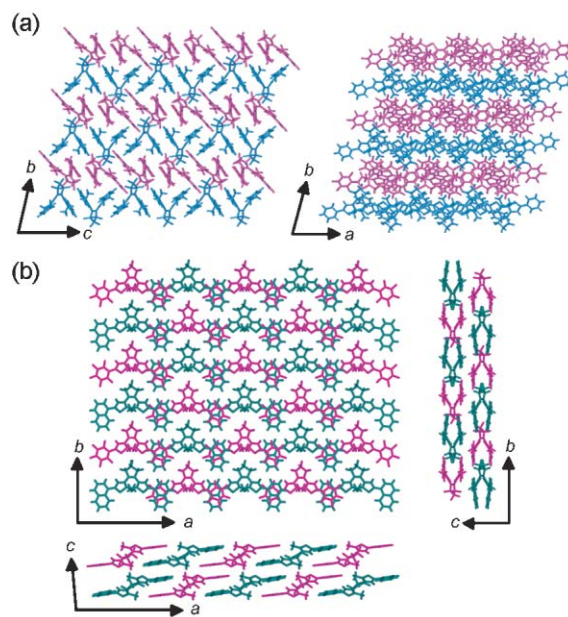


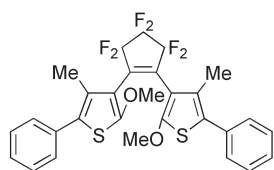
Fig. 10 Molecular packing diagrams of co-crystals **10**·**11** (a) and **10**·**12** (b). Red, blue, and green molecules indicate molecules **10**, **11**, and **12**, respectively. Reproduced by permission of Wiley-VCH (Ref. 35b).

aryl–perfluoroaryl interaction does not exist between **10** and **11** in the co-crystal.^{35a} The co-crystal of **10** and **12** was also prepared by recrystallization of a 1 : 1 mixture of the compounds. The composition ratio was 1 : 1 in the crystal. The molecular packing structure in co-crystal **10·12** is shown in Fig. 10b. The pentafluorophenyl groups of **10** and the naphthyl groups of **12** are stacked well by intermolecular aryl–perfluoroaryl interactions.^{35b} The diagrams viewed from the *a*-, *b*-, and *c*-axes indicate that **10** and **12** molecules are packed in a three-dimensional alternating arrangement to form a mosaic-like structure in the co-crystal.

Co-crystals **10·11** and **10·12** showed photochromism. Upon irradiation with UV light, the colourless co-crystals of **10·11** and **10·12** turned blue and green, respectively. These colours were thermally stable in the dark, and completely bleached upon irradiation with visible light ($\lambda > 450$ nm). The ratio of the reacted two components was monitored by HPLC. In both co-crystals **10·11** and **10·12**, components **11** and **12** selectively converted to the closed-ring isomers, and photocyclization of **10** was strongly suppressed. In homo-crystals of each compound, efficient photocyclization reactions with quantum yields of 1 took place.^{18a,34,35b} The highly selective photoreaction of **11** and **12** was also confirmed by *in situ* X-ray analysis.

Such a dramatic difference in the photoreactivity between homo-crystals and co-crystals can be explained by intermolecular excited-energy transfer in the co-crystals, as follows. Absorption edges of **11** and **12** in hexane are located at longer wavelengths than that of **10**. This means that the excited S_1 energy levels of **11** and **12** are lower than that of **10**. In the co-crystals, the two different diarylethene molecules are closely packed, and the intermolecular distance between them is less than 1 nm. Although photocyclization reactions of diarylethene derivatives in the single-crystalline phase usually proceed very fast (in less than 10 ps),¹⁹ the close intermolecular contact in the co-crystals allows the excited energy to transfer from **10** to **11** or **12**. The excited energy absorbed by **10** is efficiently transferred to **11** or **12** and the energy transfer causes the highly selective photocyclization reactions of **11** or **12** in the co-crystals.

More recently, it was found that a single crystal of diarylethene **13** (Chart 8) has a unique molecular-packing structure in which photo-reactive and photo-inactive conformer layers are alternately stacked.³⁶ This crystal includes two different conformers of **13** as a crystallographically asymmetric unit. Fig. 11a shows ORTEP drawings of the conformers. Both conformers A and B adopt an anti-parallel conformation, but the distances between the reactive carbon atoms are different, 3.65 Å and 4.93 Å for the conformers A and B, respectively. Only conformer A meets the requirement for the photocyclization.¹⁸ The conformer A can efficiently photoreact, while the



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Chart 8 Diarylethene **13**.

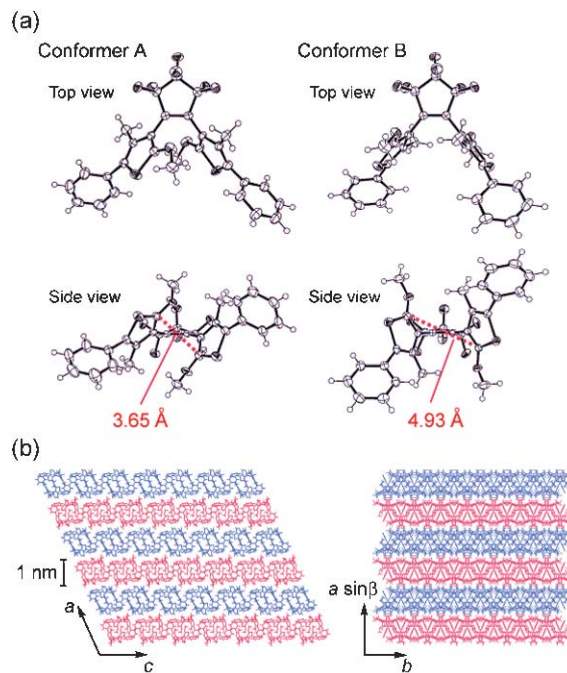


Fig. 11 ORTEP drawings (a) and molecular packing diagrams (b) of crystal **13**. Blue and red molecules in the packing diagrams indicate photoreactive and photoinactive conformers A and B, respectively. Reproduced by permission of Wiley-VCH (Ref. 36).

conformer B cannot. The two types of conformers that show extremely different photoreactivity are stacked alternately to form a nano-layered structure in the crystal, as shown in Fig. 11b. The selective photocyclization reaction was confirmed by HPLC as well as *in situ* X-ray crystallographic analyses. The photoreactivity of the molecules in each layer is controlled by molecular conformations.

Fig. 12 shows schematic illustrations of photochromic reactions in co-crystal **10·11** and crystal **13** (Fig. 12a) and co-crystal **10·12** (Fig. 12b) having well-controlled nano-structures. As a result of the selective photocyclizations, the coloured and colourless molecules, which have different refractive indices, are arranged periodically at the molecular level in the UV-irradiated crystals. Such photoreversible periodic refractive index changes in the crystalline nano-structures

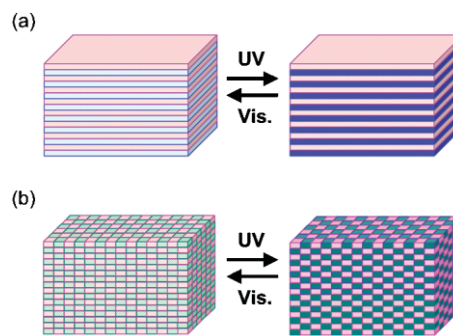


Fig. 12 Schematic illustrations of photochromic reactions in co-crystal **10·11** and crystal **13** (a) and in co-crystal **10·12** (b). Red region: **10** or conformer B of **13**, blue region: **11** or conformer A of **13**, green region: **12**. Reproduced by permission of Wiley-VCH (Ref. 35b).

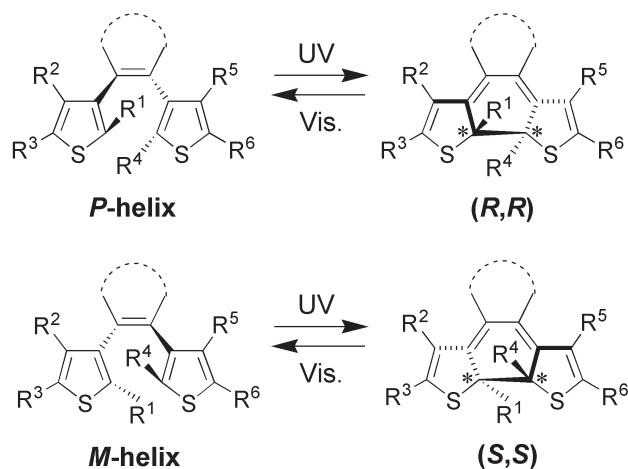
have potential application as a new type of photonic nano-device.³⁷

Diastereo- and enantio-selective photoreactions

One unique aspect of crystalline-phase reactions is a topochemical reaction.³⁸ The crystal lattice provides a matrix for reactions with stereo-, regio-, and enantio-specificity. Enantio-specific reactions can take place in chiral crystals containing chiral auxiliaries, such as chiral host molecules and covalently bonded chiral substituents.³⁹ Moreover, an assembly of achiral molecules in a chiral space group can be transformed into chiral molecules by reaction. Such an asymmetric reaction in the absence of any outside chiral influence is referred to as an absolute asymmetric synthesis.⁴⁰

Photochemical conrotatory cyclization reactions of diarylethenes produce two enantiomers of the closed-ring isomers with (*R,R*) and (*S,S*) absolute configurations originating from two asymmetric carbon atoms at the reacting positions, as shown in Scheme 2. Conrotatory cyclization reactions from *P*-helical (right-handed) and *M*-helical (left-handed) conformers of the open-ring isomers yield the (*R,R*) and (*S,S*) enantiomers, respectively. In general, the photocyclization in solution results in the formation of the two enantiomers in equal amounts. Even when a chiral substituent is introduced into the diarylethene, there is hardly any enrichment of one of the diastereomers.⁴¹ Enrichment of one of the enantiomers or diastereomers in photochemical reactions requires chiral environments. Among various approaches for enantio- or diastereo-selection, photoreactions in chiral crystals are of general use. In this section, diastereo- and enantio-selective photocyclization reactions of diarylethenes in single-crystal-line, gel, or amorphous phases are described.

The photochromic reaction of diarylethene (**S**-14) having a chiral (*S*)-3-methyl-1-penten-1-yl substituent (Chart 9) was examined.⁴² The diarylethene crystallized into a chiral crystal with orthorhombic space group $P2_12_12_1$. Fig. 13a shows an ORTEP drawing of (**S**-14) in the chiral crystal. The diarylethene molecules adopt a *P*-helical conformation. The



Scheme 2 Photochromism of diarylethene. Photocyclization reactions from *P*- and *M*-helical conformers give (*R,R*) and (*S,S*) enantiomers of closed-ring isomer, respectively.

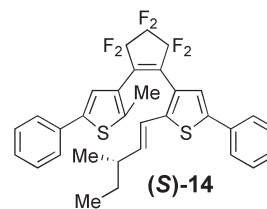


Chart 9 Chiral diarylethene (**S**-14).

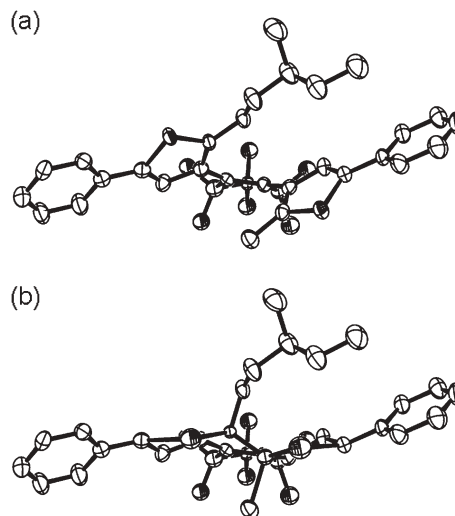


Fig. 13 ORTEP drawings of open-ring isomer in crystal (**S**-14) (a) and photogenerated (*S,R,R*) closed-ring isomer in the crystal (b). Hydrogen atoms are omitted for clarity. Reprinted with permission from Ref. 42. Copyright 2000 American Chemical Society.

chiral (*S*)-3-methyl-1-penten-1-yl substituent provided a chiral environment in the crystal. In solution, diastereo-selectivity was not observed, and the photogenerated closed-ring isomers were a mixture of equal amounts of the two diastereomers (*S,R,R*) and (*S,S,S*), as determined by HPLC analysis. However, the ratio of the two diastereomers dramatically changed in the single crystal. The reaction was highly diastereo-selective, and one of the two diastereomers was predominantly produced. The diastereomeric excess (de) value was >95%. By *in situ* X-ray crystallographic analysis of the photocyclization process, it was confirmed that the photo-product is diastereomer (*S,R,R*), as shown in Fig. 13b.

Feringa and co-workers reported a diastereo-selective photocyclization reaction of diarylethene (**R**-15) (Chart 10) in the gel phase.⁴³ The diarylethene has two (*R*)-1-phenylethylamine-derived amides as gelation scaffolds. Multiple hydrogen-bonding interactions between the amide groups induced gelation of the open-ring isomers in toluene. The gel showed strong circular dichroism around 320 nm due to exciton coupling within the aggregate. In addition, transmission electron microscopy on the gel evidenced the formation of chiral *P*-helical fibers. The chiral aggregation fixed the open-ring isomers into the *P*-helical conformation. The photocyclization reaction in the chiral aggregate induced by UV irradiation retained the chirality of the open-ring isomers to yield the closed-ring isomers with a large de value (>96%).

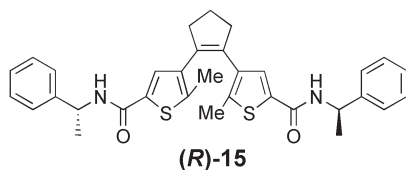


Chart 10 Chiral diarylethene **(R)-15**.

Diastereo-selective photocyclization was also observed in the bulk amorphous state. Diarylethene **(S)-16** having chiral *(S)*-*sec*-butyl groups (Chart 11) formed a stable amorphous thin film at room temperature.⁴⁴ The photocyclization reaction by UV-irradiation in the amorphous state gave a $\Delta\epsilon$ value of 25%. This suggests the existence of crystalline-like structures or short-distance regularity in the amorphous state that can't be detected by polarized microscopy or X-ray diffraction.

If achiral open-ring isomers of diarylethenes would crystallize with a chiral packing structure, absolute asymmetric photochromism, in which achiral compounds produce chiral products in the absence of any external chiral agents, could be possible. It was found that *achiral* diarylethene **17** (Chart 12) formed *chiral* single crystals.⁴⁵ Recrystallization of **17** from acetonitrile solution gave colourless needle crystals. X-ray crystallographic analysis showed that the crystals had monoclinic chiral space group $P2_1$. In addition, it was found that two kinds of crystals, **(P)-17** and **(M)-17**, which are mirror images of each other, were obtained from the same batch. In crystal **(P)-17**, all open-ring isomers are restricted to a *P*-helical conformation, on the other hand, all molecules are fixed to a *M*-helical conformation in crystal **(M)-17**. Both crystals **(P)-17** and **(M)-17** underwent photochromic reactions. Upon irradiation with UV light, the single crystals turned blue, and the blue colour disappeared upon irradiation with visible light. The enantio-selectivity of the cyclization process in solution as well as in the single crystals of **(P)-17** and **(M)-17** were examined by HPLC analysis of the photoproducts using a chiral column. Although in solution an enantio-selective photoreaction was not observed, in the chiral single crystals the enantio-selective formation of the closed-ring isomer was discerned. The chiral crystal of **(P)-17** gave optically pure *(R,R)* enantiomer, and the chiral crystal of **(M)-17** gave optically pure *(S,S)* enantiomer by topochemical photocyclization reactions in the single-crystalline phase. The enantio-selective photocyclization reaction was also proved by *in situ* X-ray crystallographic analysis. It is worth noting that the enantiomeric excess (ee) in the crystalline-state photoreactions is very high (ee >94%). This is the first example of an absolute asymmetric photochromic reaction in a crystal.

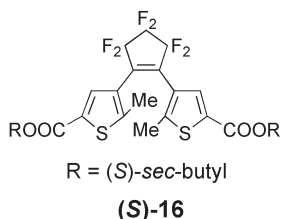


Chart 11 Chiral diarylethene **(S)-16**.

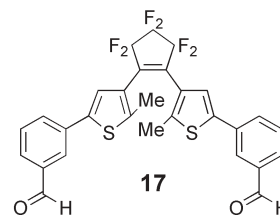


Chart 12 Diarylethene **17**.

Reversible surface morphology changes by photoirradiation

Although the structural changes of the diarylethene molecules in crystals are not remarkable, the molecules reversibly shrink to some extent upon photoirradiation. The small structural changes can induce surface morphology changes of the crystals. Fig. 14 shows (100) surface morphology changes of crystal **18**⁴⁶ and crystal **19**⁴⁷ (Chart 13). Crystal **18** shows reversible step formation upon photoirradiation, while many holes are reversibly produced in crystal **19**. The difference is ascribed to the difference in molecular alignment on the (100) surface. In crystal **18** cooperative displacement of molecules can take place, while in crystal **19** such cooperativity is lost. The surface morphology changes are also strongly dependent on the structure of molecules as well as the packing of the molecules.

Conclusions

This article highlights the single-crystalline photochromism of diarylethene derivatives. Diarylethene single crystals undergo thermally irreversible and fatigue resistant photochromic reactions. The photochromic performance reflects conformations and packing structures of the molecules in the crystals, as follows: (1) absorption spectra and photochromic quantum yields are dependent on the conformations, (2) appropriate conformation in the crystals gives a cyclization quantum yield of 1, (3) multi-component crystals provide multi-colour photochromism, (4) selective photoreactions with linearly polarized light take place in a herringbone-type crystal structure, (5) intermolecular non-covalent interactions affect molecular conformations in supramolecular assemblies and alter the absorption spectra, (6) excited-state energy transfer in nano-periodic structures induces selective photoreactions, (7) diastereo- and enantio-selective photocyclizations take place in single crystals with chiral packing structures, (8) reversible surface morphology changes are controlled by molecular structures and their packing. Such photochromic crystals that show excellent and unique performance have potential for application to various photoactive devices.

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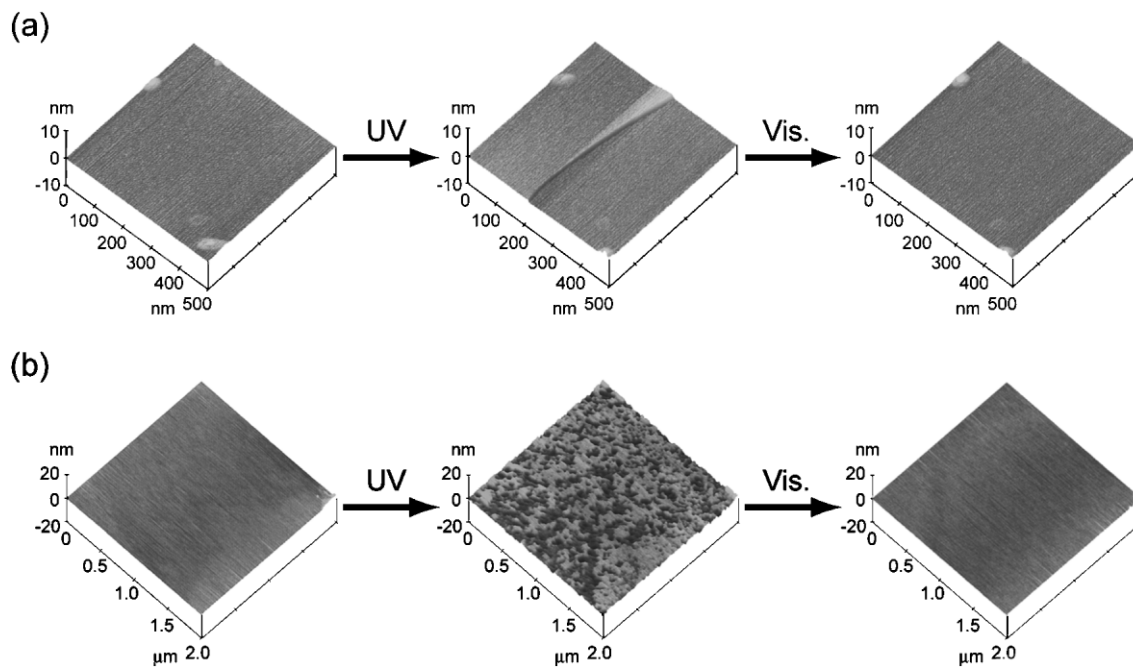


Fig. 14 Photoinduced surface morphology changes of crystals **18** (a) and **19** (b). (a) is reproduced by permission of the American Association for the Advancement of Science (Ref. 46).

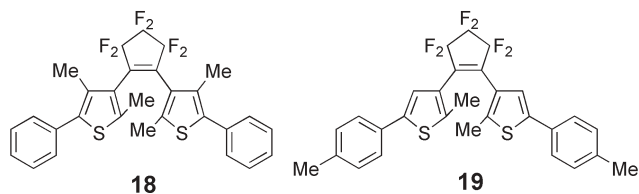


Chart 13 Diarylethenes **18** and **19**.

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Notes and references

- (a) G. H. Brown, *Photochromism*, Wiley-Interscience, New York, 1971; (b) H. Dürr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 2003; (c) H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem.*, 2001, **73**, 639–665.
- J. H. Golden, *J. Chem. Soc.*, 1961, 3741–3748.
- (a) E. Hadjoudis, M. Vittorakis and I. Moustakali-Mavridis, *Tetrahedron*, 1987, **43**, 1345–1360; (b) K. Amimoto, H. Kanatomi, A. Nagakari, H. Fukuda, H. Koyama and T. Kawato, *Chem. Commun.*, 2003, 870–871.
- A. M. Trozzolo, T. M. Leslie, A. S. Sarpotdar, R. D. Small, G. J. Ferraudi, T. DoMinh and R. L. Hartless, *Pure Appl. Chem.*, 1979, **51**, 261–270.
- (a) K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 429–438; (b) M. Kawano, T. Sano, J. Abe and Y. Ohashi, *J. Am. Chem. Soc.*, 1999, **121**, 8106–8107.
- K. Ichimura and S. Watanabe, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2220–2223.
- (a) H. Sixl and R. Warta, *Chem. Phys.*, 1985, **94**, 147–155; (b) A. Schmidt, S. Kababya, M. Appel, S. Khatib, M. Botoshansky and Y. Eichen, *J. Am. Chem. Soc.*, 1999, **121**, 11291–11299.
- Y. Mori, Y. Ohashi and K. Maeda, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3171–3176.
- J. R. Scheffer and P. R. Pokkuluri, in *Photochemistry in Organized and Constrained Media*, ed. V. Ramamurthy, VCH, Weinheim, Germany, 1991.
- (a) M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985–996; (b) M. Irie, *Chem. Rev.*, 2000, **100**, 1685–1716; (c) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759–760.
- (a) M. Irie, T. Lifka, S. Kobatake and N. Kato, *J. Am. Chem. Soc.*, 2000, **122**, 4871–4876; (b) S. Takami, S. Kobatake, T. Kawai and M. Irie, *Chem. Lett.*, 2003, 892–893.
- (a) M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, *J. Chem. Soc., Chem. Commun.*, 1990, 206–207; (b) K. Uchida, Y. Nakayama and M. Irie, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1311–1315.
- (a) H. Miyasaka, S. Araki, A. Tabata, T. Nobuto, N. Mataga and M. Irie, *Chem. Phys. Lett.*, 1994, **230**, 249–254; (b) N. Tamai, T. Saika, T. Shimidzu and M. Irie, *J. Phys. Chem.*, 1996, **100**, 4689–4692; (c) J. Ern, A. T. Bens, H.-D. Martin, S. Mukamel, D. Schmid, S. Tretiak, E. Tsiper and C. Kryschi, *Chem. Phys.*, 1999, **246**, 115–125; (d) C. Okabe, T. Nakabayashi, N. Nishi, T. Fukaminato, T. Kawai, M. Irie and H. Sekiya, *J. Phys. Chem. A*, 2003, **107**, 5384–5390.
- M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305–8309.
- (a) K. Shibata, S. Kobatake and M. Irie, *Chem. Lett.*, 2001, 618–619; (b) K. Morimitsu, K. Shibata, S. Kobatake and M. Irie, *J. Org. Chem.*, 2002, **67**, 4574–4578; (c) K. Morimitsu, S. Kobatake, S. Nakamura and M. Irie, *Chem. Lett.*, 2003, 858–859.
- S. Kobatake and M. Irie, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 195–210.
- (a) K. Uchida, Y. Nakayama and M. Irie, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1311–1315; (b) M. Irie, O. Miyatake and K. Uchida, *J. Am. Chem. Soc.*, 1992, **114**, 8715–8716.
- (a) K. Shibata, K. Muto, S. Kobatake and M. Irie, *J. Phys. Chem. A*, 2002, **106**, 209–214; (b) T. Yamada, K. Muto, S. Kobatake and M. Irie, *J. Org. Chem.*, 2001, **66**, 6164–6168; (c) S. Kobatake, K. Uchida, E. Tsuchida and M. Irie, *Chem. Commun.*, 2002, 2804–2805.
- H. Miyasaka, T. Nobuto, A. Itaya, N. Tamai and M. Irie, *Chem. Phys. Lett.*, 1997, **269**, 281–285.
- (a) T. Yamada, S. Kobatake, K. Muto and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 1589–1592; (b) T. Yamada, S. Kobatake and M. Irie, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2179–2184.

- 21 S. Kobatake, M. Morimoto, Y. Asano, A. Murakami, S. Nakamura and M. Irie, *Chem. Lett.*, 2002, 1224–1225.
- 22 A. Fernandez-Acebes and J.-M. Lehn, *Adv. Mater.*, 1999, **11**, 910–913.
- 23 K. Higashiguchi, K. Matsuda and M. Irie, *Angew. Chem. Int. Ed.*, 2003, **42**, 3537–3540.
- 24 (a) M. Morimoto, S. Kobatake and M. Irie, *Adv. Mater.*, 2002, **14**, 1027–1029; (b) M. Morimoto, S. Kobatake and M. Irie, *J. Am. Chem. Soc.*, 2003, **125**, 11080–11087.
- 25 (a) S. Kobatake, T. Yamada, K. Uchida, N. Kato and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 2380–2386; (b) S. Kobatake, M. Yamada, T. Yamada and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 8450–8456; (c) S. Kobatake, K. Shibata, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 12135–12141; (d) M. Takeshita, N. Kato, S. Kawachi, T. Imase, J. Watanabe and M. Irie, *J. Org. Chem.*, 1998, **63**, 9306–9313.
- 26 (a) M. Morimoto, S. Kobatake and M. Irie, *Chem. Eur. J.*, 2003, **9**, 621–627; (b) S. Kobatake, S. Kuma and M. Irie, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 945–951.
- 27 (a) G. R. Desiraju, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2311–2327; (b) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120–126; (c) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, **22**, 397–407.
- 28 (a) N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794–796; (b) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908; (c) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658.
- 29 (a) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525–5534; (b) E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem. Int. Ed.*, 2003, **42**, 1210–1250; (c) G. R. Desiraju and A. Gavezzotti, *J. Chem. Soc., Chem. Commun.*, 1989, 621–623.
- 30 S. Yamamoto, K. Matsuda and M. Irie, *Chem. Eur. J.*, 2003, **9**, 4878–4886.
- 31 (a) K. Matsuda, K. Takayama and M. Irie, *Chem. Commun.*, 2001, 363–364; (b) K. Matsuda, K. Takayama and M. Irie, *Inorg. Chem.*, 2004, **43**, 482–489; (c) K. Matsuda, Y. Shinkai and M. Irie, *Inorg. Chem.*, 2004, **43**, 3774–3776.
- 32 C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021.
- 33 (a) G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty and R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 248–251; (b) C. Dai, P. Nguyen, T. B. Marder, A. J. Scott, W. Clegg and C. Viney, *Chem. Commun.*, 1999, 2493–2494.
- 34 M. Morimoto, S. Kobatake and M. Irie, *Cryst. Growth Des.*, 2003, **3**, 847–854.
- 35 (a) M. Morimoto, S. Kobatake and M. Irie, *Photochem. Photobiol. Sci.*, 2003, **2**, 1088–1094; (b) M. Morimoto, S. Kobatake and M. Irie, *Chem. Rec.*, 2004, **4**, 23–38.
- 36 S. Kobatake, Y. Matsumoto and M. Irie, *Angew. Chem. Int. Ed.*, 2005, **44**, 2148–2151.
- 37 (a) J. D. Joannopoulos, R. D. Meade and J. N. Winn, *Photonic Crystals*, Princeton University Press, New Jersey, 1995; (b) J. D. Joannopoulos, P. R. Villeneuve and S. Fan, *Nature*, 1997, **386**, 143–149.
- 38 (a) K. Venkatesan and V. Ramamurthy, in *Photochemistry in Organized and Constrained Media*, ed. V. Ramamurthy, VCH, Weinheim, Germany, 1991; (b) V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, 1987, **87**, 433–481; (c) J. N. Gamlin, R. Jones, M. Leibovitch, B. Patrick, J. R. Scheffer and J. Trotter, *Acc. Chem. Res.*, 1996, **29**, 203–209; (d) K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025–1074.
- 39 (a) H. Hosomi, S. Ohba, K. Tanaka and F. Toda, *J. Am. Chem. Soc.*, 2000, **122**, 1818–1819; (b) Y. Ito, G. Kano and N. Nakamura, *J. Org. Chem.*, 1998, **63**, 5643–5647.
- 40 (a) J. R. Sheffer and M. A. Garcia-Garibay, in *Photochemistry of Solid Surfaces*, ed. T. Matsuura and M. Anpo, Elsevier, Amsterdam, 1989; (b) M. Vaida, R. Popovitz-Biro, L. Leiserowitz and M. Lahav, in *Photochemistry in Organized and Constrained Media*, ed. V. Ramamurthy, VCH, Weinheim, Germany, 1991.
- 41 T. Yamaguchi, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1997, **119**, 6066–6071.
- 42 T. Kodani, K. Matsuda, T. Yamada, S. Kobatake and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 9631–9637.
- 43 J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278–281.
- 44 T. Yamaguchi, K. Nomiyama, M. Isayama and M. Irie, *Adv. Mater.*, 2004, **16**, 643–645.
- 45 S. Yamamoto, K. Matsuda and M. Irie, *Angew. Chem. Int. Ed.*, 2003, **42**, 1636–1639.
- 46 M. Irie, S. Kobatake and M. Horichi, *Science*, 2001, **291**, 1769–1772.
- 47 T. Koga, S. Kobatake and M. Irie, unpublished data.