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Accounts

Synthesis and Properties of Photochromic Diarylethenes with Heterocyclic Aryl Groups

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A new class of thermally irreversible and fatigue resistant photochromic molecules named diarylethenes has been developed. Theoretical consideration based on the state correlation diagrams of electrocyclic reactions revealed that the thermal irreversibility is attained by introducing aryl groups that have low aromatic stabilization energy. According to the molecular design principle thermally irreversible photochromic diarylethenes having heterocyclic five-membered rings, such as furan, thiophene (or benzothiophene), or thiazole rings, have been newly synthesized. Among them, diarylethenes having benzothiophene aryl groups showed an excellent fatigue resistant property. They underwent photochromic cycles more than 1.0×10^4 times. The absorption maxima of the closed-ring forms varied from 425 to 828 nm depending on the aryl groups, substituents of the aryl groups, and the substitution position of the aryl groups to the ethane moiety. The response times of both cyclization and ring-opening reactions were less than 10 ps in solution as well as in a crystalline phase. The chemical and thermal control of photochromic reactivity was achieved by introducing intramolecular hydrogen bonding groups or oligothiophene aryl groups to the diarylethenes. Some of the dithienylperfluorocyclopentene derivatives were found to show photochromic reactivity in the crystalline phase. The reactivity was dependent on the conformation and molecular packing in the crystals.

Light-induced reversible isomerizations between two forms having different absorption spectra are referred to photochromism, and compounds capable of these reactions are called photochromic molecules.[1)]

$$\mathrm{A} \underset{h\nu',\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{B}$$

The two isomers differ from one another not only in the absorption spectra but also in refractive indices, dielectric constants, oxidation/reduction potentials, and geometrical structures. The instant property changes by photoirradiation without processing lead to their use in various optoelectronic devices,[2,3)] such as optical memory, photo-optical switching, and display. Although much effort has been made so far, photochromic molecules still await practical applications. The limitation is due to the lack of suitable molecules which fulfill the requirements for optoelectronic devices.

Fundamental requirements for such applications are thermal stability of both isomers and fatigue resistance. In general, photogenerated colored forms are thermally unstable and return to the initial colorless form in the dark. Photogenerated blue color of 6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline], for example, disappears in less than half an hour even in high T_g polymer matrices.[4)] Every effort to stabilize the colored form by controlling the properties of matrices failed.[5,6)] Aggregate formation is another approach to stabilize the colored form,[7)] but the reversibility of the system is poor. Such thermally unstable photochromic molecules and molecular systems can not be applied to optoelectronic devices.

A fatigue resistant characteristic is another indispensable property for practical applications. If the photochromic performance is lost after 100 coloration/decoloration cycles, the photochromic device is of no use. Although many molecules show photochromic reactivity, few of them keep the performance after 1000 coloration/decoloration cycles.[8)] There is no molecule which can undergo the reversible reaction more than 10^4 cycles. The essential subject of investigation is to reveal the molecular design principle for the synthesis of thermally irreversible and fatigue resistant photochromic molecules.

Additional desirable properties include gated photochromic reactivity and reactivity in the crystalline phase. The gated reactivity means the property that irradiation with any wavelength causes no molecular change, while a reaction occurs when another external stimulation, such as chem-

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[#] CREST, Japan Science and Technology Corporation.

ical, heat or light of another wavelength, is present.[9] Optical memory media require the gated reactivity to avoid erasing of the memories during storage under room light or after many readout operations.

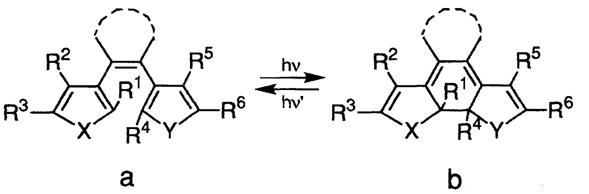
Matrices also play an important role in photochromism. Although solid state matrices are needed for the applications, in most cases polymer matrices decrease the photochromic reactivity[4] and cause undesirable side reactions. The ideal solid matrices are crystals. In crystals photochromic molecules are protected from oxygen and other impurities. Therefore, intermolecular destructive reactions are suppressed. However, photochromic molecules which show the reactivity in the crystalline phase are rare. Typical examples are *N*-salicylideneanilines,[10] 2-(2,4-dinirobenzyl)pyridine,[11] diphenylmaleonitrile,[12] and triarylimidazole dimer.[13] In most cases, the photogenerated colored isomers are thermally unstable and readily return to the initial colorless isomers at ambient temperature. It is desired to develop photochromic molecular crystals in which both isomers are thermally stable and photostimulated interconversion between them are efficient in the crystalline phase.

In this review synthesis and properties of a new class of photochromic molecules named diarylethenes with heterocyclic five membered rings will be described (Chart 1). Both isomers of the diarylethenes, open-ring and closed-ring forms, are thermally stable and cyclization/ring-opening reactions can be repeated more than 10^4 times while keeping adequate photochromic performance. Some of the diarylethenes show photochromic reactivity even in the crystalline phase. The molecules fulfill most of the requirements for optoelectronic applications.

1. Molecular Design of Thermally Irreversible Diarylethenes

In order to gain access to a guiding principle for the synthesis of thermally irreversible photochromic molecules, a theoretical study of the 1,3,5-hexatriene to cyclohexadiene type photochromic reaction was carried out.[14] Although thermal irreversibility is the key property for optoelectronic applications, existing photochromic molecules lack the property. Typical molecules of the hexatriene molecular framework are diarylethene derivatives having phenyl or heterocyclic rings. Semiempirical MNDO calculations were carried out for the diarylethene derivatives (Chart 2).

Figure 1 shows state correlation diagrams for the electrocyclic reactions from **1a** to **1b** and from **2a** to **2b** in a conrotatory mode. Full lines in the figure show that the interconnecting states have the same symmetry. According to the Woodward–Hoffman rule based on π orbital symmetries for 1,3,5-hexatriene,[15] the cyclization reaction is allowed in the conrotatory mode in the photoexcited state, as evidenced in Fig. 1. The cyclization reaction can not proceed in the ground state in either conrotatory or disrotatory mode.



a b

Chart 1.

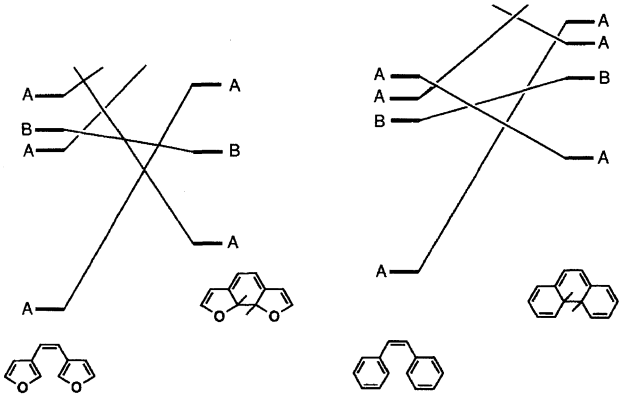


Fig. 1. The state correlation diagrams for the electrocyclic reactions in conrotatory mode.

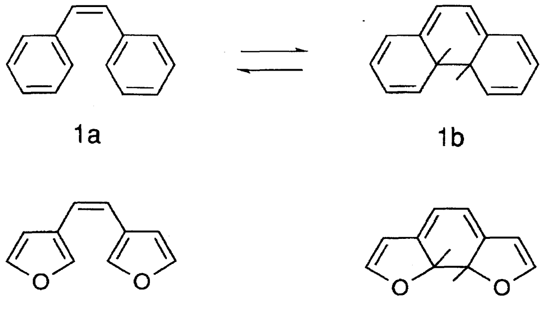


Chart 2.

What we should consider is the stability of the closed-ring forms. Full lines of Fig. 1 suggest that in both 1,2-diphenylethene and 1,2-di(3-furyl)ethene the cycloreversion reactions in the ground states have to overcome an energy barrier, and the barrier correlates with the ground state energy difference. The calculated values of the differences for 1,2-diphenylethene, 1,2-di(3-pyrrolyl)ethene, 1,2-di(3-furyl)ethene, and 1,2-di(3-thienyl)ethene are shown in Table 1. When the energy difference is large, as in the case of 1,2-diphenylethene, the energy barrier becomes small and the reaction is expected to take place readily. On the other hand, the reaction barrier becomes large when the energy difference is small as shown for 1,2-di(3-furyl)ethene. In

Table 1. Relative Ground State Energy Differences between the Open-Ring and the Closed-Ring Forms

Compd	Conrotatory
	kcal mol^{-1}
1,2-Diphenylethene	27.3
1,2-Di(3-pyrrolyl)ethene	15.5
1,2-Di(3-furyl)ethene	9.2
1,2-Di(3-thienyl)ethene	−3.3

this case the cycloreversion reaction is not expected to occur. The energy barrier, which correlates with the ground state energy difference between the open-ring and the closed-ring forms, controls the stability of the photogenerated closed-ring forms. Both the open-ring and the closed-ring forms become thermally more stable when the ground state energy of the closed-ring form is closer to that of the open-ring form.

The next question is what kind of molecular property causes the ground state energy difference. We examined the aromaticity change from the open-ring to the closed-ring forms (Chart 3). The difference between the right and left side groups was calculated, as shown in Table 2. The aromatic stabilization energy of the aryl groups correlates well with the ground state energy difference. The highest energy difference was calculated for the phenyl group and the lowest for the thienyl group. The aromaticity is the key molecular property which controls the energy barrier or the thermal stability of the closed-ring form.

The theoretical prediction was examined by the synthesis of diarylethenes with various types of aryl groups, as shown in Fig. 2.[16—24] The thermal stability was dependent on the type of aryl groups. When the aryl groups were furan, thiophene, or thiazole rings, which have low aromatic stabilization energy, the closed ring forms were thermally stable and did not return to the open-ring forms even after the storage for 3 months at 80 °C in the dark.[9,24] On the other hand, photogenerated closed ring forms of diarylethenes with phenyl or indole rings, which have rather high aromatic stabilization energy, were thermally unstable. The photogenerated yellow color of the closed-ring form of 2,3-dimesitylbutene **11b** disappeared with a half life of 1.5 min at 20 °C.[14] It quickly returned to the open-ring form. The closed-ring forms of diarylethenes with indole rings also exhibited thermally reversible reactions. The closed-ring forms **9b** and **10b** returned to the open-ring forms in the dark at 80 °C.[21] The different behavior in the thermal stability between diarylethenes with furan, thiophene, or thiazole rings and phenyl or indole rings agrees well with the theoretical prediction that the thermal stability depends on the aromatic stabilization energy of the aryl groups.

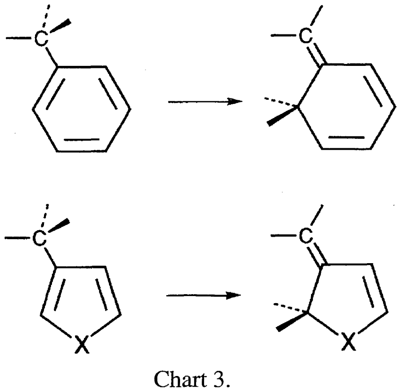


Chart 3.

Table 2. Aromatic Stabilization Energy Differences

Group	Energy/kcal mol^{-1}
Phenyl	27.7
Pyrrolyl	13.8
Furyl	9.1
Thienyl	4.7

The molecular design principle can not be applied to diarylethenes which have strong electron-withdrawing substituents.[22,23] The closed-ring forms **12b** and **13b** having dicyanoethylene substituents returned to the open-ring forms in 186 and 3.3 min at 60 °C, respectively. The thermal instability of these closed-ring forms is ascribed to the fact that the photogenerated central carbon–carbon bonds in the closed-ring forms are weakened by the electron-withdrawing substituents. The ring-opening quantum yield of 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene having CN substituents at 4-positions of the phenyl groups is much higher than that having electron-donating diethylamino substituents.[18] The stability increase in **12b** in comparison with **13b** also supports the interpretation.

The molecular design principle for thermally irreversible diarylethenes is summarized as follows. Diarylethenes with heterocyclic rings with low aromatic stabilization energy, such as furan, thiophene, or thiazole rings, having electron-donating or weakly attractive substituents undergo thermally irreversible photochromic reactions.

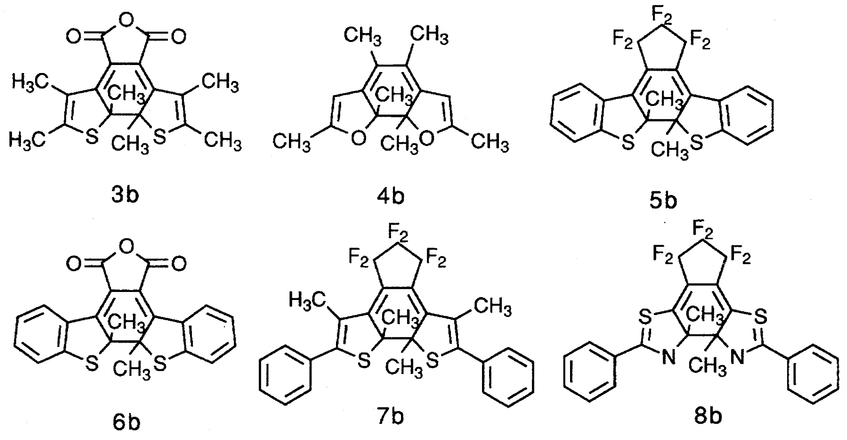
2. Synthesis

2.1 Diarylperfluorocyclopentenes. Symmetric and non-symmetric diarylethenes with various heterocyclic aryl groups were synthesized by the elimination reaction of perfluorocyclopentene with organolithium compounds. The mono- and di-substituted perfluorocyclopentenes were selectively prepared by controlling the ratio of the perfluorocyclopentene and the organolithium compound. The mono-substituted compounds can be used for the synthesis of non-symmetric diarylethenes.

A typical example of the synthesis of **7a** is shown in Scheme 1.[17,18] 2,4-Dimethylthiophene was lithilated and treated with zinc(II) chloride in ether. The ether solution was added dropwise to an anhydrous tetrahydrofuran (THF) containing iodobenzene and tetrakis(triphenylphosphine)palladium(0) to give phenylthiophene **16** in 97% yield. The phenylthiophene is also prepared by using palladium-catalyzed Suzuki coupling of thiopheneboronic acid and iodo- or bromobenzene.[23,25] The phenylthiophene **16** was halogenated by iodic acid or bromine. The lithilation of the halogenated thiophene derivative in THF at −78 °C, followed by the addition of octafluorocyclopentene, afforded 1,2-bis-(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene **7a** in 52% yield. Various types of 1,2-diarylperfluorocyclopentenes can be prepared by modification of this method.

2.2 Diarylmaleic Anhydrides. An example of the synthesis of diarylmaleic anhydride **3a** is shown in Scheme 2.[16] 2,3,5-Trimethyl-4-(chloromethyl)thiophene was prepared by the reaction of the trimethylthiophene with chloromethyl methyl ether, and converted to a cyanomethyl derivative with NaCN. The cyanomethyl compound was coupled in

Thermally Stable Molecules



Thermally Unstable Molecules

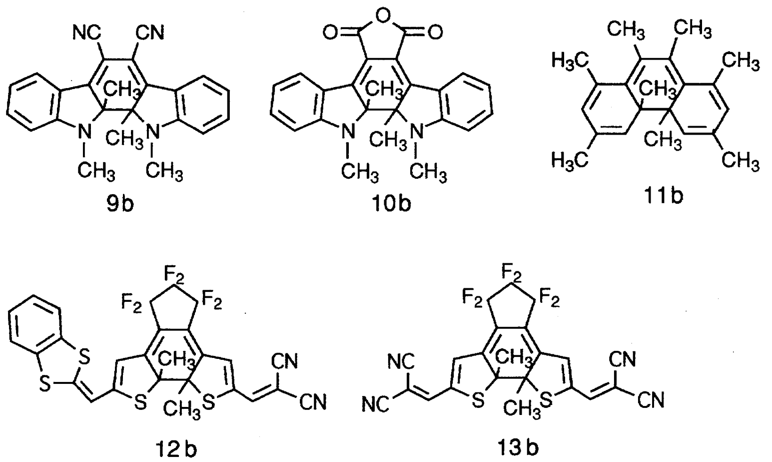
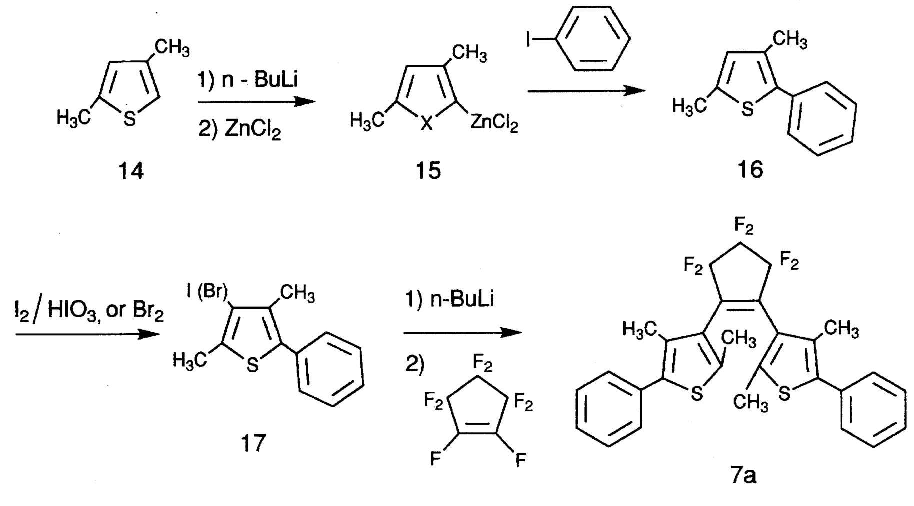
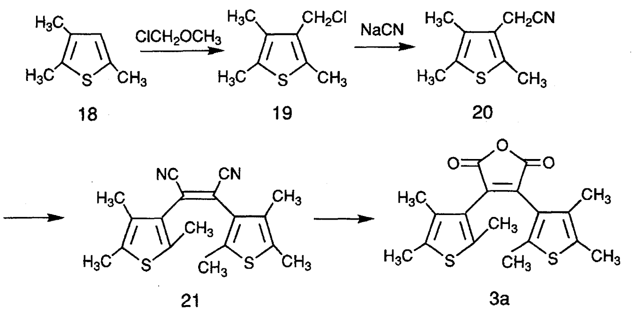


Fig. 2. Thermal stability of photogenerated closed-ring forms of diarylethenes with various types of aryl groups.



Scheme 1.



Scheme 2.

a NaOH alkaline aqueous solution in the presence of CCl_4. The 1,2-dicyano-1,2-bis(2,3,5-trimethylthiophen-3-yl)ethene **21** was hydrolyzed in an alkaline solution to produce acid anhydride derivative **3a**. The method can be applied to various diarylmaleic anhydrides.

2.3 Diarylmaleimides. Scheme 3 shows an example of the synthesis of 2,3-diaryl-*N*-(cyanomethyl)maleimide **26a**.[26] 4-Cyanomethyl-3,5-dimethyl-2-phenylthiophene **22** was prepared by a procedure similar to that used for preparing compound **20** from compound **16**. The cyanomethyl group was converted to carboxymethyl group by refluxing in concentrated hydrochloric acid. 3-[*N*-(Cyanomethyl)oxamoyl]-2-methoxybenzothiophene **25** was obtained by treating 2-methoxybenzothiophene **24** with oxalyl chloride and aminoacetonitrile. Compound **23** was converted to acid chloride using oxalyl chloride, and then mixed with compound **25** to give diaryl-*N*-(cyanomethyl)maleimide **26a**. This method is useful for the preparation of non-symmetric diarylmaleimide.

So far we have synthesized diarylethene derivatives having three different kinds of ethene moieties. The difference in the structures did not alter the basic properties of diarylethenes, thermal irreversibility and fatigue resistance (see below). Only the absorption spectra were dependent on the structure of ethene moieties.

3. Fatigue Resistant Characteristic

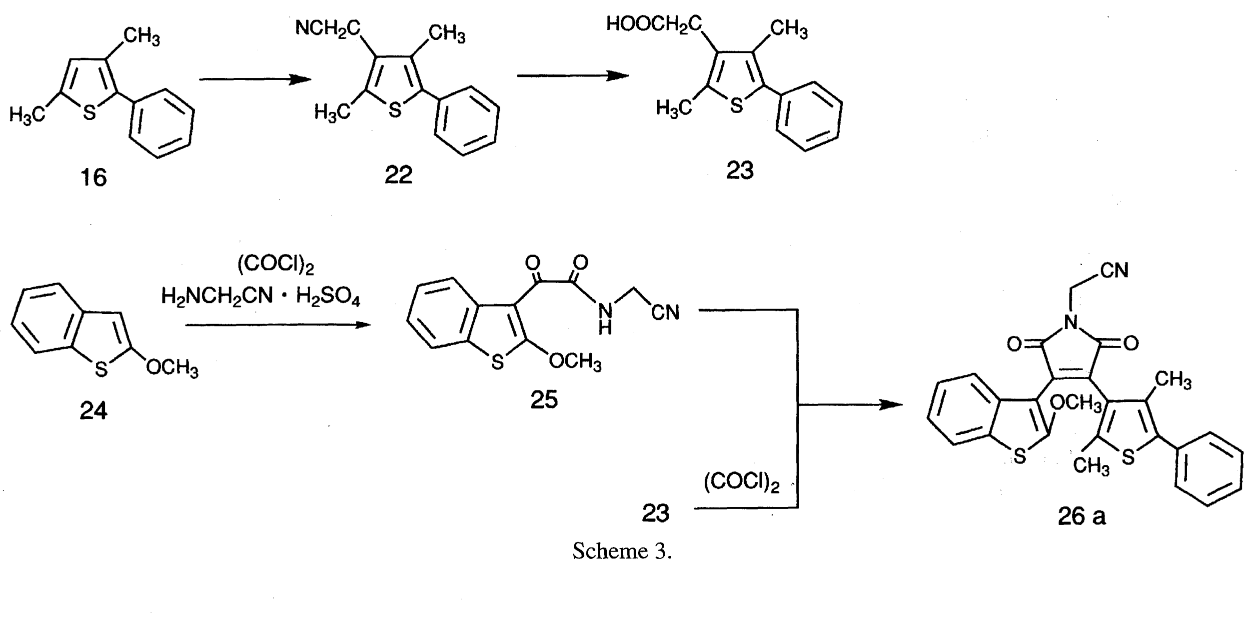
The main disadvantage of organic materials for optoelectronic applications is the lack of durability. Although the durability problem has already been overcome for liquid crystals and organic photo-conductors, it still remains for NLO (non-linear optical) and photochromic materials. Photochromic reactions are always attended by rearrangement of chemical bonds. During the bonds rearrangement, undesirable side reactions take place to some extent. This limits the durability of photochromic materials. The difficulty in obtaining fatigue resistant photochromic molecules can be easily understood by the following reaction scheme, in which a side reaction to produce B′ is involved in the forward process.

$$B' \xleftarrow{\Phi s} A \underset{\lambda_2}{\overset{\lambda_1}{\rightleftharpoons}} B$$

Even under the conditions that the side reaction quantum yield, Φs, is as low as 0.001 and B perfectly converts to A, 63% of the initial concentration of A will decompose after 1000 cycles. Thus the quantum yield for conversion to byproducts should be less than 0.0001 to repeat the cycles more than 10000 times.

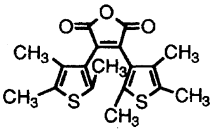
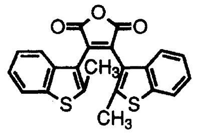
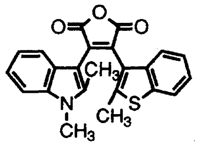
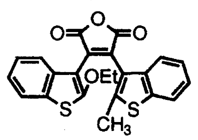
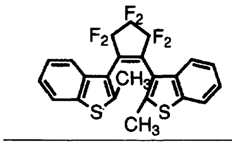
The fatigue resistant character of various diarylethenes was measured in benzene. Benzene solutions containing diarylethenes (ca. 10^{-4} mol dm^{-3}) were irradiated with shorter wavelength (λ_1) light until the absorption intensity of the colored forms reached 90% of the photostationary state. Then, the colored forms were completely bleached by irradiation with longer wavelength (λ_2) light. This operation was repeated many times.

Table 3 summarizes the result of repeatable cycle numbers in benzene. The repeatable cycle number is the number of photochromic cycles at which the absorption intensity of the colored form decreases to 80% of the first cycle. Diarylmaleic anhydride having thiophene rings **3** can not repeat the photochromic reaction more than 70 times in the presence of air. The low durability is due to the formation of endo-



Scheme 3.

Table 3. Fatigue Resistant Properties of Diarylethenes in Benzene

Compd		Repeatable cycle number	
		In iar	Under vacuum
	3	70	480
	6	3.7×10^3	1.0×10^4
	27	—	$>1.1\times10^4$
	28	$>1.0\times10^4$	—
	5	$>1.3\times10^4$	—

peroxide.[27] Photogenerated singlet oxygen reacts with the thiophene ring to produce thiophene-endoperoxide. When the thiophene rings were replaced with benzothiophene rings, the number remarkably increased. Benzothiophene has much lower reactivity to singlet oxygen. Diarylethenes having a 2-ethoxy-1-benzothiophene ring on one end had a good fatigue resistant character. 2-(1,2-Dimethyl-3-indolyl)-3-(2-ethoxy-1-benzothiophen-3-yl)maleic anhydride kept adequate photochromic performance even after 1.0×10^4 cycles in the presence of air. Diarylperfluorocyclopentene derivatives with benzothiophene aryl groups also showed excellent fatigue resistance.

4. Absorption Spectra

Figure 3 summarizes the absorption maxima of the closed-ring forms of various diarylethenes.[16—24,28,29] The closed-ring forms of bis(3-thienyl)ethene are red irrespective of the structure of the ethene moiety. Both bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene[30,31] and bis(2,4,5-trimethyl-3-thienyl)maleic anhydride[16] turned red (absorption maxima at 534 and 550 nm, respectively) upon irradiation with UV light. When phenyl groups are substituted at 5-positions of the thiophene rings, the color of the closed-ring form changed to blue ($\lambda_{\max}$=562 nm).[18] The spectral change accompanying the photochromism of 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perflurocyclopentene **7** is shown in Fig. 4. The absorption maximum further shifted to 597 nm by introducing electron-donating diethylamino groups at 4-positions of the phenyl substituents. The closed-ring form of a non-symmetric diarylethene having an indole ring on one end and a thiophene ring on the other end gave the absorption maximum at 578 nm. When an electron-donating group was introduced into the indole ring and/or an electro- withdrawing group into the thiophene ring, the absorption maxima shifted to longer wavelengths. The closed-ring form of 2, 3-diarylmaleic anhydride with a 5-methoxyindole ring on one end and a thiophene ring on the other end **34b** had its maximum at 611 nm in hexane, while the derivative with an indole ring and 5-cyanothiophene ring **35b** absorbed at 628 nm. The closed-ring having both electron-donating and -withdrawing substituents **37b** shifted the maximum to longer wavelengths at 680 nm, and the absorption edge was extended to 860 nm. The closed-ring forms of these compounds were thermally stable at 80 °C.

When a strong electron-donating CH=benzodithiole and a strong electron-withdrawing dicyanoethylene substituents were introduced into 5 and 5′ positions of the thiophene rings, the absorption maximum of the closed-ring form **12b** was further shifted to 828 nm in benzene.[22,23] This is the longest absorption band so far synthesized. The closed-ring form was, however, thermally unstable, as described before.

Although many photochromic molecules which exhibit blue and red color have been reported, the molecules which turn yellow upon UV irradiation are quite rare. 2H–Chromene[32] and spironaphthoxazine with pyrazine ring[33] are among the few such examples. For the full color display yellow-developing molecules are strongly desired. We found that the color of the closed-ring forms of dithienylethenes dramatically changes depending on the connecting position of the thiophene rings to the ethene moiety.[31] When the thiophene rings were attached to the ethene moiety at the 3-position, such as compound **31a**, the closed-ring form had an absorption at 534 nm (Scheme 4). The colorless solution turned to red upon UV irradiation. On the other hand, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene **29a** exhibited a different color change. Photoirradiation of a hexane solution containing **29a** with 366 nm led to a decrease of the absorption at 336 nm and formation of a yellow solution, in which a new band appeared at 425 nm. The blue shift of the absorption band of **29b** suggests that the π-conjugation in the closed-ring form is localized in the cyclohexadiene structure. The π-electron delocalization of **29b** is completely different from **31b**, in which π-conjugation extends through two thienyl moieties. The open-ring form **29a**, on the other hand, gave an absorption band at longer wavelengths ($\lambda_{\max}$=336 nm) compared with **31a** ($\lambda_{\max}$=234 nm). The red shift suggests that π-conjugation in the open-ring form extends throughout the molecule. The substitution position controls the absorption maxima of both isomers.

As can be seen from Fig. 3, diarylethenes can give any kind of color in the visible wavelength region.

5. Response Time

The dynamics of cyclization and ring-opening reactions of diarylethenes has been studied by using pico- and femto-

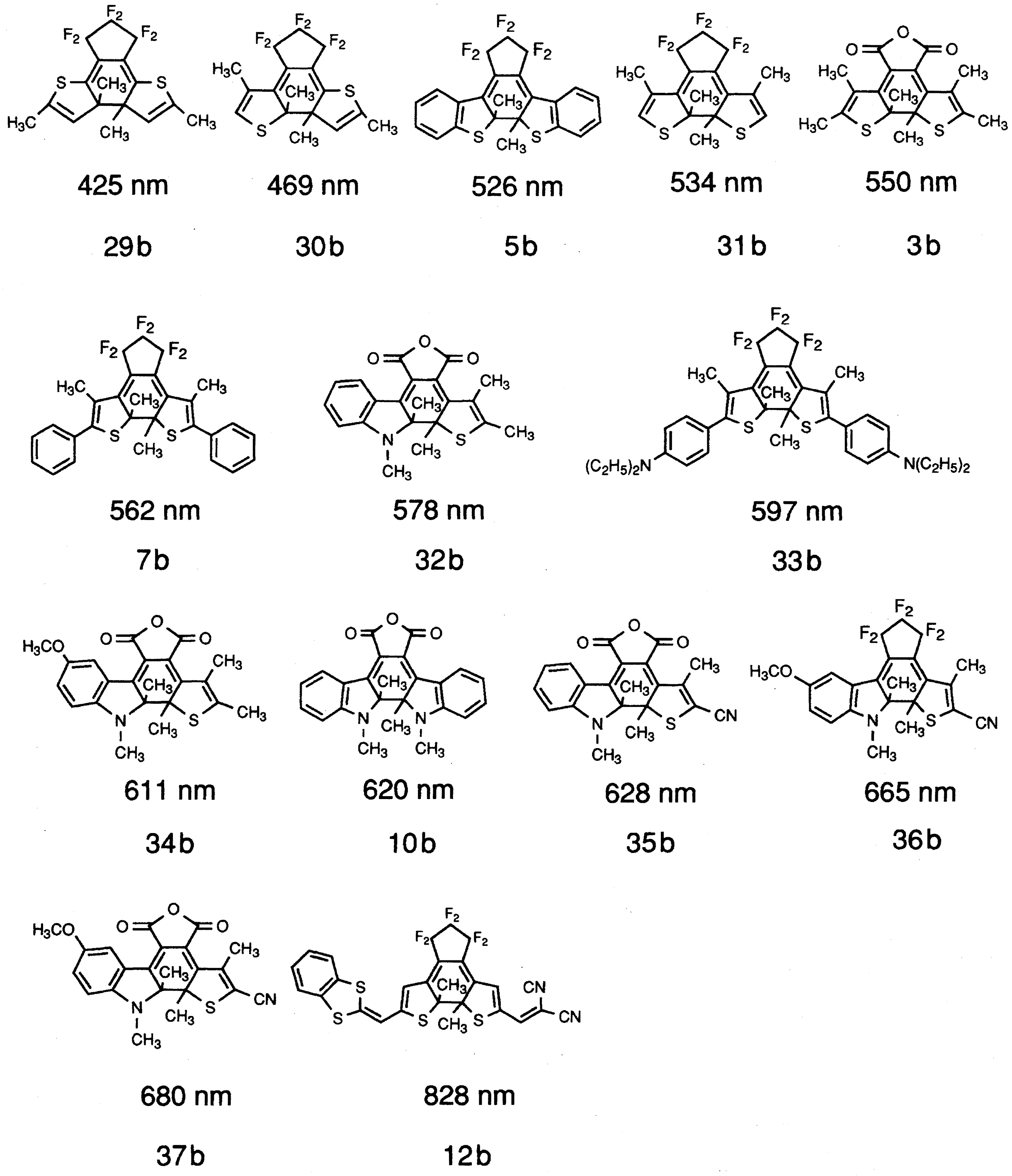


Fig. 3. Absorption maxima of the closed-ring forms of various diarylethenes.

second laser photolysis instruments. Both cyclization and ring-opening reaction rates were measured for compound **3**.[34] The open-ring form was excited with a 355 nm laser pulse (fwhm: 22 ps) in hexane and the formation of the closed-ring form was followed at 560 nm. A rapid spectral evolution in a few tens of pico-seconds was observed. This is attributable to the photocyclization reaction. The rise curve was well reproduced by taking account of the pulse duration and the time constant of formation of 8 ps. Since the laser pulse duration is rather long, it is difficult to determine the rapid time constant precisely. The result, however, clearly indicates that there exists a rapid formation process in less than 10 ps.

The ring-opening reaction was followed by exciting the closed-ring form in hexane with a 532 nm laser pulse. Immediately after the excitation depletion of the absorption around 560 nm and an increase in absorption around 600—750 nm were observed. The increased absorption is ascribable to an S_1–S_n transition. The decreased absorption is assigned to the bleaching of the closed-ring form. The bleached signal

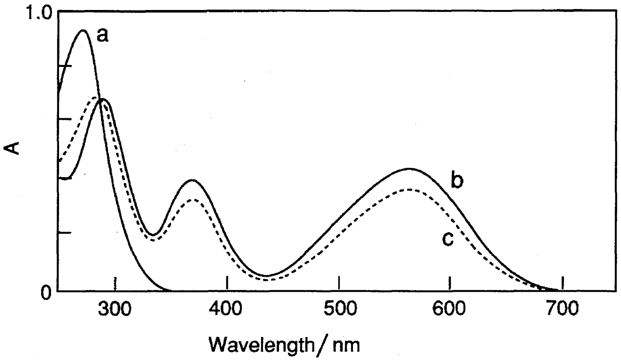
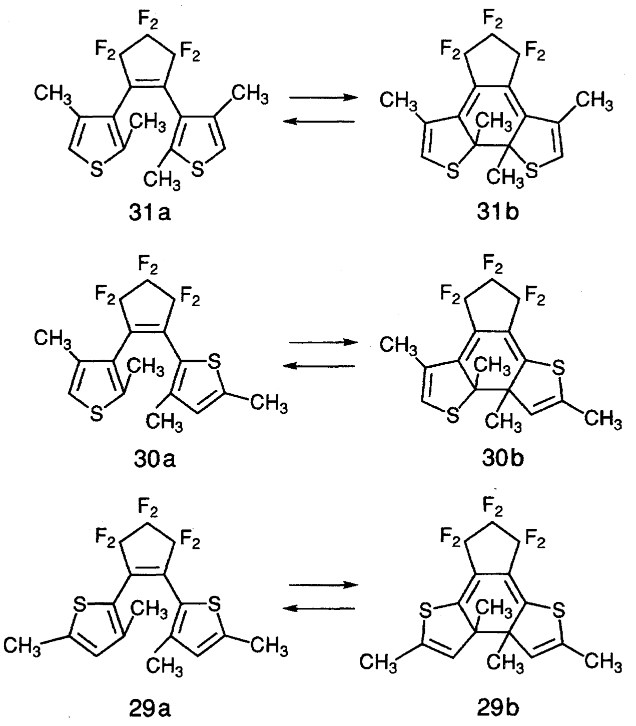


Fig. 4. Absorption spectra of hexane solutions of 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene **7a** (3.3×10^{-5} mol dm^{-3}) (a ——), **7b** (b ——), and **7b** in the photostationary state (c - - -) under irradiation with 313 nm light.



Scheme 4.

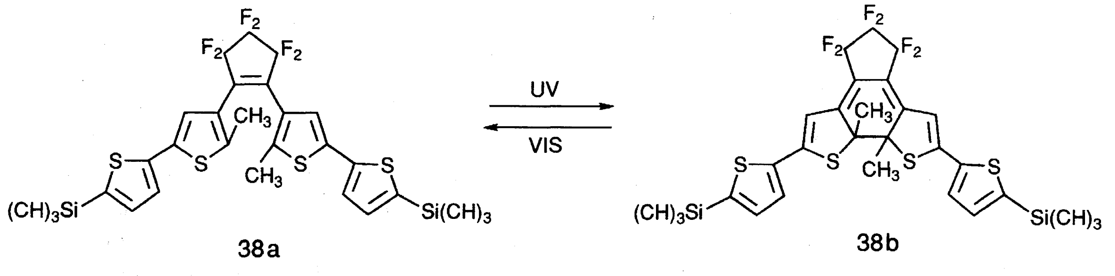
intensity slightly recovered and reached a constant value. The time constant of 2—3 ps well reproduced the recovery of the decreased absorption, indicating that the ring-opening reaction took place within 2—3 ps.

In the above measurement, the pulse duration is longer than the rates of the cyclization/ring-opening reactions. To know the rates precisely, it is desirable to employ a shorter laser pulse. The response time of the following dithienylethene **38** was measured in 1,2-dichloroethane by using a femto laser (fwhm: 180 fs) photolysis instrument (Scheme 5).[35] The absorption at 650 nm was found to increase in around 1 ps in accord with the decay of the absorption at 515 nm after irradiation with a 360 nm laser pulse. The absorption bands at 515 and 650 nm were assigned to S_1–S_n transitions of the open-ring form (or some intermediate produced from the excited state of the open-ring form) and the closed-ring form, respectively. The kinetic analysis by taking account of the pulse duration and the time constant of formation of 1.1 ps well reproduced the decay and the rise profile. This result clearly indicates that the photocyclization of the dithienylethene took place in 1 ps.

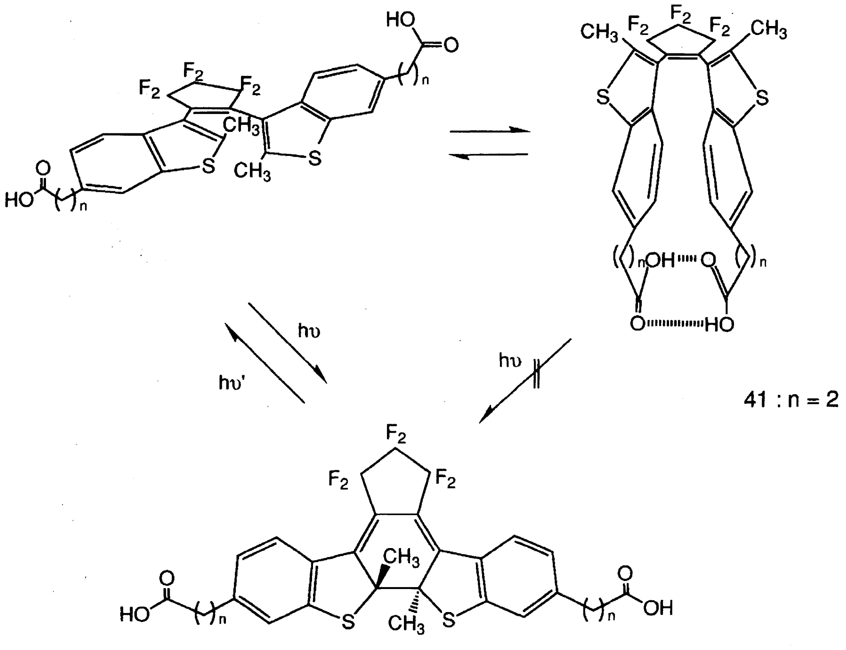
6. Gated Reactivity

6.1 An Intramolecular Locking System. Photochromic reactions, in general, proceed in proportion to the number of photons absorbed by the molecules. Such a linear-response characteristic cannot be used as the basis of opto-electronic devices, because memories or images are erased during storage under room light or after many readout operations. One possible way to avoid such inconvenience is to introduce gated photochromic reactivity to the molecules. Diarylethene derivatives having such a non-linear response property have been synthesized.

A diarylethene with heterocyclic rings has two conformations with the two rings in mirror and C_2 symmetries, and its cyclization reaction can proceed only from the conformation with the two rings in C_2 symmetry. This means that the photocyclization is prohibited if the heterocyclic rings are fixed to the mirror symmetry, or have a parallel orientation, while the reaction is allowed when the conformation converts to the C_2 symmetry, or anti-parallel orientation, as shown in Scheme 6.[36,37] The photoreaction of **41** was completely prohibited in cyclohexane. The addition of a very small amount of ethanol to the cyclohexane solution gained the photochromic reactivity. In the mixed solvents of cyclohexane and ethanol, the photocyclization quantum yield increased with the increasing ethanol content and reached a plateau value of 0.51 in the solvent containing 15 vol% ethanol. NMR measurement of the methyl protons at the 2-position of benzothienyl rings gives information concerning



Scheme 5.



Scheme 6.

the relative population of the two conformations. The signals at around 2.4 and 2.1 ppm are assigned to methyl protons in parallel and anti-parallel conformations, respectively. In cyclohexane the signal at 2.1 ppm was not observed, while it appeared by the addition of ethanol. This clearly indicates that the molecule was in a parallel conformation in cyclohexane, and it converted to an anti-parallel conformation upon the addition of ethanol. In cyclohexane the intra-hydrogen bonds fasten the molecule in the parallel conformation and make the molecule photochemically inactive. Conversely, ethanol acts as a switch to unlock the system.

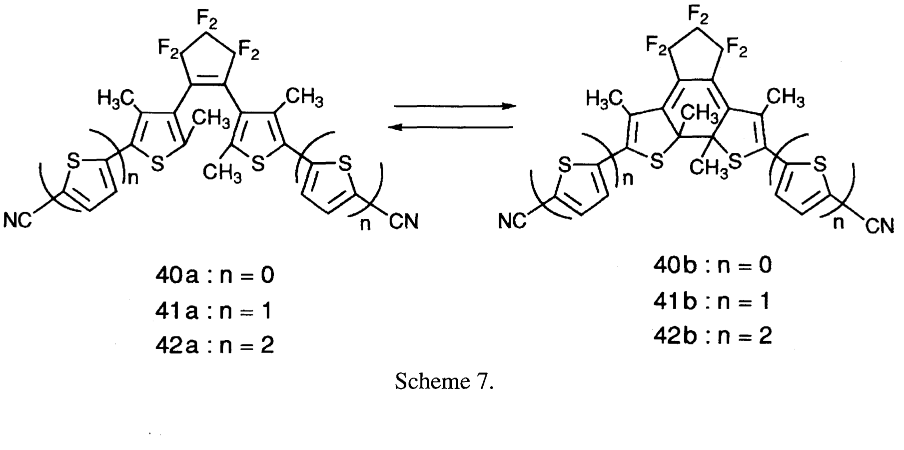
The hydrogen bonds can also be broken upon heating. In decalin the photocyclization did not occur below 60 °C, while it was clearly observed at temperatures higher than 100 °C. The molecule has both chemical- and thermal-gated reactivity.

6.2 Diarylethenes Having Oligothiophene Aryl Groups. Photochromic reactivity of diarylethenes **40**, **41**, and **42** was found to depend on the number of thiophene rings in the aryl groups (Scheme 7).[38] The cyclization and ring-opening quantum yields were measured in toluene at 25 °C. The cyclization quantum yield slightly decreased with the increasing number of the thiophene ring, as shown in Table 4. The quantum yield is as large as 0.44 for compound **40a**, while it decreased to 0.12 when a thiophene ring is attached to each thiophene ring of **40a**. The attachment of one more thiophene ring to the aryl group did not affect the cyclization quantum yield.

Table 4. Cyclization ($\Phi_{a\rightarrow b}$) and Ring-Opening ($\Phi_{b\rightarrow a}$) Quantum Yields of Dithieylethenes **40**, **41**, and **42** in Decalin

Compd	$\Phi_{a\rightarrow b}$	$\Phi_{b\rightarrow a}$		
	25 °C	25 °C	100 °C	150 °C
40	0.44	0.075	0.13	—
41	0.12	0.0013	0.0056	0.016
42	0.12	0.00013	0.0012	0.0044

The ring-opening quantum yield dramatically decreased when the number of thiophene rings was increased. The yield of 0.075 of **40b** decreased to 0.0013 when a thiophene ring was attached to **40b**. It further decreased to 0.00013



Scheme 7.

in terthiophene derivative **42b**. The very low ring-opening quantum yield of **42b** is ascribable to large extension of π -conjugation throughout the 6 thiophene moieties. The low quantum yield steeply increased as much as 34 times when the temperature was raised from 25 to 150 °C. The large temperature dependence is not due to the inherent activation energy of the ring-opening reaction in the excited state, because such large temperature dependence was not observed for **40b**. The conformational change of the oligothiophene groups by heating is considered to play an important role in the ring-opening process.

The diarylethene having terthiophene aryl groups has a thermal gated reactivity, and is useful for non-destructive readout when the diarylethene is used as the memory medium. The recorded memory can be read many times with weak laser light, which does not raise the medium temperature. The memory can be erased with a high intensity laser, which can raise the medium temperature as high as 100—150 °C.

7. Single Crystalline Photochromism

During the course of study of substituted dithienylperfluorocyclopentenes, we found that some of diarylethenes undergo photochromic reactions in the single crystalline phase (Scheme 8).[30,39,40] Another example of photochromic crystalline diarylethene is *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene–copper complex.[41]

Upon exposure to 313 nm light the powder of compound **29a** changed from white to red, and the red color disappeared by irradiation with visible light (>450 nm). In order to judge whether the reaction takes place in the real crystalline phase or in the surface defects we examined the reaction in a single crystal. A rhombus shaped crystal grown in hexane was used. Figure 5 shows a photograph of the single crystal, on which a Chinese character "Hikari-Light" is written. The line width is around 20 μm. The red character remained stable up to the melting temperature ($T_m = 120$ °C) and thermal decoloration was not discerned at room temperature. The thermally stable red character is readily erased by irradiation with visible light (>450 nm). The coloration/decoloration cycle could be repeated many times (more than 100 times) without destruction of the crystal shape.

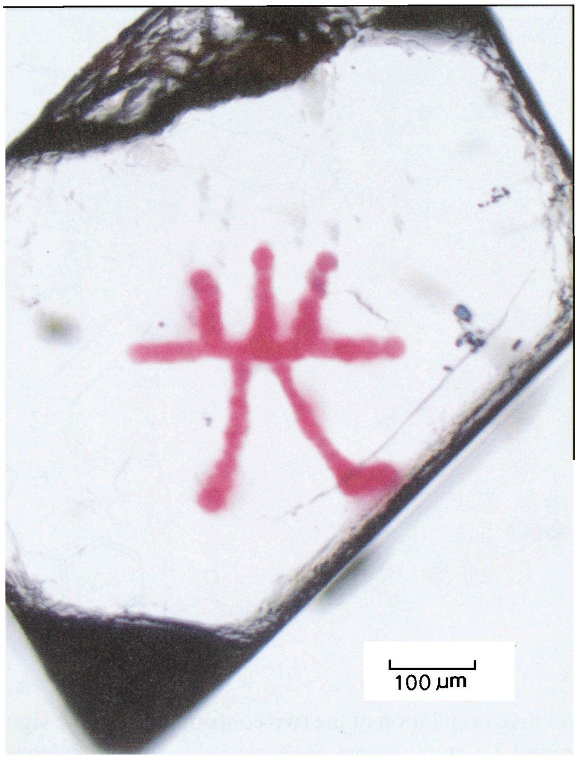
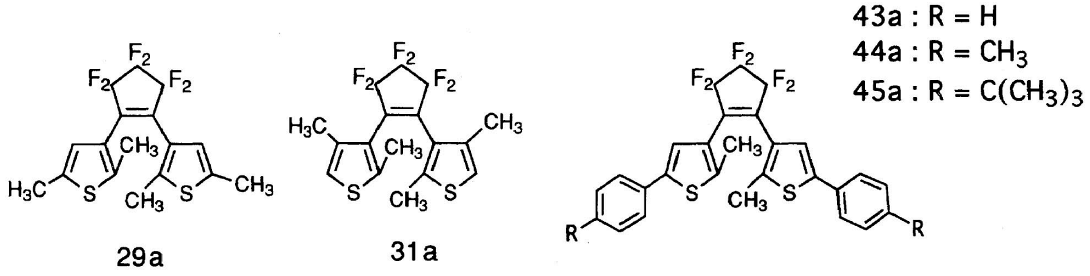


Fig. 5. The photograph of a single crystal, on which a Chinese character of "Hikari-Light" was written.

The photoreactivity in the crystalline phase was further confirmed by measuring the absorption spectrum under linearly polarized light. A colorless crystal was irradiated with 313 nm light and placed on the stage of a polarizing microscope. The polarizer and analyzer were set in parallel to each other. When the sample stage was turned, the red color intensity dramatically changed. Strong red colored appeared at 0 and 180 degrees, while the color disappeared at 90 and 270 degrees. This result clearly indicates that photogenerated colored isomers regularly align in the crystal lattice. X-Ray analysis of the crystal structure revealed that the angle dependence of the red color intensity reflects the molecular packing in the crystal.

When the thiophene rings have only two methyl groups (compounds **29a** and **31a**), the dithienylethenes underwent photochromism in the crystalline phase. But, bis(2,4,5-trimethyl-3-thienyl)perfluorocyclopentene having three methyl groups in the thiophene rings did not show any photochromic reactivity in the crystalline phase, though the reactivity in a hexane solution is very similar to each other. X-Ray analysis of the crystal structure showed that compounds **29a** and **31a** have an anti-parallel conformation, while the above non-reactive dithienylethene has a parallel conformation in the



Scheme 8.

crystalline phase. The molecules in the parallel conformation can not undergo the conrotatory photocyclization reaction. The reactivity depends on the conformation in the crystal.

Single crystals of **43a** and **45a** turned blue by irradiation with 366 nm light. The absorption maxima were similar to those of the closed-ring forms in hexane ($\lambda_{\max}=580$ nm). Although the coloration quantum yields of these three compounds are very similar to each other in a hexane solution, the reactivity strongly depended on the substituent R in the crystalline phase. When the substituent R is H or $C(CH_3)_3$, the crystal showed very quick coloration upon irradiation with 366 nm light. On the other hand, the crystal slowly turned blue and the degree of coloration remained low when R is CH_3. The crystal structure of **44a** suppressed the photocyclization. In all cases the thermally stable blue color can be bleached completely by exposing the crystals to visible light (>500 nm). Although at present it is not clear from the X-ray structure analysis, we tentatively attributed the reactivity difference to the molecular packing of the aryl groups in the crystals.

Picosecond transient absorption spectroscopy was carried out to reveal the reaction dynamics in the crystalline phase.[42] The powder of compound **29a** was irradiated with a 355 nm laser pulse (fwhm: 15 ps) and the rise of the absorption at 505 nm was followed. The absorption is due to the closed-ring form. The rise curve was well reproduced by taking into account the pulse duration and the time constant of formation of 10 ps. This result indicates that very rapid rotation of the thiophene rings is allowed in the photoexcited state even in the crystalline phase.

The crystalline photochromic materials are useful for near-field optical memory media.[43] In the near-field optical memory the media should have high contrast in very thin films (<100 nm). The bulk photochromic systems without polymer matrices can give high absorption intensity in the thin films. The thermally irreversible and fatigue resistant photochromic crystals are one of the candidates for the super-high density optical memory media.[44]

8. Conclusion

Theoretical consideration based on a molecular orbital theory predicted that the photogenerated closed-ring forms of diarylethenes are thermally stable when the aryl groups have low aromatic stabilization energy. The theoretical prediction was confirmed by the synthesis of diarylethenes having various aryl groups. Diarylethenes having heterocyclic five-membered rings, such as furan, thiophene (or benzothiophene), or thiazole rings, were found to undergo thermally irreversible photochromic reactions. Diarylperfluorocyclopentene having benzothiophene rings underwent photochromic cycles more than 1.0×10^4 times. The absorption spectra of the closed-ring forms of the diarylethenes were dependent on the aryl groups, substituents of the aryl groups and the connecting position of the aryl groups to the ethene moiety. The diarylethene derivatives can give any kind of color in the visible wavelength region from 425 to 828 nm. The response times of both cyclization and ring-opening reactions were less than 10 ps. The chemical and thermal gated photochromic reactivity was achieved by introducing intramolecular hydrogen bonding groups or oligothiophene aryl groups to the diarylethenes. Some of the dithienylethenes were found to show photochromic reactivity in the crystalline phase. The crystalline photochromic materials are potentially useful for near field optical memory media.

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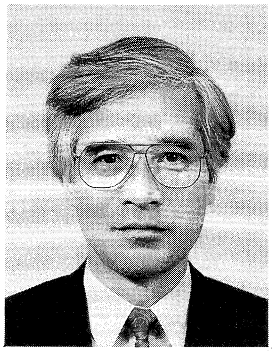

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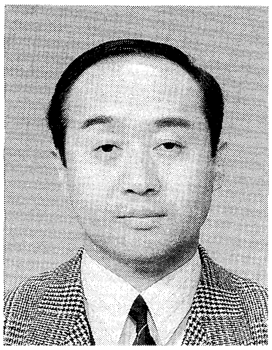

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