

# Diarylethenes for Memories and Switches

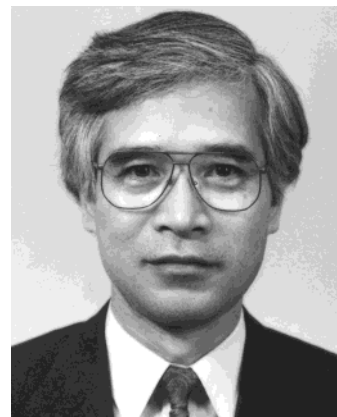
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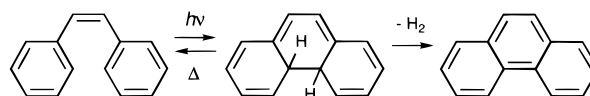
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Masahiro Irie received his B.S. (1966) and M.S. (1968) degrees from Kyoto University and his Ph.D. (1973) degree in Radiation Chemistry from Osaka University. In 1968 he joined the Faculty of Engineering, Hokkaido University, as a research associate 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 to Professor in Advanced Material Study, Kyushu University, and in 1996 he was reappointed to Professor of Chemistry with the Faculty of Engineering (the organization recently changed to the Graduate School of Engineering). His recent interests lie in development of new photochromic materials for molecular photonics and applications of near field optics. He has been named as the CREST project leader of "Development of Photochromic Systems with Perfect Performance" sponsored by Japan Science and Technology Corporation.

dihydrophenanthrene returns to stilbene in the dark in a deaerated solution. In the presence of air, however, the dihydrophenanthrene irreversibly converts to phenanthrene by the hydrogen-elimination reaction with oxygen, as shown in Scheme 1.

**Scheme 1**



## I. Introduction

Diarylethenes with heterocyclic aryl groups are newcomers to the photochromic field. They belong to thermally irreversible (P-type) photochromic compounds. The most striking feature of the compounds is their resistance to fatigue. The coloration/decoloration cycle could be repeated more than  $10^4$  times in keeping with the photochromic performance. Both properties, thermal irreversibility and fatigue resistance, are indispensable for applications to optoelectronic devices, such as memories and switches. In this review fundamental properties of the compounds and their applications to optical memories and switches are described.

Stilbene is well-known to undergo a photocyclization reaction to produce dihydrophenanthrene.<sup>1–3</sup> The

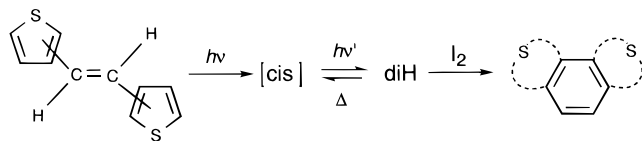
When the 2- and 6-positions of the above phenyl rings were substituted with methyl groups, the elimination reaction was suppressed and the compound underwent a reversible photocyclization reaction, that is, a photochromic reaction, even in the presence of oxygen. The lifetime of the colored dihydro-type isomer of 2,3-dimesityl-2-butene was, however, very short ( $t_{1/2} = 1.5$  min at 20 °C).<sup>4</sup> Such a thermally unstable photochromic system is not useful for optical memories and switches.

The photocyclization and hydrogen-elimination reactions can be used for the synthesis of condensed

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aromatic ring systems. During the course of a photosynthetic study of condensed ring systems including heteroatoms (Scheme 2), Kellogg et al.<sup>5</sup> found that

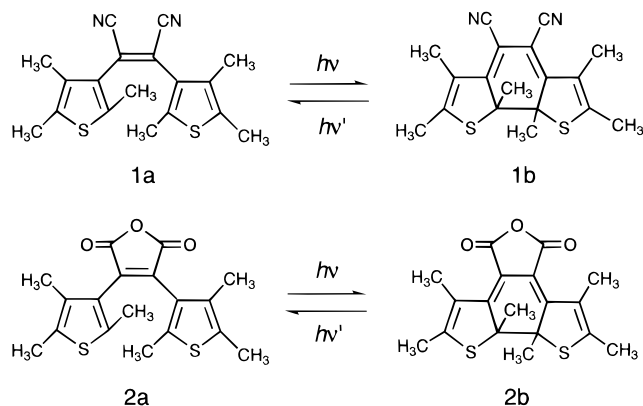
### Scheme 2



the lifetimes of the dihydro-type intermediates were prolonged by replacing the phenyl rings of stilbene with thiophene rings. They mentioned that the dihydro intermediate (diH) of 1,2-di(3-thienyl)ethene was stable for periods of 12–15 h in the dark in the absence of oxygen.

On the basis of the above suggestive observation, the following diarylethenes with thiophene rings, such as 1,2-dicyano-1,2-bis(2,4,5-trimethylthiophen-3-yl)ethene (**1a**) and 2,3-bis(2,4,5-trimethylthiophen-3-yl)maleic anhydride (**2a**) (Scheme 3), were prepared

### Scheme 3



in an attempt to construct thermally irreversible photochromic systems.<sup>4</sup> The dicyano and maleic anhydride groups were selected to shift the absorption maxima of the dihydro-type isomers to longer wavelengths. The maleic anhydride group also prohibits the cis to trans photoisomerization, which may compete with the photocyclization reaction.

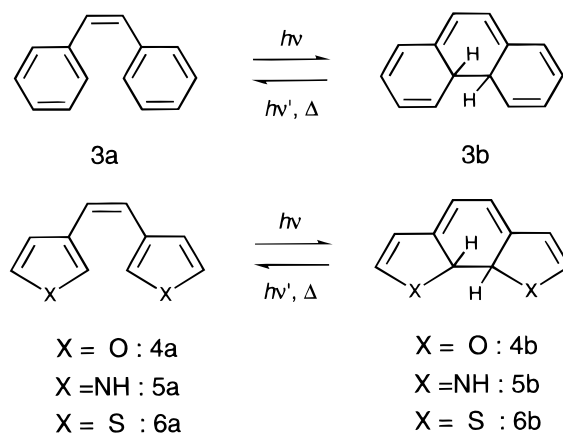
The photogenerated dihydro-type isomers, **1b** and **2b**, of the above two compounds never returned to the initial cis-type open-ring isomers in the dark for more than 3 months, even at 80 °C, but readily regenerated the open-ring isomers by irradiation with visible light ( $\lambda > 450$  nm). Hereafter, **a** and **b** refer to the open- and closed-ring form isomers, respectively. These are the first examples of thermally irreversible photochromic diarylethenes. Since then, various types of diarylethenes having thiophene, furan, indole, selenophene, and thiazole aryl groups have been prepared. Most of them show thermally irreversible and fatigue-resistant photochromic reactions. In the following, molecular design, synthesis, properties, and applications are reviewed.

## II. Molecular Design Principle

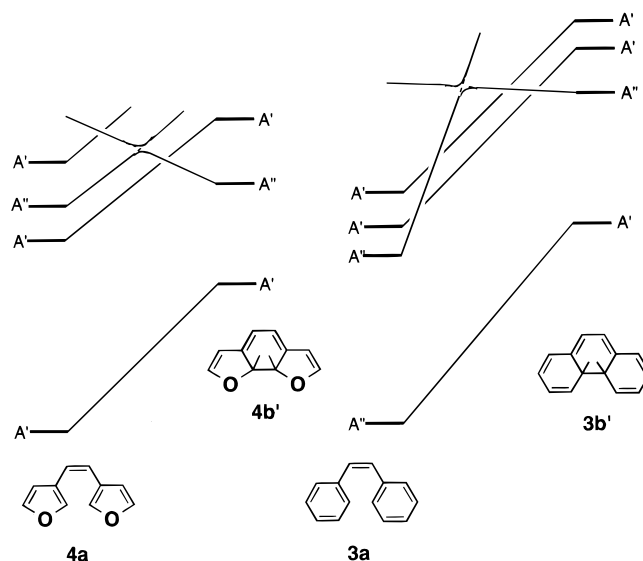
Although thermal irreversibility is the key property for the applications of photochromic compounds to

memories and switches, most existing photochromic compounds lack the property, and any guiding principle for the design of such compounds has not been established. To gain access to a guiding principle for the synthesis of thermally irreversible photochromic compounds, a theoretical study on 1,3,5-hexatriene to cyclohexadiene-type photochromic reactions was carried out.<sup>6</sup> Typical compounds having a 1,3,5-hexatriene molecular framework are diarylethenes having phenyl or heterocyclic five-membered rings. Semiempirical MNDO calculations were carried out for several diarylethenes, such as 1,2-diphenylethene (**3a**), 1,2-di(3-furyl)ethene (**4a**), 1,2-di(3-pyrrolyl)ethene (**5a**), and 1,2-di(3-thienyl)ethene (**6a**), together with their closed-ring isomers (Scheme 4).

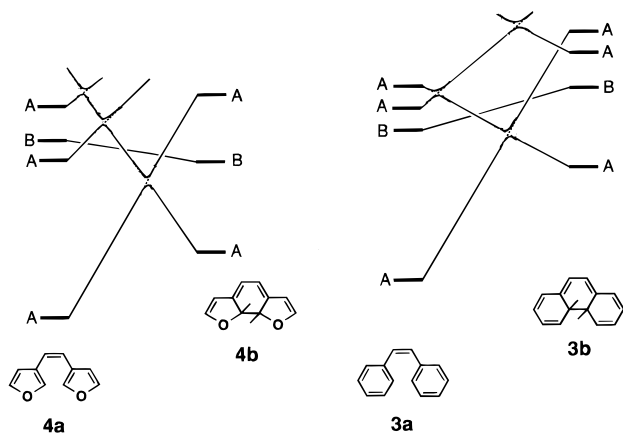
### Scheme 4



According to the Woodward–Hoffmann rule based on  $\pi$ -orbital symmetries for 1,3,5-hexatriene, a conrotatory cyclization reaction is brought out by light and a disrotatory cyclization by heat.<sup>6</sup> Figures 1 and 2 show the state correlation diagrams for the electrocyclic reactions from **3a** to **3b'** (**3b**) and **4a** to **4b'** (**4b**) in disrotatory and conrotatory modes, respectively. Full lines in the figures show that the



**Figure 1.** State correlation diagrams for the electrocyclic reactions in disrotatory mode. **3b'** and **4b'** are the closed-ring isomers, in which two hydrogens attached to the central carbons are in a cis configuration.



**Figure 2.** State correlation diagrams for the electrocyclic reactions in conrotatory mode. **3b** and **4b** are closed-ring isomers, in which two hydrogens attached to the central carbons are in a trans configuration.

**Table 1. Relative Ground-State Energy Differences between the Open- and Closed-Ring Isomers<sup>b</sup>**

compound		disrotatory (kcal/mol)	conrotatory (kcal/mol)
1,2-diphenylethene	<b>3</b>	41.8	27.3
1,2-di(3-pyrrolyl)ethene	<b>5</b>	32.3	15.5
1,2-di(3-furyl)ethene	<b>4</b>	27.0	9.2
1,2-di(3-thienyl)ethene	<b>6</b>	12.1	-3.3

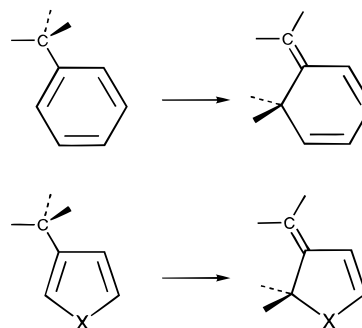
interconnecting states belong to the same symmetry groups. As can be seen from Figure 1, orbital symmetry allows the disrotatory cyclization in the ground state from **3a** to **3b'** and **4a** to **4b'**. The relative ground-state energies of the products are, however, 27.0 and 41.8 kcal/mol higher than the respective energies of the reactants. The large energy barriers practically prohibit the ground-state cyclization reactions in both cases.

No large energy barriers exist in the cyclization processes in the  $S_1$  state for **3a** and  $S_2$  state for **4a**, as shown in Figure 2. This means that the cyclization reactions of **3a** and **4a** are allowed in the photoexcited states.

Next, what should be considered is the stability of the photogenerated closed-ring isomers. Full lines in Figure 2 suggest that in both **3b** and **4b** the cyclereversion reactions in the ground states have to overcome energy barriers, and the barriers correlate with the ground-state energy differences. The calculated values of the differences for **3**, **4**, **5**, and **6** are shown in Table 1. When the energy difference is large, as in the case of 1,2-diphenylethene (**3**), the energy barrier becomes small and the cyclereversion reaction readily takes place. On the other hand, the reaction barrier becomes large when the energy difference is small, as shown for 1,2-di(3-furyl)ethene (**4**). In this case the cyclereversion reaction is not expected to occur. The energy barrier, which correlates with the ground-state energy difference between the open- and the closed-ring isomers, controls the stability of the photogenerated colored closed-ring isomers.

The important question is what kind of molecular property change causes the ground-state energy difference. The aromaticity change from the open- to

**Scheme 5**



the closed-ring isomers was examined. Scheme 5 shows the structural change of the aryl groups in the reaction from the open- to closed-ring isomers. The difference in the energy between the above right- and left-side groups was calculated, as shown in Table 2.

**Table 2. Aromatic Stabilization Energy Differences<sup>6</sup>**

group	energy (kcal/mol)
phenyl	27.7
pyrrolyl	13.8
furyl	9.1
thienyl	4.7

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 isomers.

From the above consideration, it was concluded that the thermal stability of both isomers of diarylethene-type photochromic compounds can be attained by introducing heterocyclic aryl groups, which have low aromatic stabilization energies. This is the molecular design principle of thermally irreversible diarylethenes.

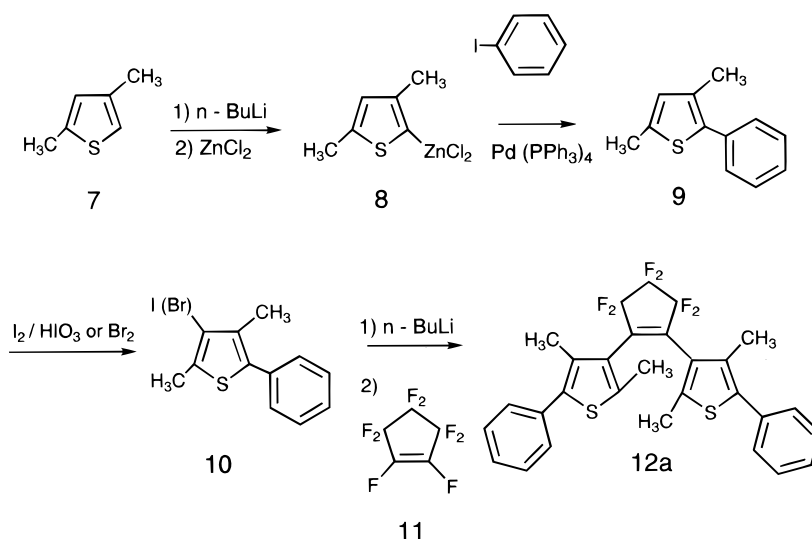
### III. Synthesis

#### A. Diarylperfluorocyclopentenes

The most commonly used diarylethenes are diaryl-perfluorocyclopentenes.<sup>8</sup> Symmetric and nonsymmetric diarylethenes with various heterocyclic aryl groups were synthesized by the elimination reaction of perfluorocyclopentenes with aryllithium. The reaction yield is usually moderate, but in some cases a very high yield, more than 99%, has been reported.<sup>9</sup> A typical synthetic route is shown in Scheme 6.<sup>10</sup>

2,4-Dimethylthiophene (**7**) was lithiated and treated with zinc(II) chloride in ether. The ether solution was added dropwise to anhydrous tetrahydrofuran (THF) containing iodobenzene and tetrakis(triphenylphosphine)palladium(0) to give phenylthiophene (**9**) in 97% yield. The phenylthiophene is also prepared by using palladium-catalyzed Suzuki coupling of thiopheneboronic acid and iodo- or bromobenzene.<sup>11,12</sup> The phenylthiophene (**9**) was halogenated and then lithiated. The lithiated thiophene derivative was

## Scheme 6

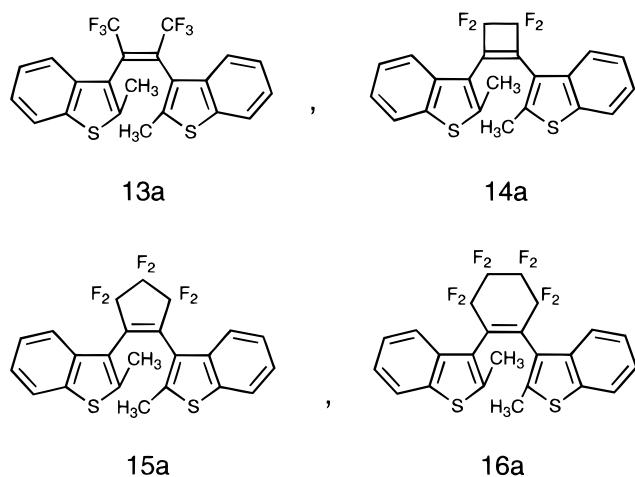


reacted with octafluorocyclopentene (**11**) at  $-78^\circ\text{C}$  to give 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene (**12a**) in 52% yield. Various types of 1,2-diarylperfluorocyclopentenes can be prepared by modification of this process.

Monosubstituted perfluorocyclopentenes were selectively prepared by controlling the ratio of perfluorocyclopentene and aryllithium. The monosubstituted compound can be used for the synthesis of nonsymmetric diarylethenes.<sup>13–17</sup>

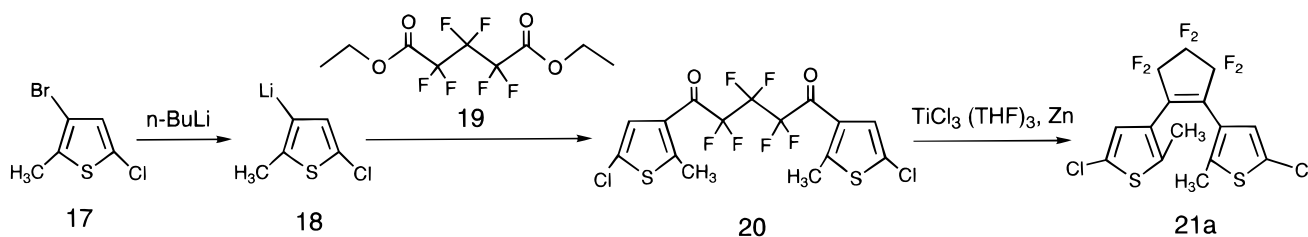
The cycloalkene size can be changed from a four- to six-membered ring (Scheme 7).<sup>8,18–20</sup>

## Scheme 7



The absorption maxima of the closed-ring isomers were shifted to longer wavelengths upon decreasing

## Scheme 8

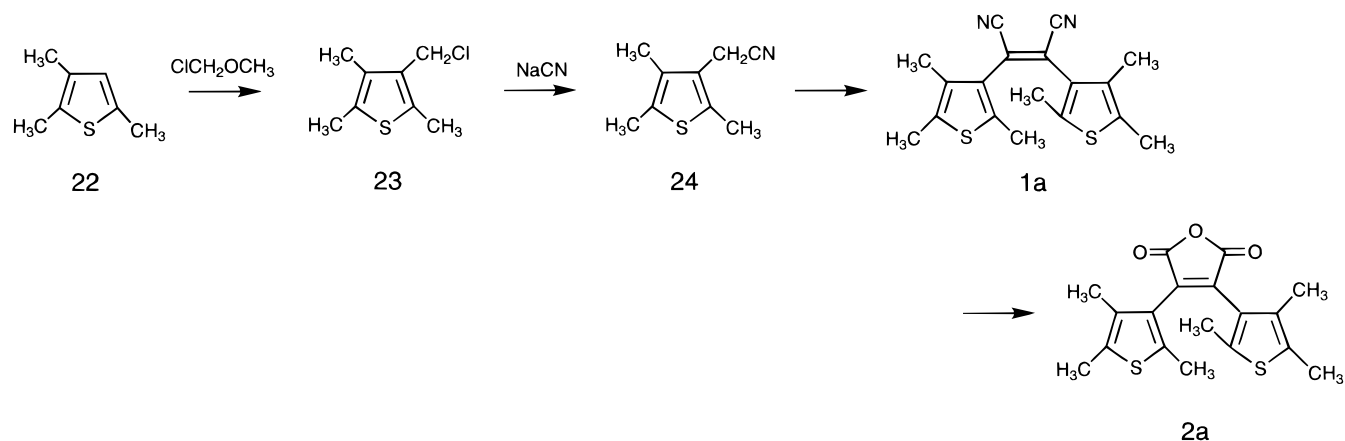


the ring size. The closed-ring form of bis(perfluoromethyl) derivative **13b**, which has no ring structure, has an absorption maximum at 449 nm. The maximum at 510 nm of the closed-ring form of six-membered ring derivative **16b** was shifted to 526 nm for the five-membered ring derivative **15b** and further to 532 nm for the four-membered ring derivative **14b**. From the absorption spectral shift data it is inferred that the ring size controls the planarity and thus the extent of  $\pi$ -conjugation in the closed-ring isomers. The cyclization quantum yield was dependent on the ring size, and the highest value was observed for the six-membered ring derivative.<sup>19</sup> Taking two factors into account, the absorption maximum of the closed-ring form and the cyclization quantum yield, the five-membered ring is the most appropriate cycloalkene structure.

Recently a new synthetic route based on the acylation of a thiophene derivative, followed by a McMurry coupling,<sup>21</sup> has been proposed. The new route is shown in Scheme 8.<sup>22</sup>

A lithiated thiophene derivative **18** was reacted with **19** at  $-78^\circ\text{C}$ , and cyclization of the product **20** was carried out by a titanium-mediated coupling using  $\text{TiCl}_3(\text{THF})_3$  and  $\text{Zn}$  in THF at  $40^\circ\text{C}$ . The intramolecular McMurry coupling was also used for the synthesis of 1,2-diheteroaryl-substituted cyclopentenes,<sup>23,24</sup> which have hydrogens instead of the fluorines of diarylperfluorocyclopentenes. The photochromic performance, such as fatigue resistance and spectral splitting of the two isomers, of these diarylcyclopentene derivatives was inferior to that of the diarylperfluorocyclopentene derivatives.<sup>24</sup>

## Scheme 9



## B. Diarylmaleic Anhydrides and Diarylmaleimides

Anhydride ring structures, such as maleic anhydride or maleimide, can also be used as the cycloalkene groups, which prevent the *cis* to *trans* photoisomerization. An example of the synthetic route of a diarylmaleic anhydride is shown in Scheme 9.<sup>4</sup>

2,3,5-Trimethyl-4-(chloromethyl)thiophene (**23**) was prepared by reaction of the trimethylthiophene (**22**) with chloromethyl methyl ether and converted to cyanomethyl derivative **24** with NaCN. The cyanomethyl derivative **24** was coupled in a NaOH alkaline aqueous solution in the presence of  $\text{CCl}_4$ . The 1,2-dicyano derivative **1a** was hydrolyzed in an alkaline solution to produce acid anhydride derivative **2a**. The method can be applied to various diarylmaleic anhydrides.<sup>25–27</sup>

Maleimide derivatives can be prepared by using oxalyl chloride and aminoacetonitrile as shown in Scheme 10.<sup>28</sup>

In summary, three different kinds of diarylethenes, 1,2-diaryperfluorocyclopentenes, 1,2-diarylmaleic anhydrides, and 1,2-diarylmaleimides, were synthesized. The difference in the structure did not alter the basic photochromic performance, such as thermal irreversibility and fatigue resistance. Only the ab-

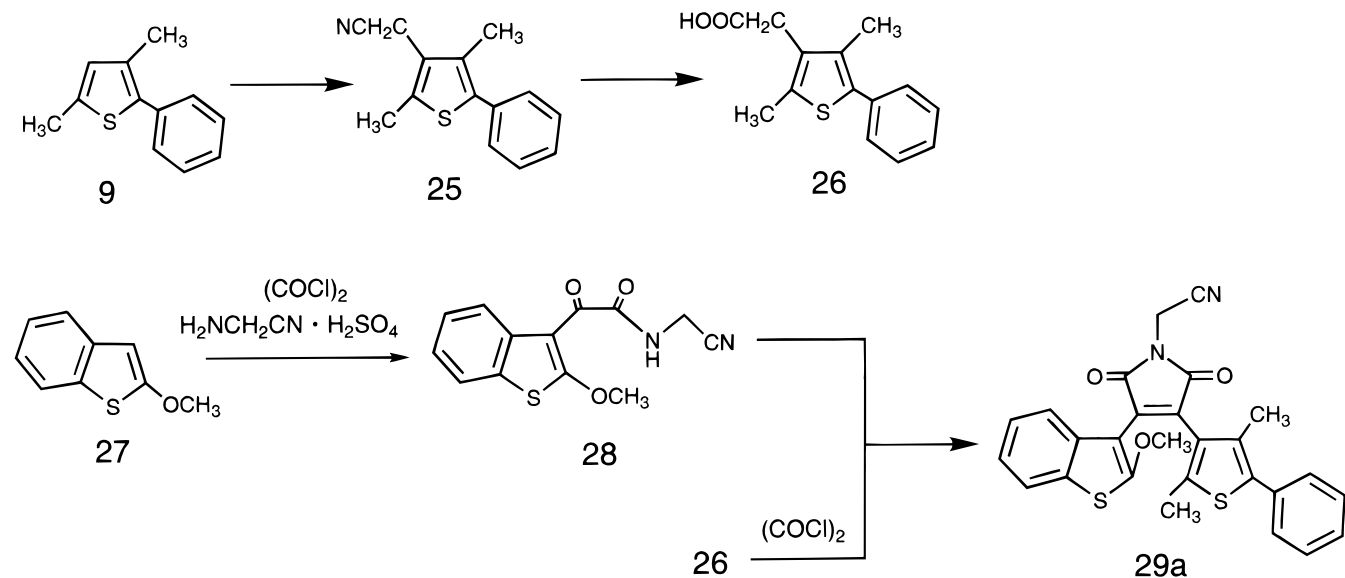
sorption spectra were shifted to longer wavelengths when maleic anhydride or maleimide cycloalkene groups were used.

## IV. Properties

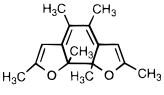
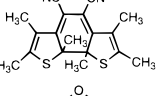
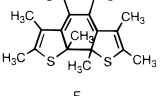
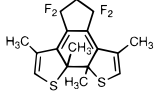
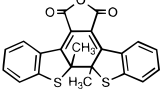
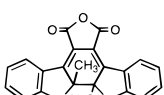
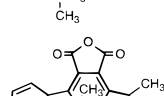
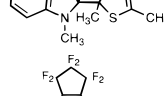
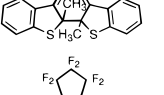
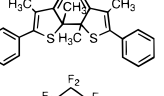
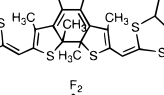
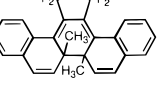
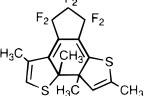
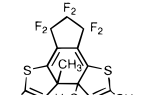
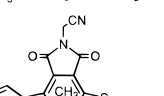
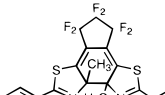
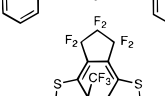
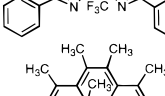
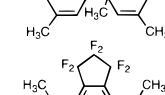
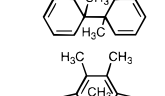
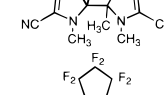
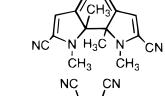
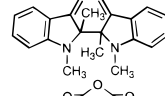
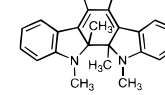

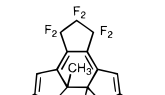
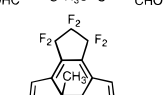
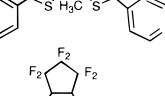
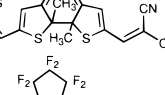
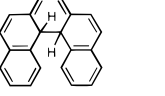
Despite the favorable situation provided by recent progress of optical memory and switch technologies, organic photochromic compounds still await practical applications. The limitation is due to lack of suitable compounds which meet the following technical requirements for the optoelectronic devices: (1) Archival storage capability and stability of both isomers (thermal stability); (2) Low fatigue (can be cycled many times without significant loss of performance); (3) High sensitivity and rapid response; (4) Nondestructive readout capability; (5) Sensitivity at diode laser wavelengths.

Among the requirements, the most important ones are the thermal stability of both isomer, and the fatigue resistance. In general, photogenerated colored isomers are thermally unstable and return to the initial isomers in the dark. These thermally reversible compounds are classified as T-type compounds. Although several attempts have been carried out to stabilize the photogenerated unstable isomers by

## Scheme 10



**Table 3. Thermal Stability of Closed-Ring Isomers of Diarylethenes<sup>a</sup>**

Compounds	Lifetime, $t_{1/2}$	Compounds	Lifetime, $t_{1/2}$
	30b	Stable	
	1b	> 90 days at 80 °C > 15 h at 140 °C	
	2b	> 90 days at 80 °C > 5 years at r. t	
	31b	Stable	
	32b	Stable	
	33b	Stable	
	34b	Stable	
	15b	Stable	
	12b	Stable	
	35b	Stable	
	36b	> 500 h at 70 °C	
	37b	Stable	
	38b	Stable	
	39b	Stable	
	40b	> 40 h at 70 °C	
	41b	> 80 h at 100 °C	
	42b	> 80 h at 100 °C	
	43b	1.5 min at 20 °C	
	44b	15 min at 25 °C	
	45b	32 min at 20 °C	
	46b	37 s at r.t.	
	47b	~ 20 h at 80 °C	
	48b	3 h at 80 °C	
	49b	3.3 min at 60 °C	
	50b	573 min at 60 °C	
	51b	247 min at 60 °C	
	52b	186 min at 60 °C	
	53b	43 min at 70 °C	
	54b	15 min at -150 °C	
	55b	~ 20 h at 70 °C	

<sup>a</sup> Stable means that the lifetime is longer than 12 h at 80 °C.

dispersing them in high  $T_g$  polymer matrices,<sup>29–31</sup> the stability is not enough for practical applications. Aggregate formation is another approach to stabilize the colored isomers,<sup>32</sup> but the reversibility of the system is poor. It is strongly desired to develop photochromic compounds in which both isomers are intrinsically stable. Furylfulgides and diarylethenes with heterocyclic aryl groups belong to such thermally irreversible (P-type) compounds. The difference between furylfulgides and diarylethenes is the fatigue resistance. In most cases, coloration/decuration cycles of furylfulgides are limited to less than 100 cycles.<sup>33</sup> Diarylethenes having heterocyclic aryl groups are thermally irreversible and fatigue resistant as described below.

### A. Thermal Stability

Table 3 summarizes the lifetimes of the closed-ring isomers of various diarylethenes in solution in the dark.<sup>4,6,8,10,11,25–27,34–42</sup> All of the compounds reported so far have not shown any thermochromism. The open-ring isomers are thermally stable, as predicted by the theoretical calculation (see section II). The thermal stability of the colored closed-ring isomers is dependent on the type of aryl groups. When the aryl groups are furan, thiophene, selenophene, or thiazole rings, which have low aromatic stabilization energies, the closed-ring isomers are thermally stable and do not return to the open-ring form isomers even at 80 °C. On the other hand, photogenerated closed-ring isomers of diarylethenes with pyrrole, indole, or phenyl rings, which have rather high aromatic stabilization energies, are thermally unstable. The photogenerated blue closed-ring isomer of 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene (**46b**) returned to the open-ring isomer in 37 s ( $=t_{1/2}$ ) at room temperature.<sup>41</sup> The closed-ring isomers of bis(3-indolyl)ethenes, **47b** and **48b**, also exhibited thermally reversible reactions at 80 °C.<sup>26</sup> The different thermal stability behavior of the closed-ring isomers between diarylethenes with furan, thiophene, or thiazole rings and pyrrole, indole, or phenyl rings agrees well with the theoretical prediction.<sup>6</sup> The detailed theoretical calculation for the reaction **2a**  $\rightleftharpoons$  **2b** also confirmed that the thermal irreversibility is attributable to an avoid crossing at a high energy in the ground state.<sup>43</sup>

It is worthwhile to note the difference in stability between **36b** and **44b**.<sup>36</sup> Although the red color of **44b** disappeared in 15 min ( $=t_{1/2}$ ) at 25 °C, the absorption at 471 nm of **36b** remained stable for more than 500 h at 70 °C. The energy differences between the open- and the closed-ring isomers were calculated using MOPAC AM1 to be 30.27 and 43.87 kcal/mol for **36** and **44**, respectively. The energy difference of the naphthyl derivative **36** is much smaller than that of the phenyl derivative **44**. In the closed-ring isomer **36b**, styryl-type structures are involved. The relatively stable styryl structures are considered to decrease the energy of the closed-ring isomer **36b**.

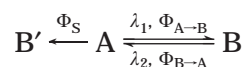
As presented in Table 3, some diarylethenes which have strong electron-withdrawing substituents deviate from the general rule.<sup>11,37</sup> The closed-ring isomers of **49b** and **52b** having dicyanoethylene substituents

returned to the open-ring isomers in 3.3 and 186 min at 60 °C, respectively. The dithienylethenes having pyridinium ions **51b** and formyl substituents **50b** also underwent thermally reversible photochromic reactions. The thermal instability of these closed-ring isomers is ascribed to the fact that the photogenerated central carbon–carbon bonds in the closed-ring isomers are weakened by the electron-withdrawing substituents.

When bulky substituents are introduced at 2-positions of the benzothiophene rings, the red closed-ring isomer **55b** was found to become thermally unstable.<sup>42</sup> The red-color disappeared in  $\sim 20$  h ( $=t_{1/2}$ ) at 70 °C, while any such instability was not observed for the closed-ring form **15b** of the methyl-substituted derivative. The bulky substituents are considered to weaken the photogenerated central carbon–carbon bond.

### B. Fatigue Resistance

Photochromic reactions are always accompanied by rearrangement of chemical bonds. During the rearrangement, undesirable side reactions take place to some extent. This limits the number of cycles of photochromic reactions. The difficulty in obtaining fatigue-resistant photochromic compounds can be easily understood by the following reaction sequence, in which a side reaction to the product **B'** is involved in the forward process.

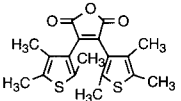
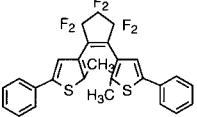
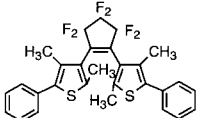
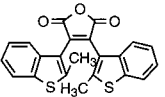
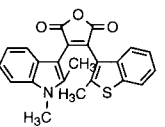
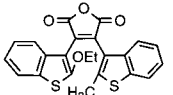
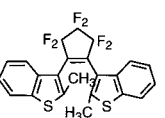
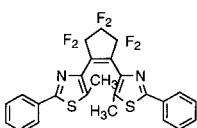
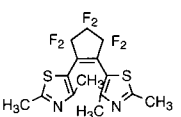
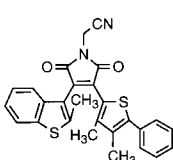
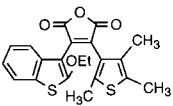
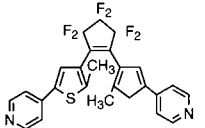


Even if the side reaction quantum yield,  $\Phi_S$ , is as small as 0.001 and **B** perfectly converts to **A** ( $\Phi_{\text{B} \rightarrow \text{A}} = 1$ ), 63% of the initial concentration of **A** will decompose after 1000 coloration/decuration cycles. Thus, the quantum yield of conversion to byproducts should be less than 0.0001 to repeat the cycles more than 10 000 times. This is not an easy task.

Fatigue resistance can be measured in the following experiment.<sup>44</sup> A benzene solution containing a diarylethene ( $\sim 10^{-4}$  mol/L) is irradiated with UV light of wavelength  $\lambda_1$ , which can excite the open-ring isomer, until the absorbance of the closed-ring isomer reaches 90% of the photostationary state, and then the colored closed-ring isomer is completely bleached by irradiation with visible light of wavelength  $\lambda_2$ . This operation is repeated many times, and after each 100 cycles, the absorbance of the open-ring isomer (or closed-ring isomer) is measured. In the case that the decomposition products have an absorption in the wavelength region of the open-ring isomer, the absorbance of the colored closed-ring isomer is monitored. The repeatable cycle number can be defined as the number of photochromic cycles at which the absorbance change of the open-ring isomer (or the colored closed-ring isomer) decreases to 80% of the first cycle.

Table 4 summarizes the results of repeatable cycle numbers in benzene and other media.<sup>4,8,15,25,39,40,44–46</sup> 1,2-Di(2,3,5-trimethylthiophen-3-yl)maleic anhydride (**2a**) as well as 1,2-di(2-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene (**56a**) decomposed in less

**Table 4. Fatigue-Resistant Property of Diarylethenes in Benzene and Other Media**

Compd	Repeatable Cycle Number <sup>a)</sup>		
	in air	under vacuum	
	2a	70	480
	56a	80 (in hexane)	200 (in hexane) > 10 <sup>4</sup> (in crystal)
	12a	200 (in hexane) ( <i>n</i> <sub>1/2</sub> = 500)	> 850 (in hexane)
	32a	3.7 x 10 <sup>3</sup>	1.0 x 10 <sup>4</sup>
	33a		> 1.1 x 10 <sup>4</sup>
	57a	> 1.0 x 10 <sup>4</sup>	
	15a	> 1.3 x 10 <sup>4</sup> (in methylcyclohexane)	
	40a	> 4 x 10 <sup>3</sup> (in hexane)	
	58a	> 4 x 10 <sup>3</sup> (in hexane)	
	39a	> 5 x 10 <sup>3</sup> (in hexane)	
	59a	3.0 x 10 <sup>4</sup> (in polystyrene)	7.0 x 10 <sup>4</sup> [ in polystyrene protected with PVA in the presence of singlet oxygen quenchers ]
	60a	~ 1500 (1/e) (in poly(butyl acrylate-co- acrylic acid))	

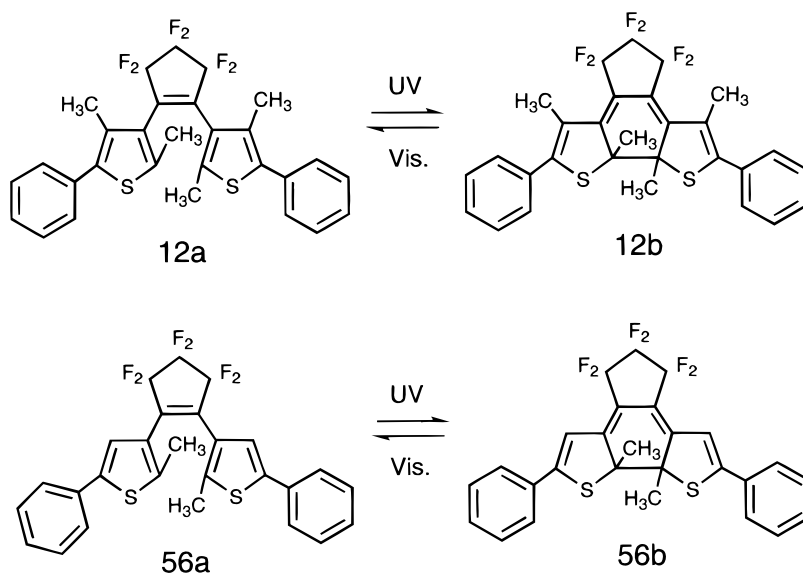
<sup>a</sup> The number of photochromic cycles at which the absorbances of the closed-ring isomers decrease to 80% of the first cycle. *n*<sub>1/2</sub> is the number of cycles at which one-half of the open-ring isomers decompose.

than 80 cycles in the presence of air.<sup>4,46</sup> The low durability is due to the formation of endoperoxide.<sup>45</sup>

Six-membered ring formation (see below) may also contribute to the degradation process. When the



## Scheme 11



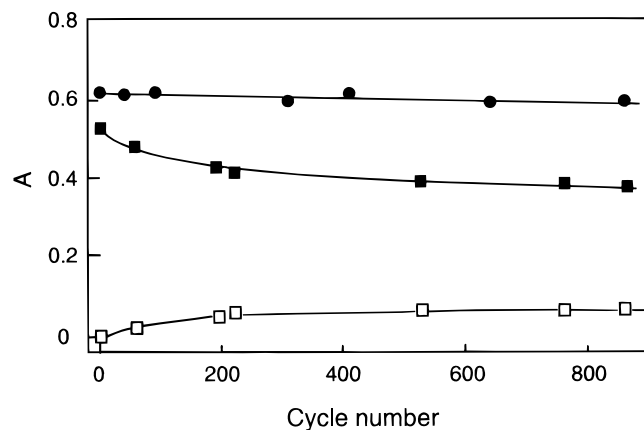
thiophene rings were replaced with benzothiophene rings, the cycle number remarkably increased.<sup>8,25</sup> Benzothiophene has a much lower reactivity to singlet oxygen, and the six-membered ring cannot be produced from the benzothiophene derivatives.

It is worth noting the difference in fatigue resistance of compounds **12a** and **56a** (Scheme 11).<sup>46</sup> Compound **12a** has methyl groups at the 4- and 4'-positions of the thiophene rings, while compound **56a** has no methyl groups at these positions. Figure 3 shows the cycle number dependence of absorbances of the bleached samples. The absorbance of **12a** remained almost constant even after 850 cycles, while the absorbance of **56a** gradually declined. At the same time a photostable violet product with an absorption maximum at 547 nm was formed. The photostable byproduct could be isolated by HPLC and was found by elemental analysis and molecular mass determination to be isomeric with compound **56a**. The molecular structure of the byproduct was determined by X-ray crystallographic analysis to be a six-

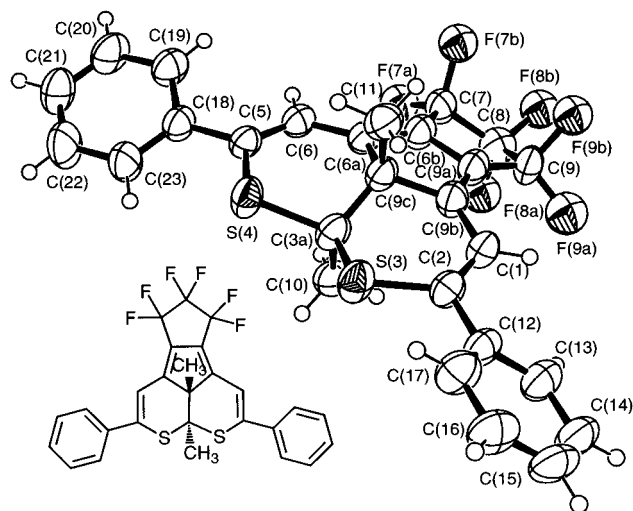
membered condensed ring structure as shown in Figure 4. The byproduct was more efficiently produced from the closed-ring form by UV irradiation. Such byproduct formation is the main fatigue process of dithienylethenes, which have no methyl groups at the 4- and 4'-positions of the thiophene rings, in the absence of oxygen. The methyl substituents at the 4- and 4'-positions are considered to prevent rearrangement of the thiophene rings to the six-membered condensed ring.

Compound **56** undergoes photochromism even in the crystalline phase. In the crystal, formation of the byproduct was not discerned even after 10 000 cycles. In the crystalline lattice the rearrangement is prohibited and oxygen diffusion is suppressed. Crystalline photochromic materials have a very high fatigue resistance. In a polymer matrix the degradation of **60**, which has no methyl substituents at the 4- and 4'-positions, was suppressed to some extent.<sup>47</sup>

The fatigue-resistant character of diarylethene **61** (Scheme 12) was examined in a Langmuir–Blodgett (LB) film.<sup>15</sup>

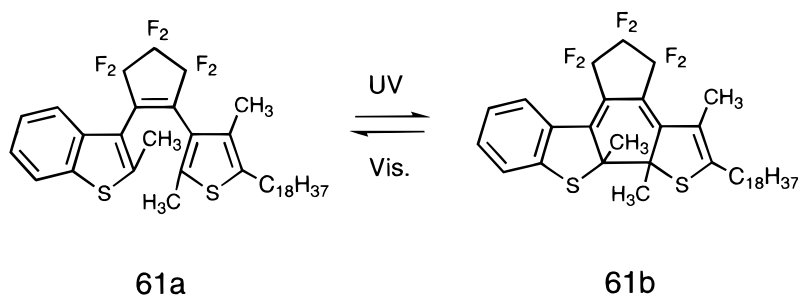


**Figure 3.** Fatigue resistance of **12** and **56** in deaerated hexane solution. Absorbances of **12a** (●) and **56a** (■) were plotted after irradiation with visible light. The visible absorbance at 547 nm (□), which still remained after visible irradiation of the hexane solution containing **56**, was also plotted. (Reprinted with permission from ref 46. Copyright 1999 The Royal Society of Chemistry.)



**Figure 4.** ORTEP view of the byproduct and its chemical structure. (Reprinted with permission from ref 46. Copyright 1999 The Royal Society of Chemistry.)

## Scheme 12



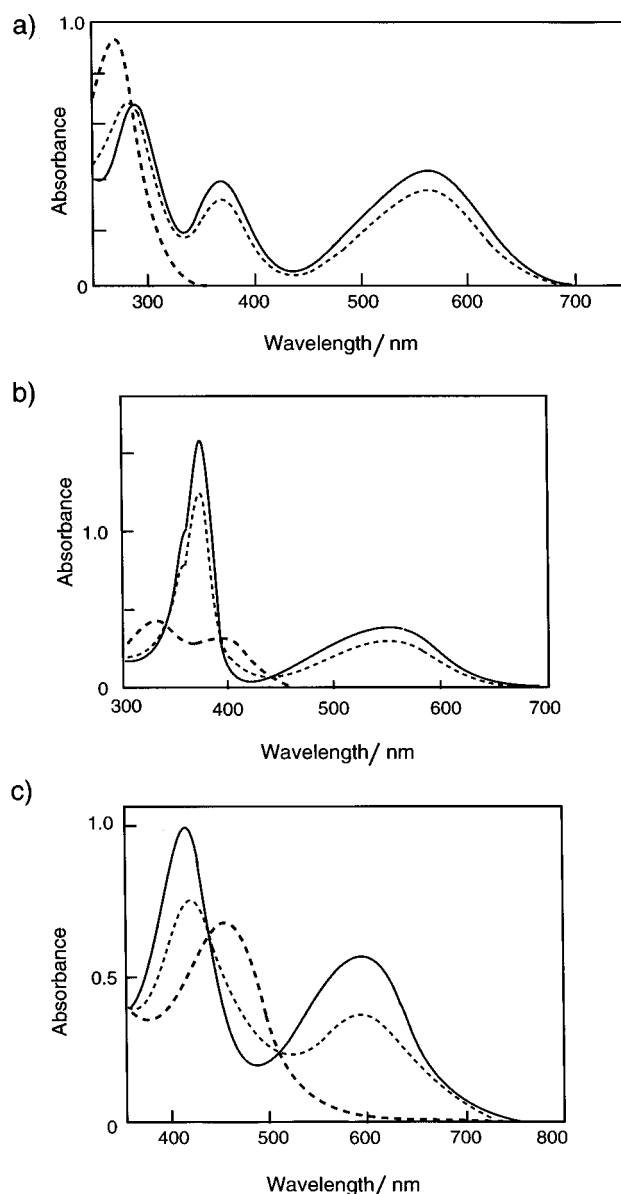
The excitation energy transfer method in an LB double-layer film consisting of acceptor monolayer containing photochromic chromophores and monolayer containing a fluorescent oxacarbocyanine was employed to measure the fatigue resistance. The method to detect fluorescence from the donor monolayer is highly sensitive and useful to detect photochromic reactions in the acceptor monolayer. The fluorescence intensity is modulated by the photochromic reactions in the acceptor layer. Upon irradiation with UV light, the spirobenzopyran LB film underwent a prompt bleaching to one-half of the initial fluorescence intensity change after 1500 s while the fluorescence intensity change in the diarylethene-containing LB films remained constant for 10 000 s. The quantum yield of byproduct formation was estimated to be less than  $0.25 \times 10^{-5}$ .

## C. Absorption Spectrum

Figure 5 shows the typical absorption spectral changes of diarylethene derivatives **12**, **2**, and **34** in hexane or benzene.<sup>10,48,27</sup> In general, the open-ring isomers of diarylethenes have absorption bands at shorter wavelengths. Upon irradiation with UV light, new absorption bands appear at longer wavelengths, which are ascribed to the closed-ring isomers. Most diarylethenes show very large spectral shifts upon photoisomerization from the open- to the closed-ring isomers ( $>6500 \text{ cm}^{-1}$ ). In the closed-ring isomers,  $\pi$ -electrons delocalize throughout the two condensed thiophene rings and further extend to the substituents. The absorption spectra of the closed-ring isomers depend on the substituents of the thiophene rings.

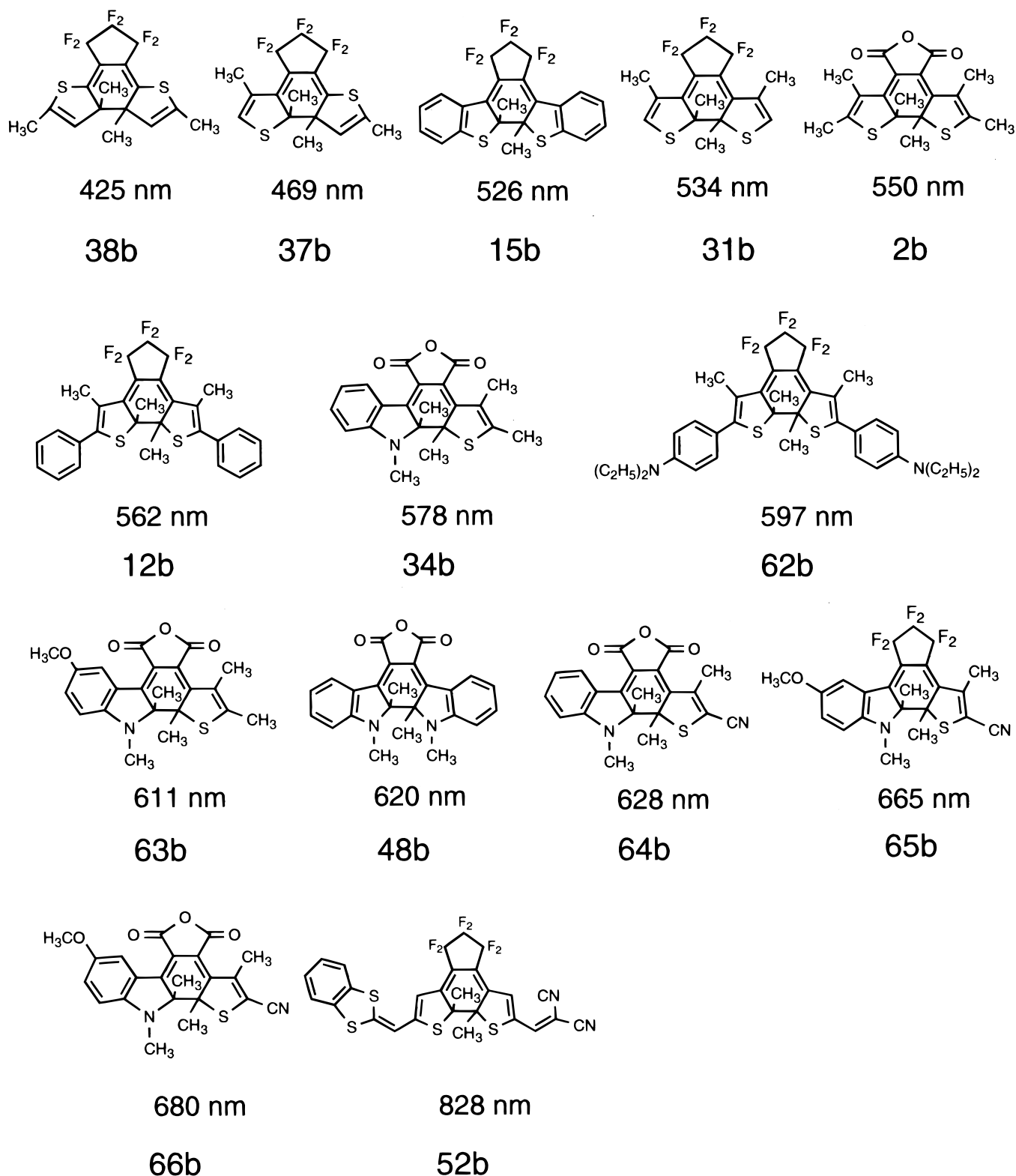
The absorption spectra of the open-ring isomers also depend on the upper cycloalkene structures. The open-ring isomers of maleic anhydride or maleimide derivatives show spectral shifts to longer wavelengths in comparison with the perfluorocyclopentene derivatives. The maleic anhydride derivatives **34** underwent the cyclization reaction by irradiation with visible light of 450–500 nm, as shown in Figure 5.

From the viewpoint of applications to optical memory media, it is desired to develop photochromic compounds that have sensitivity in the wavelength region 650–830 nm. The effect of substitution on the absorption maximum was examined in an attempt to develop near-infrared light-sensitive photochromic compounds. Figure 6 summarizes the typical absorption maxima of the closed-ring isomers.<sup>4,8,10,11,13,25–27,37,49</sup>



**Figure 5.** Absorption spectra of open-ring (---) and closed-ring (—) isomers and at the photostationary state (---) by irradiation with (a) 313, (b) 405, and (c) 491 nm light. (a) **12** in hexane. (b) **2** in hexane. (c) **34** in benzene. (Reprinted with permission from ref 27. Copyright 1991 The Chemical Society of Japan.)

Both 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene (**31b**) and 2,3-bis(2,4,5-trimethyl-3-thienyl)-maleic anhydride (**2b**) turned red upon irradiation with UV light. The absorption maxima of **31b** and



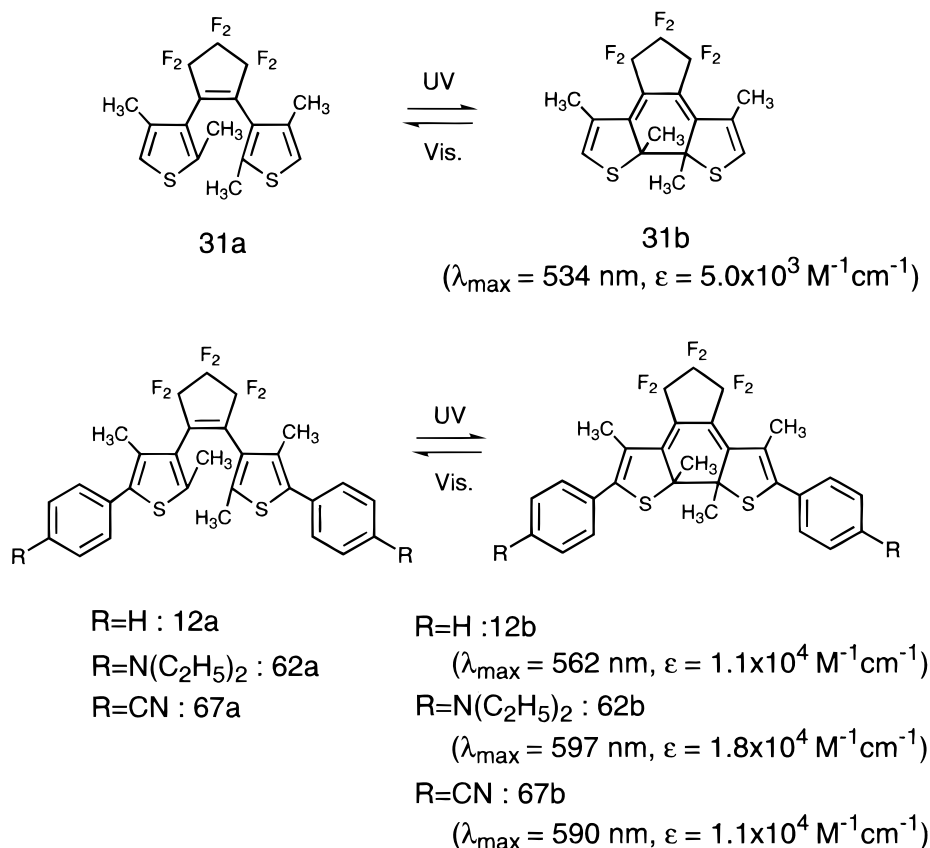
**Figure 6.** Absorption maxima wavelengths of the closed-ring isomers of diarylethenes.

**2b** were at 534 and 550 nm in benzene, respectively. When phenyl groups were substituted at the 5- and 5'-positions of the thiophene rings, the color of the closed-ring isomer **12b** changed to blue ( $\lambda_{\max} = 562$  nm). The absorption maximum was further shifted to 597 nm by incorporating electron-donating diethyl-amino groups at the 4- and 4'-positions of the phenyl substituents.<sup>10</sup> The closed-ring isomer of symmetric 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride (**48b**)

has an absorption maximum at 620 nm. The closed-ring isomer was, however, thermally unstable. In an attempt to obtain thermally stable photochromic compounds having absorptions at longer wavelengths, several nonsymmetrical diarylethenes having an indole ring on one end and a thiophene ring on the other end were prepared.

2-(1,2-Dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)maleic anhydride (**34b**) gave an absorption

## Scheme 13



maximum at 578 nm.<sup>27</sup> When an electron-donating group was introduced into the indole ring and/or an electron-withdrawing group into the thiophene ring, the absorption maximum was shifted to longer wavelengths. The closed-ring isomer **63b** having an electron-donating group had its maximum at 611 nm, while the derivative having a 5-cyanothiophene ring **64b** absorbed at 628 nm. The closed-ring isomer having both electron-donating and -withdrawing substituents **66b** shifted the maximum to 680 nm, and the absorption edge was extended to 860 nm. The closed-ring isomers of these compounds were stable at 80 °C.

When a strong electron-donating CH=benzodithiole substituent and a strong electron-withdrawing dicyanoethylene substituent were introduced into the 5- and 5'-positions of the thiophene rings, the absorption maximum of the closed-ring isomer **52b** was further shifted to 828 nm in benzene.<sup>11,37</sup> This is the longest absorption band so far reported. The closed-ring isomer was, however, thermally unstable. It returned to the open-ring isomer in 186 min ( $=t_{1/2}$ ) at 60 °C.

When we apply diarylethenes to full color display, it is indispensable to synthesize yellow-developing compounds. The absorption maximum of the closed-ring isomer was found to depend on the substitution positions of the thiophene or thiazole rings to the ethene moiety. When the thiophene rings were attached to the ethene moiety at the 2-positions, the  $\pi$ -conjugation is localized in the central cyclohexadiene structure in the closed-ring isomer and does not extend to substituents at the 5-positions. This was

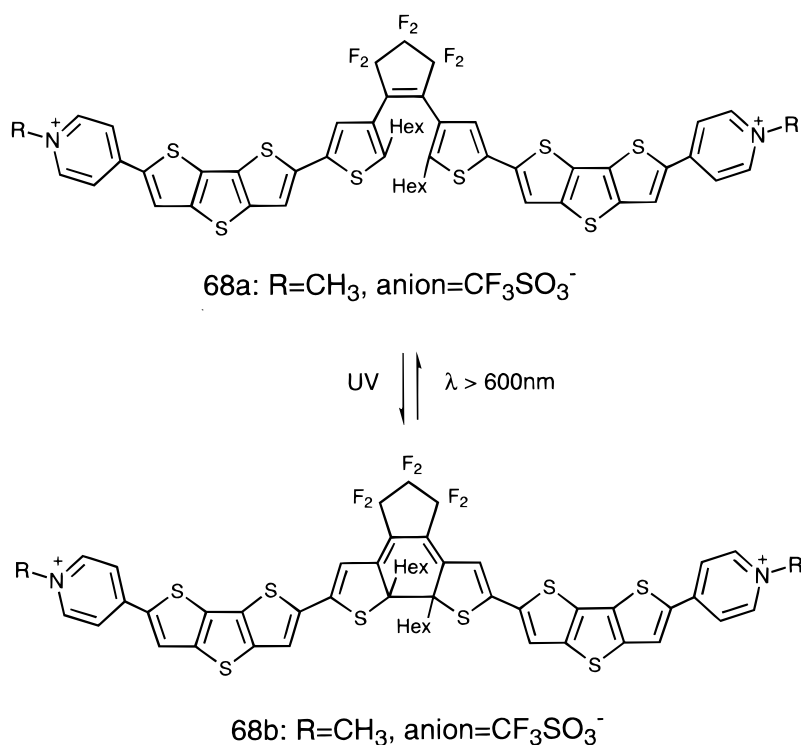
confirmed by the fact that the absorption maxima of the closed-ring isomers do not depend on the substituents at the 5-positions.<sup>39,40</sup> Both methyl and phenyl substituents exhibited almost similar absorption maxima.

It is interesting to compare the absorption bands of the open- and closed-ring isomers of **31** and **38**, in which the substitution position of the thiophene rings to the ethene moiety is different.<sup>13</sup> Photoirradiation of a hexane solution of **38a** with 366 nm light 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 absorption maximum is blue shifted as much as 109 nm in comparison with the maximum of **31b**, in which thiophene rings are attached to the ethene moiety at the 3-position. The open-ring isomer **38a**, on the other hand, gave an absorption band at a longer wavelength than **31a**. The red shift indicates that  $\pi$ -conjugation in the open-ring isomer extends more in the molecule. In **31a** the  $\pi$ -conjugation is localized in each thiophene ring. The substitution position controls the absorption maxima of both isomers.

Another important absorption characteristic is the molar absorption coefficient. High sensitivity requires high molar absorption coefficients and high quantum yields. Several diarylperfluorocyclopentenes with various electron-donating or -withdrawing substituents (Scheme 13) were synthesized to examine the effect of the substituents on the absorption coefficients ( $\epsilon$ ,  $\text{M}^{-1} \text{ cm}^{-1}$ ).

The  $\epsilon$  value of **31b** is rather low ( $5.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). The  $\epsilon$  value increased twice and the absorption

## Scheme 14



maximum was shifted to a longer wavelength as much as 28 nm when phenyl groups were introduced at the 5- and 5'-positions of the thiophene rings (**12b**). It further increased to  $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  when electron-donating *N,N*-diethylamino groups were substituted at *para*-positions of the phenyl rings. The  $\epsilon$  value of **62b** is 3.6 times larger than that of the unsubstituted form of **31b**. When the diethylamino groups were protonated by the addition of trifluoroacetic acid, the  $\epsilon$  value decreased to 55% of the neutral form. On the other hand, electron-withdrawing cyano substituents did not affect the  $\epsilon$  value, as observed for **67b**, which has the same  $\epsilon$  value as that of the unsubstituted derivative.

Electron-rich dithieno(thiophene) groups (Scheme 14) are also effective in increasing the  $\epsilon$  value of the closed-ring form.<sup>50,51</sup> Compound **68b** has a very large  $\epsilon$  value ( $\lambda_{\text{max}} = 704 \text{ nm}$ ;  $\epsilon = 4.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) in acetonitrile.

Successive increases in the absorption coefficients and spectral shift to longer wavelengths of the closed-ring isomer were observed in the diarylethenes (Scheme 15) having oligothiophene<sup>51,52</sup> or polyene<sup>53</sup> groups.

In the case of oligothiophene derivatives, the  $\epsilon$  value increased as much as 4 times and the absorption maximum shifted as much as 65 nm by increasing the number of thiophene rings from one to three. When polyene structures were introduced at the 5- and 5'-positions of thiophene rings, the  $\epsilon$  value also increased. The absorption maximum position of the closed-ring isomers was almost saturated with four double bonds as observed for **74b**, since the overall  $\pi$ -conjugation is already large. Introduction of electron-rich substituents or large- $\pi$ -conjugation systems is effective to increase the  $\epsilon$  values.

## D. Quantum Yield

A diarylethene with five-membered heterocyclic rings has two conformations with the two rings in mirror symmetry (parallel conformation) and in  $C_2$  symmetry (antiparallel conformation).<sup>4,10,25</sup> The photocyclization reaction can proceed only from the antiparallel conformation (Scheme 16).

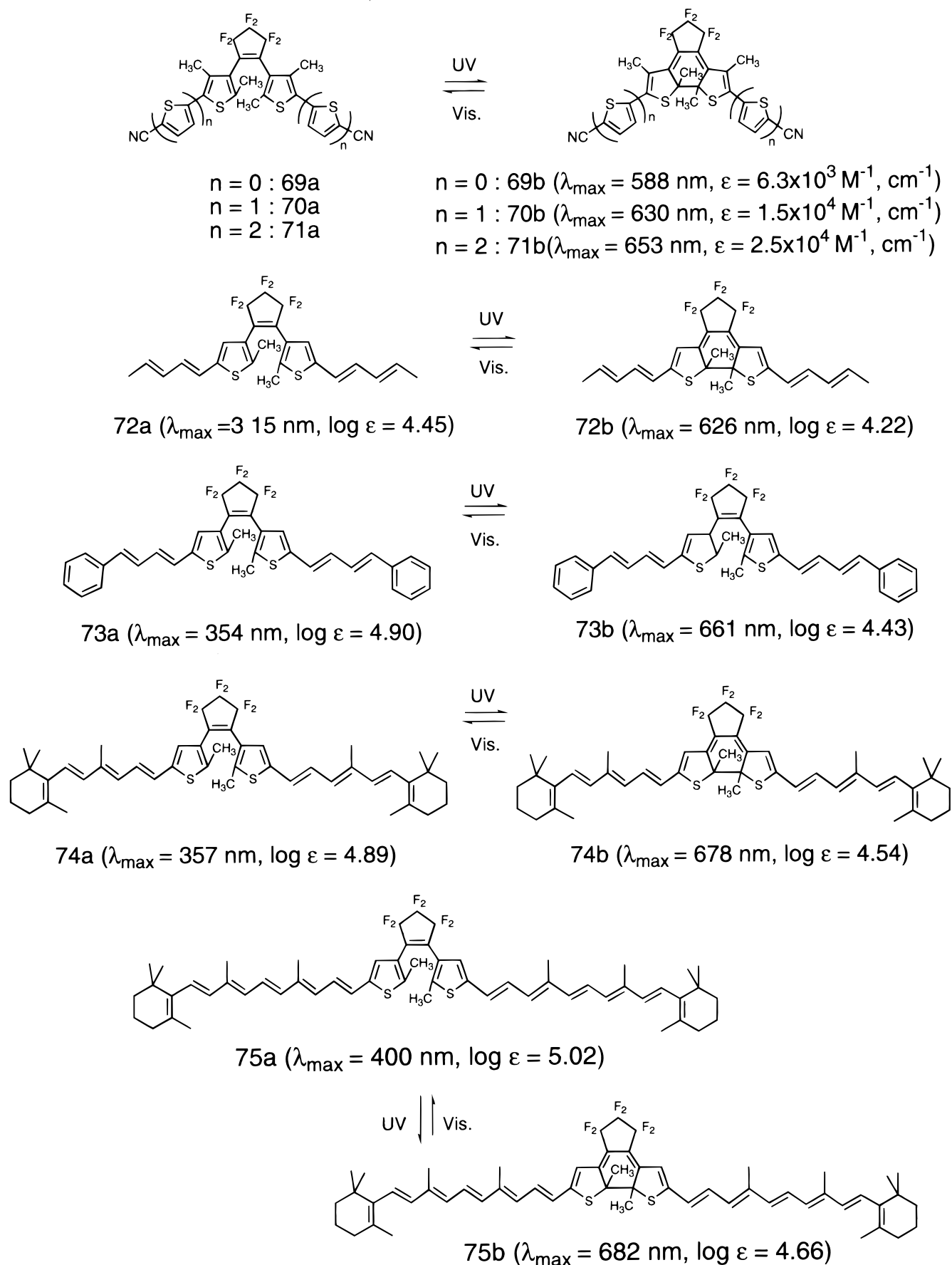
In general, the population ratio of the two conformations is 1:1. Therefore, the cyclization quantum yield cannot exceed 0.5. The quantum yields of 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene derivatives (Scheme 13) are shown in Table 5.<sup>10</sup> In these derivatives two conformations exist in an equal ratio. This means that the quantum yields of **12a** and **67a** are very close to the maximum value. Almost all photoexcited antiparallel conformations undergo the cyclization reaction. In other words, the actual quantum yields are close to 1.

When the ratio of the antiparallel conformation is increased, the quantum yield is also expected to increase. There are two possible approaches to increase the ratio. One approach is to change the ratio by introducing bulky substituents to the thiophene rings.

The ratio of the two conformations was found to change by introducing bulky isopropyl substituents at the 2- and 2'-positions of the benzothiophene rings.<sup>42</sup> The increase of the antiparallel conformation was confirmed by measuring the NMR signals of the methyl protons. The antiparallel conformation ratio increased from 0.65 to 0.94 by the introduction of isopropyl substituents. Accordingly, the cyclization quantum yield increased from 0.35 to 0.52.

The quantum yield was also found to increase by incorporating the dithienylethenes into a polymer backbone.<sup>54</sup> Polymer **76a** (Scheme 17) having dithie-

## Scheme 15



nylenes in the main chain was synthesized and the quantum yield of cyclization reaction measured.

A cyclization quantum yield as large as 0.86 has been reported. The authors<sup>54</sup> ascribed such a large cycliza-

## Scheme 16

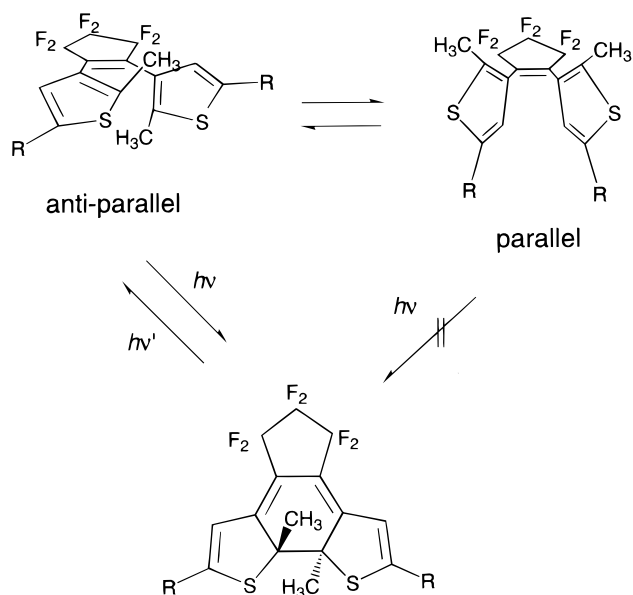
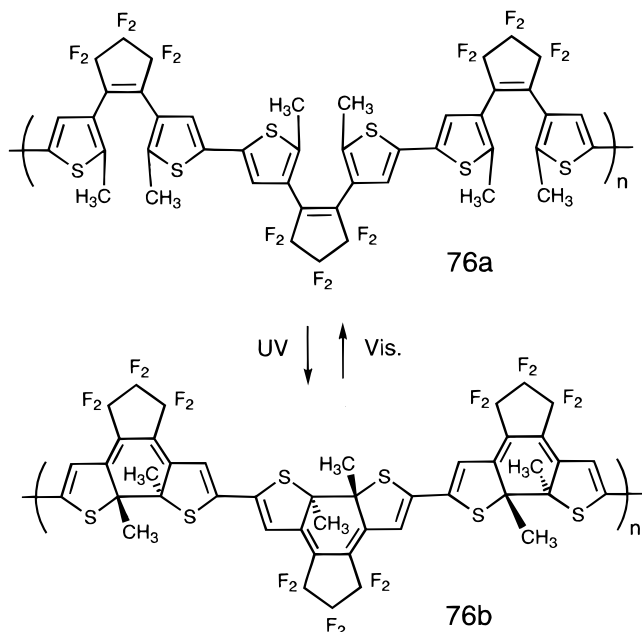


Table 5. Quantum Yields of Cyclization and Cycloreversion Reactions

compound	quantum yield	
	cyclization	cycloreversion
<b>31</b>	0.21	0.13
<b>12</b>	0.46	0.015
<b>62</b>	0.37	0.0025
<b>67</b>	0.50	0.018

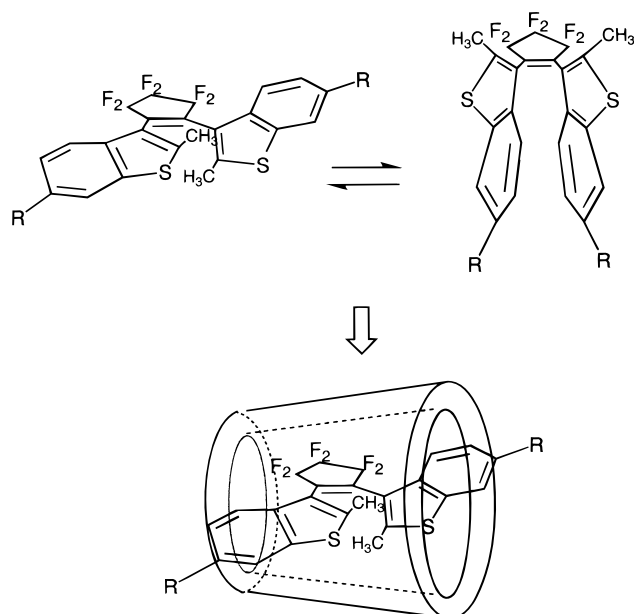
## Scheme 17



tion quantum yield to the fact that only the antiparallel conformation can exist in the polymer backbone. This is the largest cyclization quantum yield so far reported.

Another approach to increase the antiparallel conformation ratio is to include the diarylethene molecule in confined space. The molecule in the antiparallel conformation has an extended rodlike structure, while the molecule in the parallel confor-

## Scheme 18



mation has a cubic structure. When the space size fits to the rodlike structure and is too small to accept the cubic structure, the diarylethene molecule included in the space is forced to have only the antiparallel conformation, as shown in Scheme 18.

Cyclodextrins have cavities whose sizes are dependent on the number of glucopyranose units and can include various types of organic molecules by hydrophobic interactions in aqueous media. To aqueous solutions containing 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentenes having sulfuric acid substituents at the 6- and 6'-positions were added  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins, and the ratio change of the two conformations was examined by NMR measurement.<sup>55-57</sup> In the case of  $\beta$ -cyclodextrin, an appreciable increase in the ratio of the antiparallel conformation was observed. By the addition of 10 equiv of  $\beta$ -cyclodextrin, the antiparallel conformation ratio increased from 0.64 to 0.94. The addition of  $\alpha$ -cyclodextrin did not change the ratio. The result indicates that the cavity of  $\beta$ -cyclodextrin is suitable for the antiparallel conformation whereas that of  $\alpha$ -cyclodextrin is too small to include the compound. In the case of  $\gamma$ -cyclodextrin, the ratio increased to 0.80. The cyclization quantum yield was found to increase from 0.32 to 0.49 by the addition of  $\beta$ -cyclodextrin and to 0.45 by the addition of  $\gamma$ -cyclodextrin. Such an increase was not observed for  $\alpha$ -cyclodextrin. The enhancement of quantum yields in the presence of cyclodextrins is ascribed to the favorable antiparallel conformation in the cyclodextrin cavities.

The cycloreversion quantum yields of dithienylethenes **69b**–**71b** (Scheme 15) were dependent on the  $\pi$ -conjugation length of the aryl groups.<sup>52</sup> When the number of thiophene rings in the aryl groups increased, the quantum yield of the cycloreversion reaction dramatically decreased as shown in Table 6. The yield of 0.075 of **69b** decreased to 0.0013 when a thiophene ring was attached to **69b**. It further decreased to 0.00013 in terthiophene derivative **71b**. The very low cycloreversion quantum yield of **71b** is

**Table 6. Quantum Yields of Cyclization and Cycloreversion Reactions**

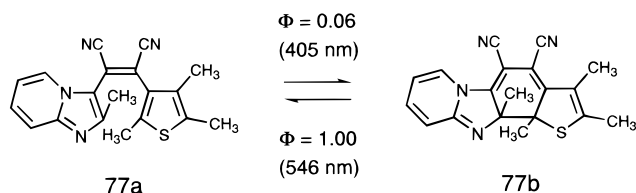
compound	quantum yield	
	cyclization	cycloreversion
<b>69</b>	0.44 <sup>a</sup>	0.075 <sup>a</sup>
<b>70</b>	0.12 <sup>a</sup>	0.0013 <sup>a</sup>
<b>71</b>	0.12 <sup>a</sup>	0.00013 <sup>a</sup>
<b>72</b>	0.76 <sup>b</sup>	$2.8 \times 10^{-4}$ <sup>b</sup>
<b>73</b>	0.59 <sup>b</sup>	$3 \times 10^{-5}$ <sup>b</sup>
<b>74</b>	0.34 <sup>c</sup>	0
<b>75</b>	$5.3 \times 10^{-3}$ <sup>c</sup>	0

<sup>a</sup> In decaline. <sup>b</sup> In toluene. <sup>c</sup> In dichloromethane.

ascribed to large extension of  $\pi$ -conjugation throughout the six thiophene moieties. The antibonding nature in the excited singlet state of the central photogenerated carbon-carbon bond decreases with the extension of  $\pi$ -conjugation, and the weak antibonding character is considered to decrease the cycloreversion quantum yields.

A similar decrease in the cycloreversion quantum yields was also observed for the diarylethenes having polyene groups (Scheme 15), as shown in Table 6.<sup>53</sup> The decrease is also ascribed to the long extension of  $\pi$ -conjugation in the molecules.

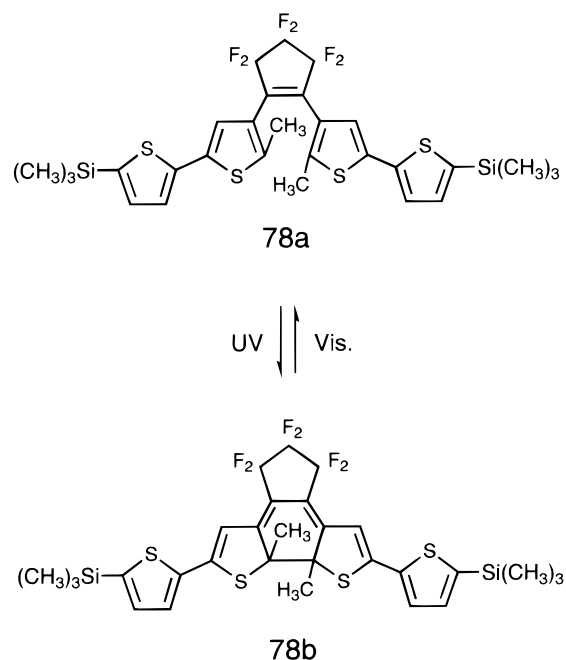
A very large cycloreversion quantum yield ( $\Phi = 1.0$ ) has been reported<sup>58</sup> for **77b** (Scheme 19).

**Scheme 19**

## E. Response Time

The dynamics of cyclization and cycloreversion reactions of diarylethenes has been studied by using pico- and femtosecond laser photolysis experiments. Both cyclization and cycloreversion reactions were measured for compound **2**.<sup>59</sup> The open-ring isomer was excited with a 355 nm laser pulse (fwhm = 22 ps) in hexane, and the formation of the closed-ring isomer was followed at 560 nm. A rapid spectral evolution in a few tens of picoseconds was observed. This is attributable to the photocyclization reaction. The rise curve was reproduced by taking into account the pulse duration and the time constant of formation ( $\tau = 8$  ps). Considering the rather long pulse duration, it is concluded that the rise process is faster than 10 ps.

The cycloreversion process was also measured by exciting the closed-ring isomer with a 532 nm laser pulse. Immediately after the excitation, an increase in the absorption around 560 nm and a decrease in absorption around 600–750 nm were observed. The increased absorption is ascribed to an  $S_1 \rightarrow S_n$  transition. The bleached signal was partly recovered and reached a constant value. The time constant of 2–3 ps reproduced the recovery of the decreased absorption, indicating the cycloreversion reaction took place within 2–3 ps.

**Scheme 20**

In the above experiment, the pulse duration is longer than the cyclization/cycloreversion reactions. It is necessary to use a shorter laser pulse to know the precise cyclization and cycloreversion rates. The cyclization time of diarylethene **78a** (Scheme 20) was measured by using a femtosecond laser (fwhm = 180 fs).<sup>60</sup>

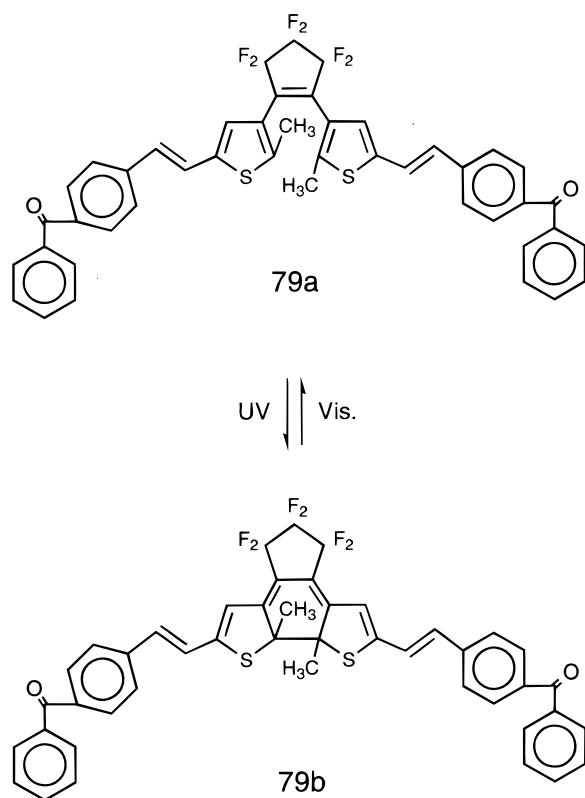
The absorption at 650 nm was found to rise in ca. 1 ps in accord with the decay of the absorption at 515 nm after irradiation with 360 nm laser light. The absorption bands at 515 and 650 nm were assigned to  $S_1 \rightarrow S_n$  transition of the open-ring isomer and the  $S_0 \rightarrow S_1$  transition of the closed-ring isomer, respectively. The rise and decay curves were reproduced by taking into account the pulse duration and the time constant of formation ( $\tau = 1.1$  ps). This result indicates that cyclization proceeds very rapidly in 1 ps. Very rapid photocyclization reaction (<3 ps) was also observed for **60a** in ethanol as well as in a polymer film.<sup>47</sup>

The cycloreversion reaction of diarylethene **79b** (Scheme 21) was measured in  $\text{CH}_2\text{Cl}_2$  by using a femtosecond laser.<sup>61</sup>

The closed-ring isomer of the compound has a broad absorption band at 625 nm ( $S_0 \rightarrow S_1$ ) and a sharp band at 360 nm ( $S_0 \rightarrow S_4$ ). Upon irradiation with a 100 fs pulse with a central wavelength of 650 nm, bleaching of the two bands and population of the  $S_1$  state were instantaneously induced. Recovery of the bleached  $S_0$  state and decay of the  $S_1$  state along with an increase of the absorption due to the open-ring isomer at around 350 nm were carefully measured. Very fast decay of the  $S_1$  state and rise of the open-ring isomer with a time constant of 2.1 ps were observed. The absorption bands of the closed-ring isomer recovered with a time constant of ca. 10 ps. During the first 500 fs, the  $S_1 \rightarrow S_5$  absorption spectrum at around 500 nm showed a blue shift from 540 to 480 nm. The dynamic of the transient absorption spectrum was interpreted as follows. Upon

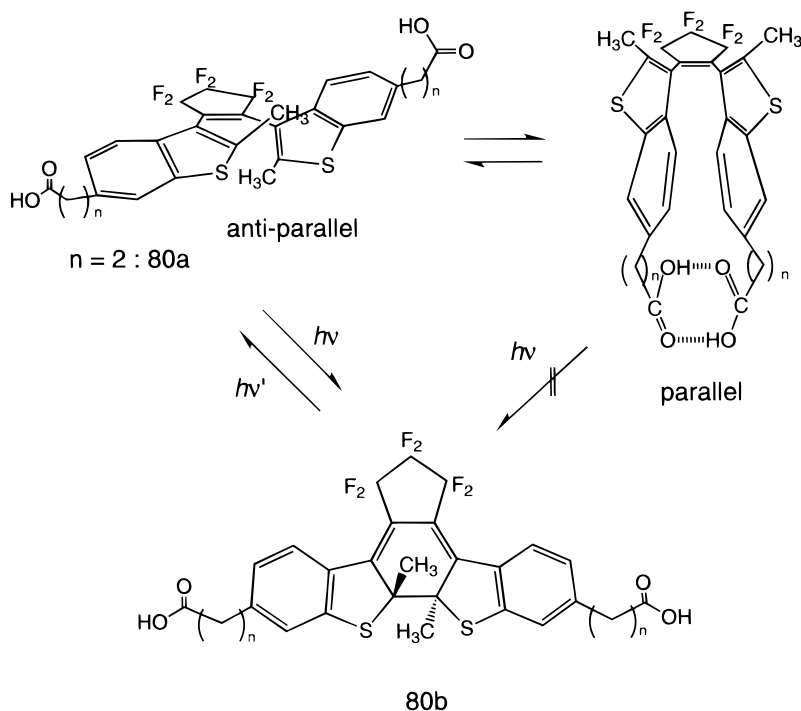


Scheme 21



photoexcitation with a 650 nm laser pulse, the initially prepared vibrational structure relaxed to two equilibrium states, a disrotatory twisted intermediate state and a conrotatory twisted prestate, and the cycloreversion reaction took place from the conrotatory prestate in 2.1 ps. The remaining disrotatory and conrotatory states returned to the closed-ring ground state in around 10 ps.

Scheme 22



The laser pulse experiments revealed that both the cyclization and cycloreversion reactions take place very rapidly in less than a few picoseconds.

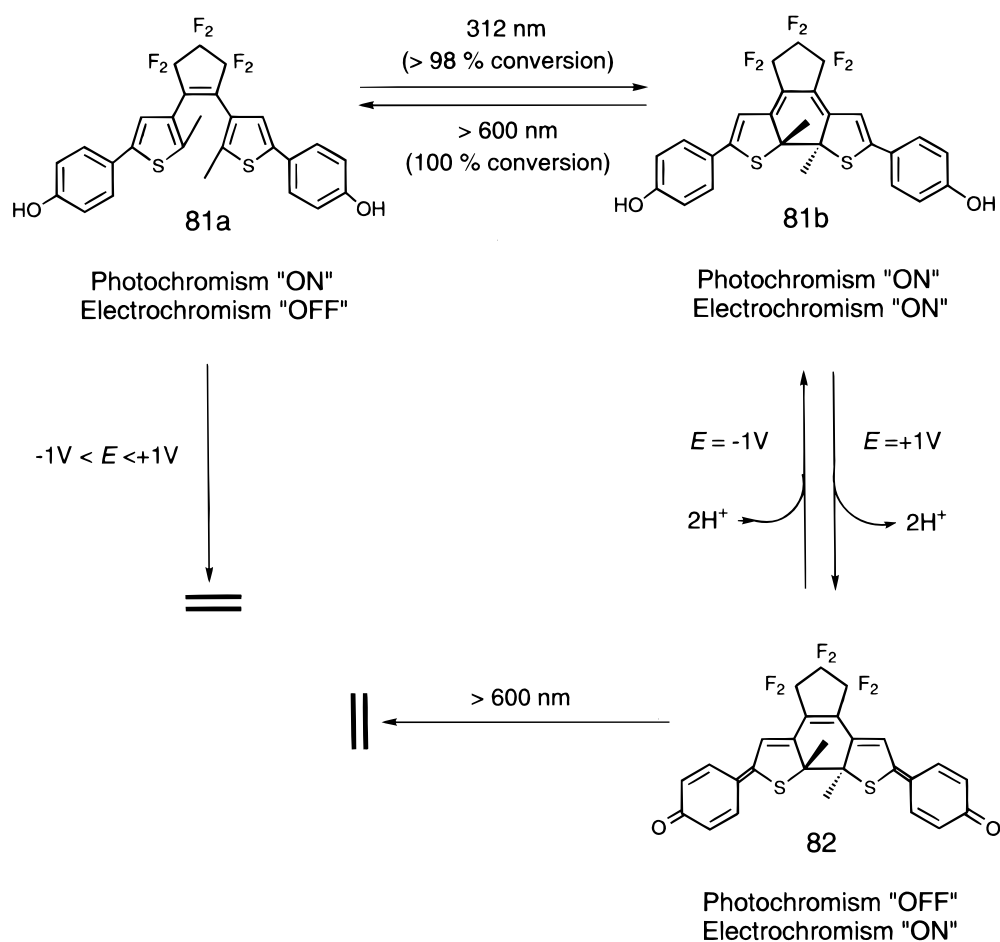
## F. Gated Reactivity

One of the main reasons why photochromic compounds cannot be used as practical optical memory media is that the compounds lack nondestructive readout capability. Photochromic reactions, in general, proceed in proportion to the number of photons absorbed by the compounds. Such a linear-response characteristic cannot be used as the basis of memory media because recorded memories are destroyed after many readout operations. One possible way to avoid such an inconvenience is to introduce gated photochromic reactivity to the photochromic systems. Several attempts to develop gated diarylethene photochromic systems have been reported.<sup>52,62–66</sup>

A diarylethene with heterocyclic aryl groups has two conformations with the two rings in mirror and  $C_2$  symmetries, and the cyclization reaction can proceed only from the  $C_2$  symmetry, as described in section D. The photocyclization is prohibited when the compound is fixed in the mirror symmetry conformation. This means that compounds having special substituents which reversibly fix the conformation undergo gated photochromic reactions, as shown in Scheme 22.<sup>62,63</sup>

The photochromic reaction of **80a** was completely prohibited in cyclohexane because the compound is fixed in mirror symmetry, or parallel conformation, by the intramolecular hydrogen bonding. The addition of a very small amount of ethanol to the cyclohexane solution gained photochromic reactivity. In the mixtures of cyclohexane and ethanol with a different ethanol content, the photocyclization quantum yield increased with the increasing ethanol

## Scheme 23



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- and 2'-positions of the benzothiophene rings gives information concerning the relative population of the two conformations. In cyclohexane only a low-field singlet signal at 2.4 ppm due to the parallel conformation was observed, while a new high-field signal at 2.1 ppm due to the antiparallel conformation appeared by addition of ethanol. This clearly indicates that the compound is in a parallel conformation in cyclohexane and converts to an antiparallel conformation upon addition of ethanol. In cyclohexane the intramolecular hydrogen bonding fastens the compound in the parallel conformation and makes the compound photochemically inactive. Conversely, ethanol acts as a molecular trigger to unlock the system.

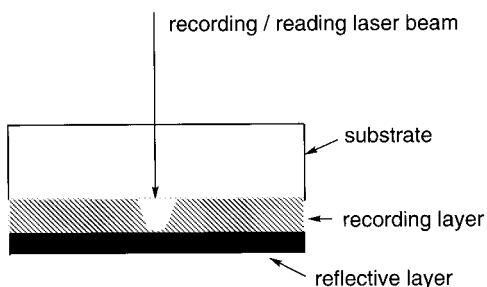
The hydrogen bonds can also be broken upon heating. In decaline, the photocyclization did not occur below 60 °C while it was clearly observed above 100 °C. This compound has both chemical- and thermal-gated reactivity.

As already described in the section D, the cycloreversion quantum yields of **69b**–**71b** depend on the number of thiophene rings.<sup>52</sup> It dramatically decreased to 0.00013 in a terthiophene derivative **71b**. The very low cycloreversion quantum yield was found to steeply increase as much as 34 times when the temperature was raised from 25 to 150 °C.<sup>52</sup> The large temperature dependence is not due to the

inherent activation energy of the cycloreversion reaction in the excited state, because such a large temperature dependence was not observed for **69b**, which has only one thiophene ring in both aryl sides. The conformational change of the oligothiophene groups by heating is considered to play an important role in the cycloreversion process. The recorded memory in this system can be read many times with a weak irradiance laser, which does not raise the medium temperature. The memory can be erased with a high irradiance laser, which can raise the medium temperature as high as 100–150 °C.

Dual-mode-type switching systems, which combine two reversible processes that can be addressed by two independent stimuli, can be used for nondestructive readout. A molecule having photochromic and electrochromic active units (Scheme 23) was synthesized.<sup>64,65</sup>

Upon irradiation with 312 nm light, an acetonitrile solution containing **81a** turned deep blue, for which absorption maxima were observed at 590 and 340 nm. The absorption is due to the closed-ring isomer **81b**. The conversion was over 98%. The blue color disappeared by irradiation with >600 nm light. The electrochemical activity of the two isomers **81a** and **81b** was examined in acetonitrile. Whereas the opening isomer was electrochemically inert within the –1 to +1 V domain, the closed-ring isomer, which is extended hydroquinone, had a reversible oxidation wave at +0.72 mV (with respect to SCE) correspond-



**Figure 7.** Structure of a photochromic memory medium.

ing to the formation of quinonoid form **82**. The quinonoid form **82** was photochemically stable. Irradiation of the acetonitrile solution of **82** with  $>600$  nm light for 8 h resulted in less than a 2% decrease in the absorbance at the maximum. Under comparable conditions, the closed-ring isomer **81b** completely decolorized within 10 min. Thus, in the reduced hydroquinone form **81b**, the system is photochromic, while oxidation to the quinonoid form **82** can be used to effectively block the photochemical coloration. Such multimode switching was also observed in a mixture of photochromic systems.<sup>66</sup>

## V. Memories

### A. Optical Disk Memory

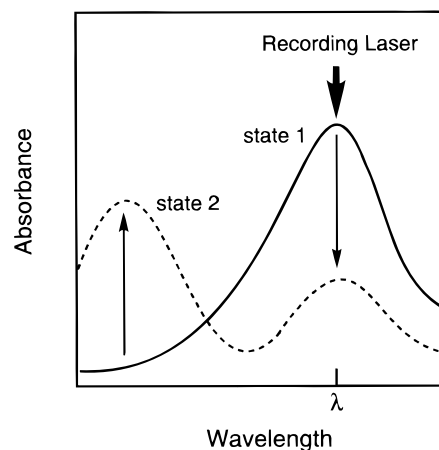
Optical data storage refers to systems that use laser light to record as well as to reproduce information. Current erasable optical data storage systems are based on magneto-optic (MO)<sup>67</sup> and phase-change (PC)<sup>68</sup> effects. Both MO and PC recording systems utilize heat-mode effects. In the systems, focused light energy is converted into heat energy on the recording medium and increases the medium temperature above Curie-point or melting temperatures. Physical property changes accomplished by the heating are used as the memories.

In contrast to the above heat-mode recording systems, photochromic optical memories are based on a photon-mode recording method. Physical property changes, such as transmittance, reflectance, or fluorescence changes, induced by photochemical reactions are utilized as the bases of memories. Photon-mode recording has various advantages over heat-mode recording in terms of resolution, speed of writing, and multiplex recording capability, such as wavelength, polarization, and phase.

Several papers related to the technical applications of photochromic materials to optical memory media have been published.<sup>69–76</sup> The recording sensitivity, possible data transfer rate, and readout repeatability were simulated by using physical and chemical parameters of a diarylethene recording medium and experimentally confirmed.<sup>69</sup>

The memory medium has the structure shown in Figure 7. Figure 8 shows the model absorption spectrum of the medium. An initial state 1 is shown by a solid line, and recorded state 2 is shown by a broken line. Assuming that the molecules corresponding to state 1 only absorb at wavelength  $\lambda$ , the reflectance  $R$  is expressed as

$$R = \exp(-2.303\epsilon C2L) \quad (4.1)$$



**Figure 8.** Absorption spectral change of a recording layer by irradiation with a laser of wavelength  $\lambda$ .

Here, we assume perfect reflectance of the reflective layer.  $\epsilon$  ( $M^{-1} \text{ cm}^{-1}$ ),  $C$  (M), and  $L$  (cm) are the absorption coefficient, concentration of diarylethene dye, and thickness of the recording layer, respectively. When we irradiate the medium with writing light (power  $P$  (W), wavelength  $\lambda$  (m)) for an infinitesimal time  $dt$ , the medium absorbs the following number of photons

$$dn = P\lambda(1 - R) dt/hc \quad (4.2)$$

where  $c$  is the light speed (m/s). When the reaction quantum yield is  $\Phi$ , the following number of molecules reacts:

$$dN = dn \cdot \Phi \quad (4.3)$$

The number of molecules in the irradiated volume  $LS$  is equal to  $CLSN_a \times 10^{-3}$ .  $N_a$  is Avogadro's constant. The number of reaction molecules is therefore given by

$$dN = dC \cdot LSN_a \times 10^{-3} \quad (4.4)$$

From the above relations we obtain the following equation

$$\partial C/\partial t = -P\lambda\Phi(1 - R)/hcLSN_a \times 10^{-3} \quad (4.5)$$

Using the derivative of eq 4.1, the following differential equation is deduced

$$\partial R/\partial t = 2\alpha P\lambda\epsilon\Phi R(1 - R)/S \quad (4.6)$$

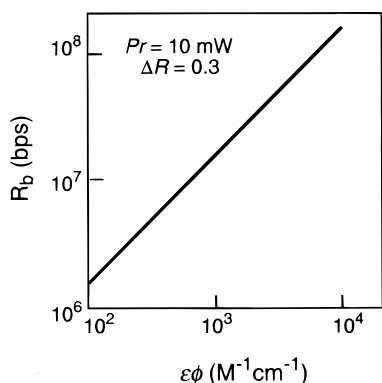
where  $\alpha = 2.3 \times 10^3/N_a hc$ . Then

$$R = [1 + \text{const} \times \exp(-2\alpha F\lambda\epsilon\Phi)]^{-1} \quad (4.7)$$

where the total irradiation flux  $F$  is defined as  $Pt/S$ . From the above equations, the maximum data transfer rate  $Rb$  bit per second (bps) is derived as follows

$$Rb = (2\alpha Pr\lambda\epsilon\Phi/S) \ln((R_m(1 - R_i)/(1 - R_m)R_i)^{-1}) \quad (4.8)$$

where  $R_m$  and  $R_i$  are the reflectances of the recorded mark and the land, respectively. Under the condition that  $\Delta R (=R_m - R_i)$  is 0.3,  $P$  is 10 mW at 633 nm, and the numerical aperture of objective lens ( $NA$ ) is



**Figure 9.** Data transfer rate  $R_b$  under the following conditions:  $\lambda = 633$  nm,  $P_r = 10$  mW, and  $\Delta R = 0.3$ . (Reprinted with permission from ref 69. Copyright 1994 Publication Board, Japanese Journal of Applied Physics.)

0.5, we obtain the data transfer rate or the writing speed as shown in Figure 9. When  $\epsilon\Phi = 1000$   $M^{-1}cm^{-1}$ ,  $R_b$  is more than 10 Mbps. This value is comparable to current MO and PC disks.

The change of reflectance  $R_m(m)$  of the recorded mark and  $R_l(m)$  of the land after  $m$  readout operations with a laser power of  $P_{rep}$  can be calculated by eq 4.7 as follows

$$P_{rep}(\min) = (SNR_0 \cdot 2eB/\eta\gamma)R_a/(\Delta R)^2$$

where  $SNR$ ,  $B$ ,  $\eta$ ,  $\gamma$ ,  $R_a$ , and  $\Delta R$  are the signal-to-noise ratio required, the bandwidth, the photoelectron conversion efficiency, the pick-up efficiency, the initial average reflectance, and the initial reflectance change, respectively.

Under the conditions that  $\Delta R = 0.3$ ,  $R_a = 0.3$ ,  $SNR = 400$  (26 dB),  $\eta = 0.4$ ,  $\gamma = 0.8$ , and  $B = 5$  MHz, the number of readout cycles reaches  $10^6$  when the readout laser power is 10 nW.

The above numerical simulation was confirmed experimentally using a polystyrene film containing 2-(1-octyl-2-methyl-3-indolyl)-3-(2,3,5-trimethyl-3-thienyl)maleic anhydride (**83**) (Scheme 24) as the memory medium.<sup>69</sup>

#### Scheme 24

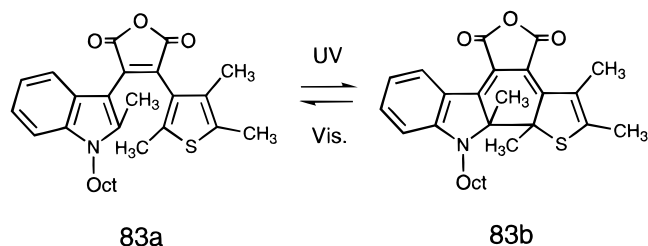
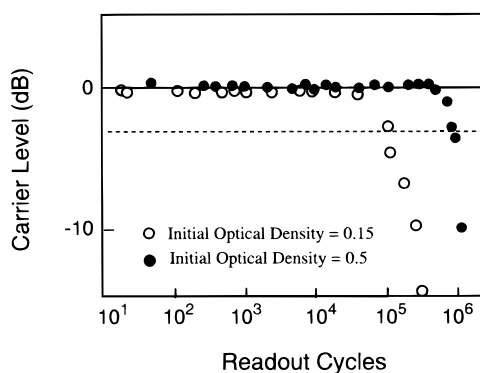
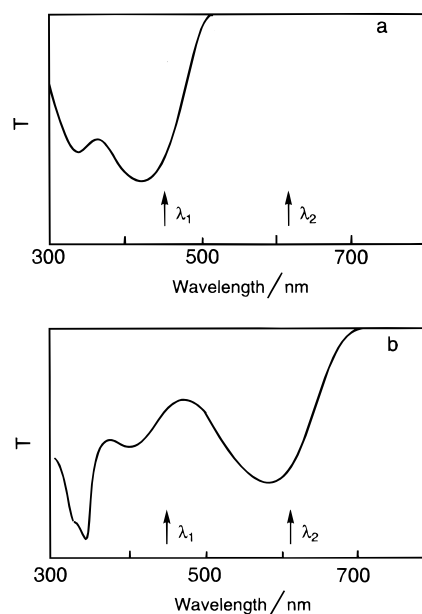


Figure 10 shows the result of readout cycle dependence of the carrier levels using 20 nW readout laser power at 633 nm. When the initial optical density is as high as 0.5, it is possible to read the memory more than  $10^6$  using the super low power laser irradiance.

Another approach to avoid readout instability in disk memory systems is to use thermal-gated photochromic compounds.<sup>70</sup> The method is as follows. Recording light  $\lambda_1$  converts the molecules in the recording area from A to B, and the transmittance at  $\lambda_2$  decreases as shown in Figure 11. The unre-



**Figure 10.** Readout cycle dependence of the carrier levels. (Reprinted with permission from ref 72. Copyright 1995 Publication Board, Japanese Journal of Applied Physics.)



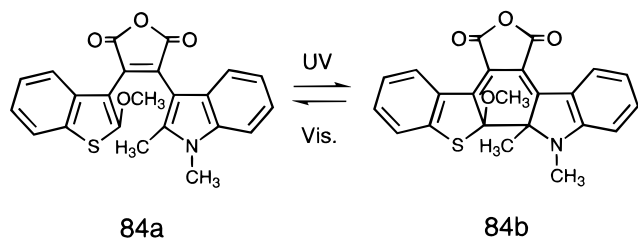
**Figure 11.** Transmittance spectra of (a) unrecorded and (b) recorded areas. (Reprinted with permission from ref 70. Copyright 1993 Publication Board, Japanese Journal of Applied Physics.)

recorded area has only A isomers. Therefore, the area shows no absorption at  $\lambda_2$ . The transmittance (or the reflectance) difference at  $\lambda_2$  between the recorded and unrecorded areas is used as the readout signal. During the reading, however,  $\lambda_2$  light causes the photoreaction of B to A. After many readout operations, the transmittance of the recorded area is increased and finally the memory is destroyed. When the photochromic medium has a threshold temperature  $T_c$  higher than room temperature in the reaction process from A to B, it becomes possible to keep the signal intensity constant even after many readout operations. A high-irradiance laser light is used for writing. The laser heats the medium above  $T_c$  and enables the conversion from A to B. The contrast between the recorded and unrecorded areas is read using two lasers,  $\lambda_1$  and  $\lambda_2$ , with the former having reduced irradiance. As a result of coupling between the B form and the readout  $\lambda_2$  laser, the recorded area is held at a higher temperature ( $T > T_c$ ) relative to the unrecorded area which has no absorption at  $\lambda_2$ .

Simultaneous irradiation with the  $\lambda_1$  laser ensures that reversion from B to A by the  $\lambda_2$  laser is canceled in the recorded areas by effective rewriting by the  $\lambda_1$  laser. Therefore, the decreased transmittance of the recorded area remains constant. Isomerization from A to B by the  $\lambda_1$  laser minimally occurs at the unrecorded areas because no thermal bias is provided in the unrecorded areas by the  $\lambda_2$  laser. Using this method, the contrast between the recorded and unrecorded areas remains almost constant even after many readout operations.

The effectiveness of the above reading method was experimentally confirmed using a polystyrene film containing 2-(2-methoxybenzo[*b*]thiophen-3-yl)-3-(2-dimethyl-3-indolyl)maleic anhydride (**84**) (Scheme 25).<sup>70</sup> The polystyrene memory medium has a ther-

### Scheme 25

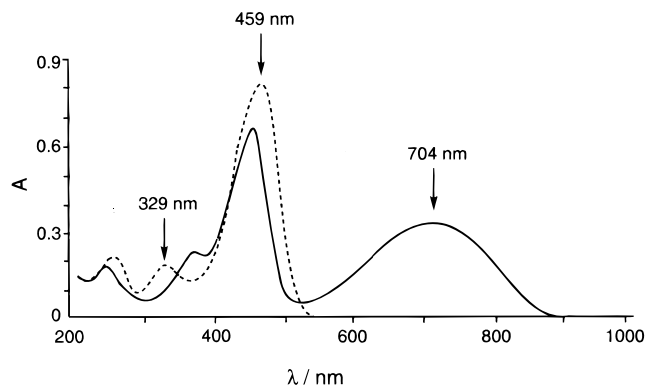


mal reaction threshold. The conversion in the photostationary state under irradiation with 458 nm light was very low ( $\sim 7\%$ ) at room temperature, while it was over 40% at temperatures above 140 °C. The temperature dependence is ascribable to the polarity and mobility changes of the polymer matrix upon heating.

Writing was carried out using a high-power laser of 476.5 nm, and the recorded marks were read using two lasers (476.5 nm, 0.13 mW; 633 nm, 0.05 mW). The reflectance difference between the recorded and unrecorded areas remained almost constant, even after  $10^6$  readout operations. This is an effective method to read memory many times without a decrease of the signal-to-noise ratio.

### B. Fluorescence and IR Readout

Several methods using fluorescence or infrared absorption as readout signals have been proposed to avoid the destructive readout. A diarylethene having dithieno(thiophene) units **68a** (Scheme 14)<sup>50,51</sup> shows fluorescence in the open-ring form. Figure 12 shows the absorption spectra of **68a** and **68b**. Irradiation of the main band of the open-ring isomer **68a** at 400–500 nm gave no reaction, while the cyclization reaction proceeded by irradiation at wavelengths less than 400 nm. The closed-ring isomer had an intense broad absorption band at 704 nm. Cycloreversion reaction occurred by irradiation with  $> 600$  nm light. The open-ring isomer was found to have a strong emission at 589 nm when excited in the 400–500 nm region. In contrast, the closed-ring isomer displayed only a weak fluorescence (less than 3% of the intensity of **68a**). The large fluorescence intensity change between the open- and closed-ring isomers makes it possible to use the change as the readout signal. When the fluorescence can be detected without



**Figure 12.** Absorption spectra of **68a** (---) and **68b** (—) in methanol. (Reprinted with permission from ref 50. Copyright 1995 Wiley-VCH.)

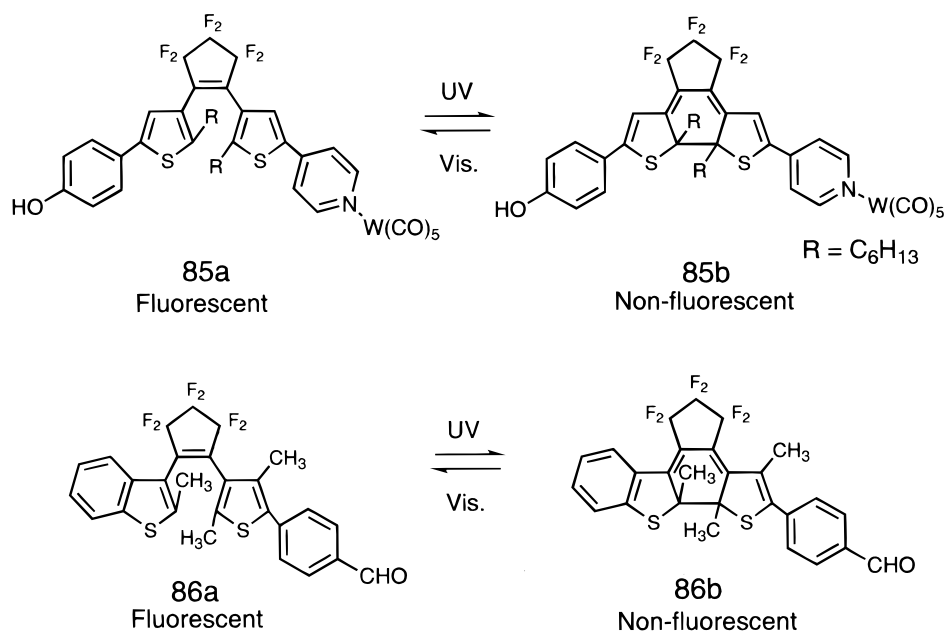
influencing the ratio of the two isomers, the readout method becomes nondestructive. The absorption band at 459 nm of the open-ring isomer was photochemically inactive. However, the analogous band of the closed-ring isomer ( $\lambda_{\text{max}} = 454$  nm) had low activity; a slow conversion of less than 10% per hour was observed. When the irradiation was performed with a narrow range of the excitation wavelength, the cycloreversion reaction was very slow ( $< 2\%$  per 30 min irradiation). Although the system has no perfect performance of nondestructive readout, a very large number of fluorescence reading can, in principle, be performed before significant change takes place.

The fluorescence intensity modulation by the photoisomerization has also been observed for diarylethene **85** and **86** (Scheme 26).<sup>77,78</sup>

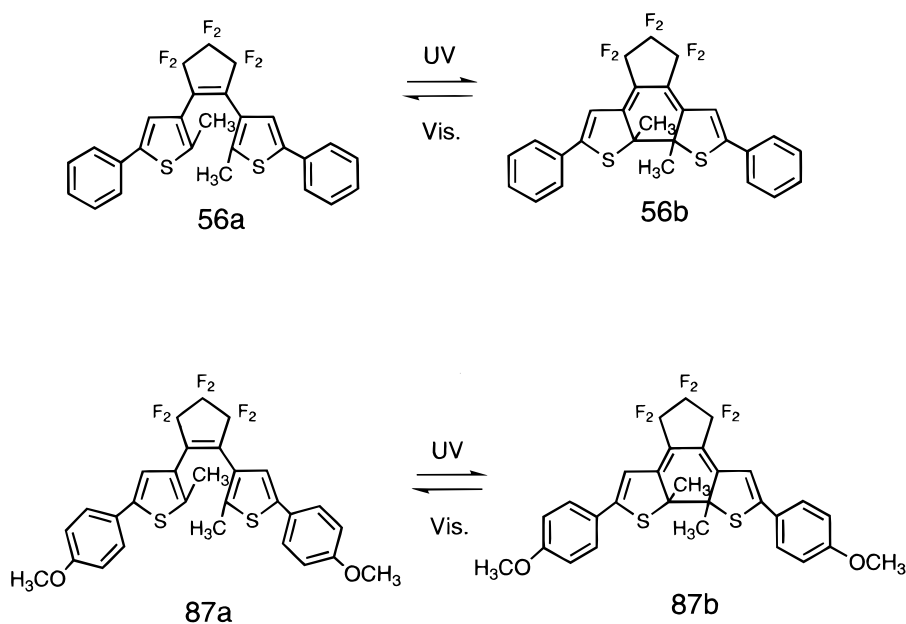
When the difference between the open- and closed-ring isomers can be detected by the light whose energy cannot cause any molecular change, the recorded information can be read many times without destruction.<sup>79,80</sup> The infrared spectra of the open- and closed-ring isomers of **56** and **87** were measured (Scheme 27).<sup>80</sup>

The C=C stretching region ( $1400\text{--}1650\text{ cm}^{-1}$ ) is highly selective and suitable for detecting the difference. In the spectral region, the open-ring isomer **56a** has three bands at 1637, 1592, and  $1544\text{ cm}^{-1}$ . The first one is due to the C=C bond of perfluorocyclopentene, and the others can be ascribed to the double bonds of the thiophene rings. In the closed-ring forms, three new bands appeared at 1612, 1574, and  $1503\text{ cm}^{-1}$ , which are assigned to the C=C bonds of the newly generated conjugated system. Although it is possible to detect the difference of the two isomers by the infrared spectra, the spectral intensity is rather weak. To increase the spectral intensity, various substituents were introduced to the 5- and 5'-positions of the thiophene rings. Enhancement of the spectrum was observed for **87** (Scheme 27). The closed-ring isomer has a strong absorption at  $1495\text{ cm}^{-1}$  with an intensity of  $\sim 300\,000$  dark (cm/mol). The band was not observed in the open-ring isomer. Conceptually it is proposed to construct an optical memory system in which the information is written and erased by UV and visible photons that activate the photochromic process; the reading is achieved by infrared photons unable to cause any molecular rearrangement.

## Scheme 26



## Scheme 27



## C. Near-Field Memory

Continuous efforts have been made to increase the recording density of optical memories. Various approaches have been proposed to recording: decreasing the spot diameter by use of short-wavelength lasers,<sup>81</sup> three-dimensional recording,<sup>82,83</sup> and multiwavelength recording.<sup>71</sup> One of the approaches to the ultrahigh-density optical memory is near-field optical recording. Recording density in conventional optical recording is limited by the diffraction limit of light and numerical aperture of the lens, and the spot size cannot be reduced to less than the wavelength of light. Therefore, efforts have been focused to develop shorter wavelength lasers.<sup>81</sup> In near-field recording, in contrast, the recording mark size depends only on the diameter of the probe tip aperture. Therefore, the recording density can be increased at will, in principle, if the small size aperture tip is

available. So far the memory media that have been used for the near-field optical recording are magneto-optical<sup>85</sup> or phase-change<sup>86</sup> media. These media are based on a heat-mode recording method. The heat-mode recording requires a high-power recording light and the transfer rate is slow. Another recording method is a photon-mode recording based on a photochemical reaction of the medium.<sup>87,88</sup> A photochromic medium is one of the candidates for the photon-mode near-field recording, which offers advantages with regard to resolution and writing speed.

Two kinds of diarylethene amorphous films were prepared, and near-field recording was carried out on the media.<sup>88</sup> One recording medium was polystyrene film containing **15a** (dye/polymer = 20 wt %). For the optical recording the film was first colored homogeneously by irradiation with UV light (300 nm <  $\lambda$  < 400 nm), and then bleached by 529 nm light

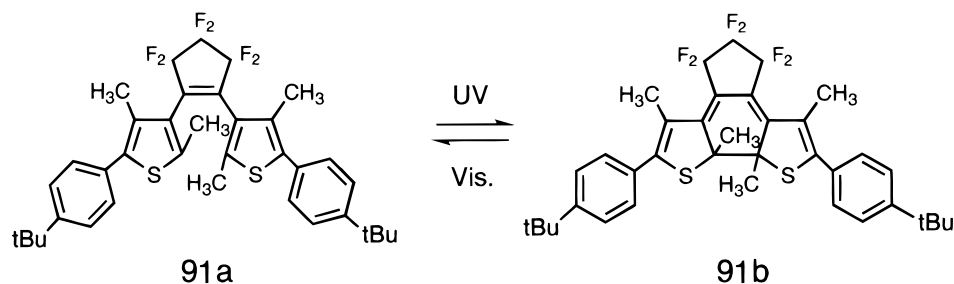
**Table 7. Refractive Index Change Along with the Photoisomerization**

Compounds	$\Delta n$
	1 $1.5 \times 10^{-3}$ (633 nm, 3 wt% conversion in amorphous polyolefin)
	14 $2.8 \times 10^{-3}$ (633 nm, 2 wt% conversion in PMMA) $1.5 \times 10^{-3}$ (633 nm, 3 wt% conversion in amorphous polyolefin) $5 \times 10^{-4}$ (1300 nm, in polyfluoroethyl methacrylate containing 10wt% dye after UV irradiation)
	87 $3.5 \times 10^{-3}$ (633 nm, after UV irradiation in sol-gel film) $3.0 \times 10^{-3}$ (785 nm, after UV irradiation in sol-gel film)
	88 $1.8 \times 10^{-3}$ (1300 nm, in PMMA film containing 50 wt% dye after UV irradiation)
	89 $3.9 \times 10^{-3}$ (1300 nm, in PMMA film containing 50 wt% dye after UV irradiation)
	90 $4.0 \times 10^{-2}$ (785 nm, in sol-gel film. see the text)
	91 $3.8 \times 10^{-2}$ (817 nm, in bulk amorphous film)

from the micropipet, the diameter of which was 100 nm. The mark size diameter was  $\sim 1 \mu\text{m}$ . The film thickness used was  $1.5 \mu\text{m}$ . In such a thick medium, light scattering resulted in a large mark size. To obtain smaller marks, the medium thickness should be reduced to the mark size demanded. However, in dye/polymer systems it is impossible to reduce the film thickness less than  $1.5 \mu\text{m}$  because sufficient contrast cannot be obtained.

Some of the diarylethenes are known to undergo photochromism in bulk amorphous or single-crystalline states. In such bulk systems, sufficient contrast can be obtained even when the film thickness is less than 300 nm. The recording medium was prepared by vacuum evaporation of **12a** (Scheme 6) on a glass substrate and used for the near-field recording. The film was first colored by irradiation with UV light ( $300 \text{ nm} < \lambda < 400 \text{ nm}$ ) and then bleached with 529

## Scheme 28



nm light from a small probe tip. The mark size diameter was as small as  $\sim 100$  nm. The mark could be erased by irradiation with UV light. The result represents a 60-fold improvement in recording density compared with current conventional MO and PC recording systems.

## VI. Switches

### A. Photooptical Switching—Refractive Index Change

Upon photoirradiation, photochromic compounds reversibly change not only the absorption spectra but also other physicochemical properties, such as refractive indices, dielectric constants, oxidation/reduction potentials, and geometrical structures, upon photoirradiation. These property changes can be potentially applicable to photonic devices. Among the properties, refractive index change is the most important character for the applications. Photochromic compounds which change the refractive indices in the near-infrared region are widely useful for optical waveguide components, such as optical switches, variable frequency filters, variable attenuators, and phase shifters. For such applications a self-holding ability, or in other words thermal irreversibility, is indispensable. When the compounds have a thermally irreversible photochromic character, they provide a new class of highly integrated optoelectronic systems for optical communication, signal processing, and interconnection. Diarylethenes undergo thermally irreversible photochromic reactions. Therefore, the compounds are the most promising candidates for the applications.

Keeping such applications in mind, several research groups have measured the refractive index changes of diarylethenes.<sup>98,101</sup> Table 7 summarizes the values and measuring conditions. For dye/polymer systems, the maximum refractive index change was  $3.9 \times 10^{-3}$  at 1300 nm.<sup>93</sup> The relatively low refractive index change is due to low conversion in polymer matrices. The quantities of diarylethenes which can be dispersed in polymer matrices are limited to less than 30 wt %, and the open- to closed-ring photoisomerization conversion is suppressed. Taking into account the conversion, the relation between the weight fraction ( $f$ ) of photoisomerized compound and the refractive index change ( $\Delta n$ ) at 633 nm is expressed for **15** (Scheme 7) in PMMA as follows<sup>90</sup>

$$\Delta n = 0.128f$$

This relation means that the refractive index change

can be enlarged in bulk amorphous photochromic systems or in solid matrices containing a high concentration of diarylethenes.

Diarylethene **91** (Scheme 28) undergoes photochromism even in a bulk amorphous system.<sup>97</sup> The  $T_g$  was measured to be 68 °C. The closed-ring isomer was isolated by HPLC and coated on a glass substrate by a dip-coating method using hexane as a solvent. The refractive index was measured at 817 nm before and after visible ( $\lambda > 500$  nm) irradiation. The initial refractive index of 1.589 changed to 1.551 after visible irradiation. The photoinduced refractive index change was as large as  $3.8 \times 10^{-2}$ . The refractive index again increased by irradiation with UV ( $\lambda = 366$  nm) light, though the recovery was around 80%. After the first cycle, the refractive index reversibly changed from 1.55 to 1.58 by alternate irradiation with visible/UV light. Amorphous diarylethenes are useful materials not only for switches but also for other optoelectronic applications.<sup>99–101</sup>

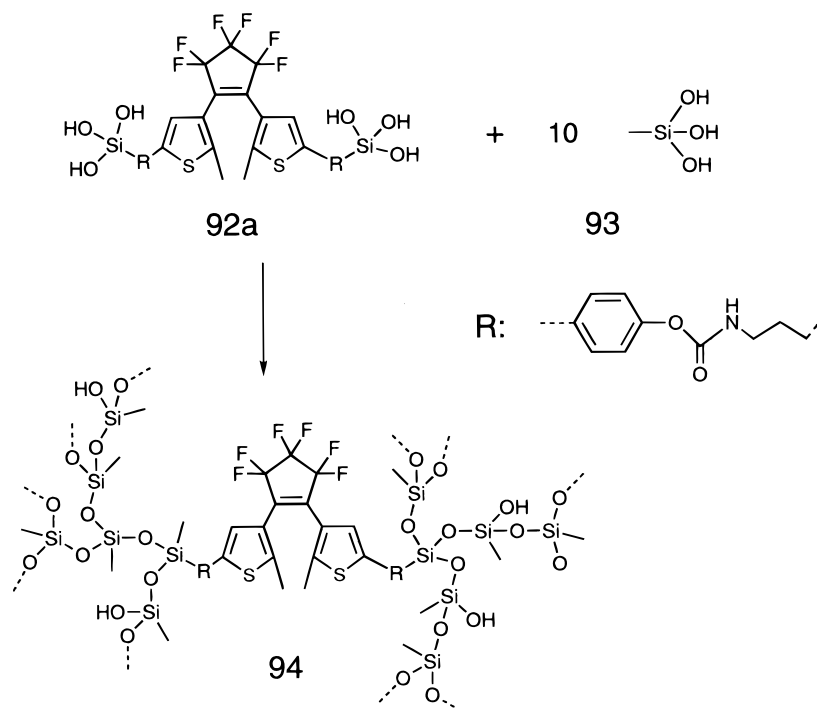
A sol-gel technique was used to prepare hybrid organic-inorganic xerogels containing a high concentration of dithienylethenes.<sup>95,96</sup> The sol-gel technique is useful in constructing photochromic solid materials.<sup>98</sup> The sol-gel materials were prepared based on the co-condensation between the hydrolyzed species of the diarylethene derivative **92a** and of methyltriethoxysilane precursors as shown in Scheme 29.<sup>96</sup>

The sol containing the diarylethenes and methyltrimethoxysilanes in THF was poured onto the substrate for spin coating, and thin films ( $\sim 0.5$   $\mu\text{m}$ ) were prepared on various substrates. Plain glass substrates were used for UV-visible absorption measurement, and some of them were previously gold coated for refractive index and thickness measurements. The absorption measurement indicated that the conversion from the open- to the closed-ring isomers at the photostationary state by irradiation with 313 nm light was as large as 95% even in the gel matrix. The refractive index was measured at 785 nm. The film thickness of the sample was 0.65  $\mu\text{m}$ . The colorless open-ring isomer had a refractive index of  $n = 1.533$ , while it increased to  $n = 1.573$  by irradiation with UV light. The refractive index change was as large as  $4 \times 10^{-2}$ . This large  $\Delta n$  value is promising for photooptical applications. Several optical components were designed and fabricated, such as gratings and waveguides (directional couplers and Mach-Zender interferometers) using the gels containing dithienylethenes.

For the dye/polymer systems, the refractive index changes are rather low, as shown in Table 7. Even so, the refractive index change can be applied to



## Scheme 29



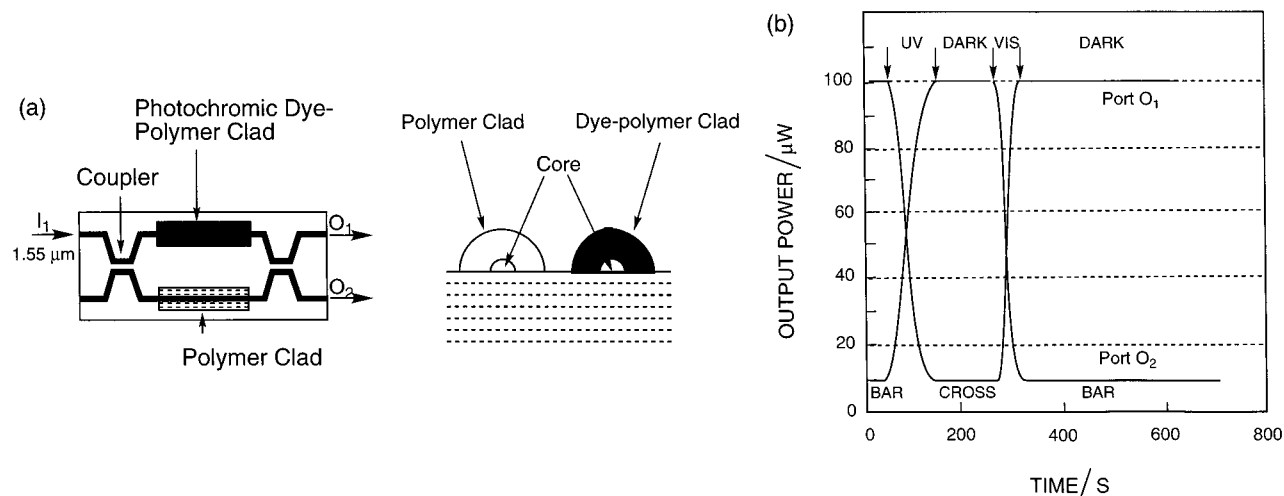
photooptical switching devices. A self-holding and optical-optical  $2 \times 2$  photochromic switch using a Mach-Zender interferometer was constructed.<sup>91,94</sup> The device was fabricated using a silica-based integrated optic Mach-Zender interferometer with a cladding polymer containing diarylethenes as shown in Figure 13. The refractive indices of the two polymer claddings were adjusted to that of the silica glass cladding by changing the copolymerization ratio of poly-(trifluoroethyl methacrylate-*co*-methyl methacrylate). One polymer cladding contained 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**15**).

Cross-bar switching was achieved by alternate irradiation with ultraviolet (313 nm) and visible ( $\lambda > 500$  nm) light, as shown in Figure 13. The switching was self-holding, and the cross talk ratio of the

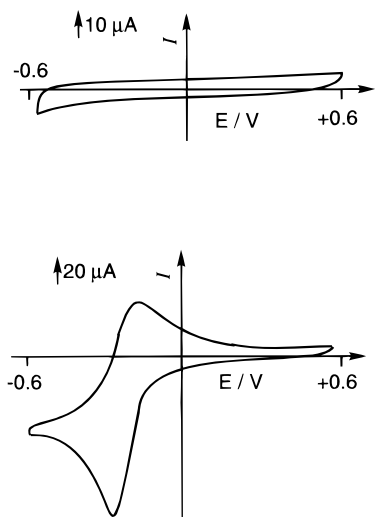
switching was  $-12$  dB at  $1.55 \mu\text{m}$ . At the material level, self-holding at  $80^\circ\text{C}$  was confirmed. According to the calculation a refractive index change as large as 0.00014 is required for full switching. The observed refractive index change was approximately 0.0003, which was enough for full switching operation. The switching time of the system was 20–30 s. This new optical switch can be applied for switching the route of optical fiber networks. For such application, a high switching rate is not required.

### B. Photoelectrochemical Switching

Reversible modulation of electrochemical properties by photoirradiation is of basic importance for the development of molecular electronic devices. Such a function can be introduced into a molecule by incor-



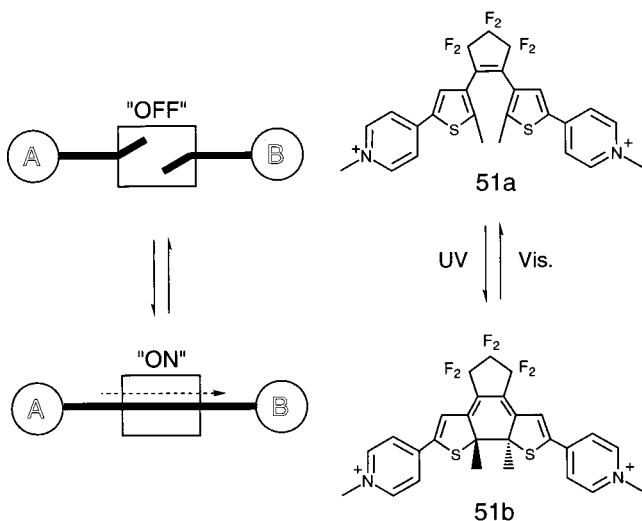
**Figure 13.** (a) Schematic view of the photooptical switching device. (b) Relation between output power and irradiation time. UV and visible light were alternatively irradiated. (Reprinted with permission from ref 91. Copyright 1994 American Institute of Physics.)



**Figure 14.** Cyclic voltammograms for the open- (top) and the closed-ring (bottom) isomers of **51** in acetonitrile (supporting electrolyte  $\text{NBu}_4\text{BF}_4$ ). (Reprinted with permission from ref 37. Copyright 1993 The Royal Society of Chemistry.)

porating a photochromic unit. Incorporation of an appropriate photochromic switching unit capable of reversibly interrupting the conjugation into a polyene molecular wire permits reversible modulation of the properties through irradiation at selected frequencies. A switching device that can control electron flow in a molecular system<sup>11,37</sup> is shown in Scheme 30.

#### Scheme 30

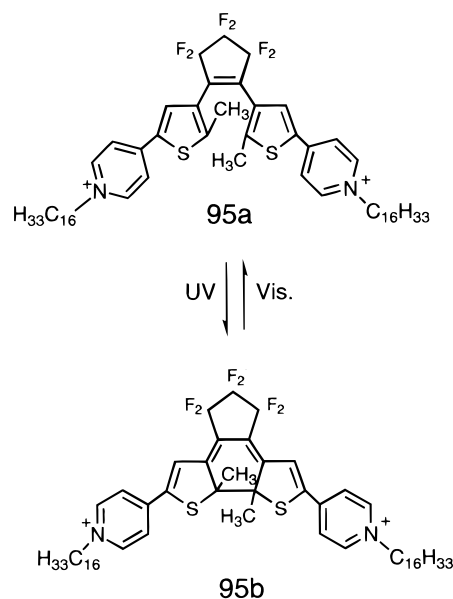


In the open-ring isomer, two pyridinium ion groups are electronically separated from each other and there is no appreciable interaction between them. This is the "off" state. On the other hand, in the photogenerated closed-ring isomer,  $\pi$ -conjugation delocalizes between two pyridinium ion groups and the absorption spectrum shifts to a longer wavelength from 352 to 662 nm. This is the "on" state. Cyclic voltammetry indicated that whereas no electrochemical process occurred for the open-ring isomer in the +0.6 to -0.6 V region, a clear reversible and mono-electronic reduction wave was observed for the closed-ring isomer at a potential  $E_{1/2} = -230$  mV vs standard calomel electrode, as shown in Figure 14.

The compound represents a prototype of a switching molecular wire in which the electron flow can be reversibly switched by photoirradiation. Such a switching response was also observed for a diarylethene having oligothiophene aryl groups **78**<sup>102</sup> (Scheme 20).

When such photoswitching chromophores are immobilized on an electrode, vectorial electron flow from the electrode to electroactive species in solution can be controlled by photoirradiation.<sup>103,104</sup> Using *n*-octadecanethiol-modified gold electrode incorporated with diarylethene **95** (Scheme 31) the vectorial

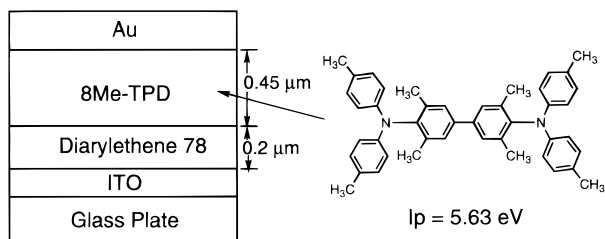
#### Scheme 31



electron transport from the electrode to hexacyanoferrate(III) in solution could be switched by photoirradiation.

Hole injection efficiency from a metal electrode to an organic film can be controlled by inserting a thin film of a diarylethene derivative between metal and organic charge-transport layer.<sup>105</sup> As described above, the  $\pi$ -conjugation length of diarylethene derivatives changes upon photoisomerization. This means that the ionization potentials also depend on the isomers. Diarylethene **78** (Scheme 20) was prepared, and the ionization potentials of the open- and closed-ring isomers were measured. The ionization potential of the closed-ring form was determined to be 5.82 eV. The potential of the open-ring isomer was estimated to be 6.8 eV from the oxidation potential changes of the compound in an acetonitrile solution: 1.57 V for the open-ring isomer and 0.63 V for the closed-ring isomer.<sup>102</sup> The two isomers have a very large ionization potential change.

Photoswitching of hole injection from the metal electrode to the organic layer was carried out using the device shown in Figure 15. When the diarylethene is in the open-ring form, any hole injection from ITO to the organic layer was not observed. On the other hand, an appreciable increase in the current on the order of sub-mA was observed by irradiation with UV light. Very thin diarylethene film, as thin as 0.2  $\mu\text{m}$ , controlled the hole injection efficiency by photoirradiation. This result is potentially ap-

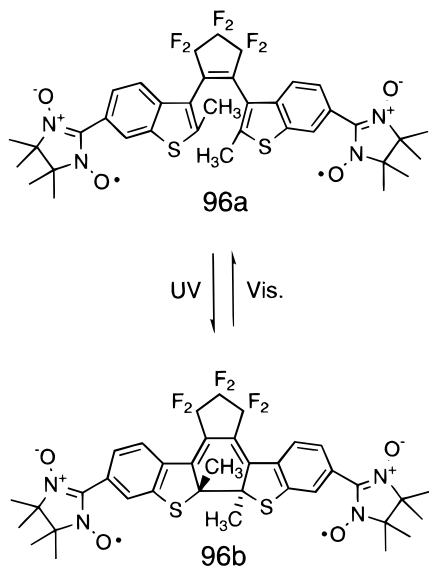


**Figure 15.** Structure of the device for the measurement of electric-field dependence of the current density for the diarylethene **78** film.

plicable to memory-type organic photoconductors. Photoconductivity could also be controlled by incorporating diarylethene **1** in a conductive polymer poly-(9,9-dihexadecylfluorene).<sup>106</sup>

The concept of controlling the interaction between terminally functionalized polyenes can also be applied to magnetic interaction.<sup>107</sup> For this purpose, diarylethenes having two nitronyl nitroxide radicals **96** were prepared and the intramolecular magnetic interaction was compared in the open- and closed-ring forms. An appreciable difference in the interaction was observed between the open- ( $2J/k_B = -2.2$  K) and the closed-ring ( $2J/k_B = -11.6$  K) isomers (Scheme 32).

#### Scheme 32

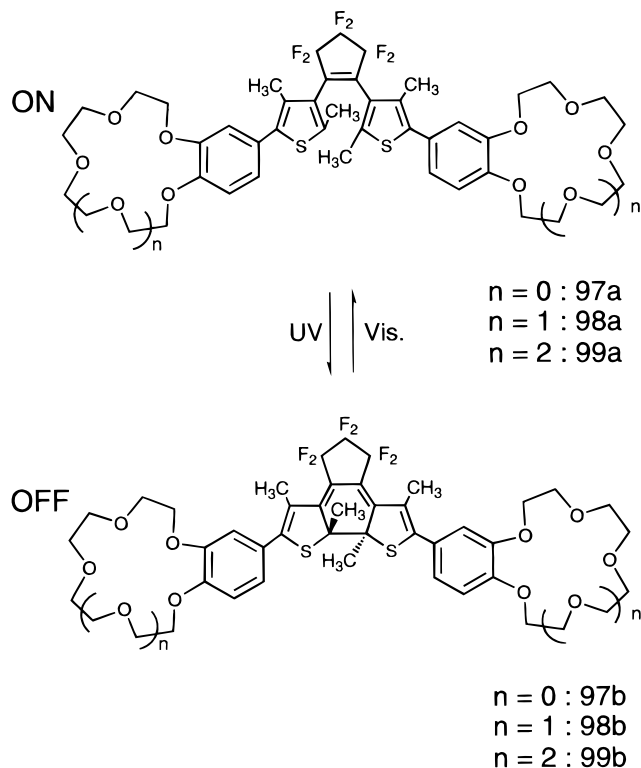


### C. Host–Guest Interaction

Switching of host–guest interactions by photoirradiation potentially enables us to carry out active transportation of guest molecules. Photochromic compounds, such as thioindigo, azobenzene, and anthracene, have been widely used as switching moieties. Diarylethenes can also be used as the switching unit when two crown units were introduced,<sup>108–111</sup> as shown in Scheme 33.

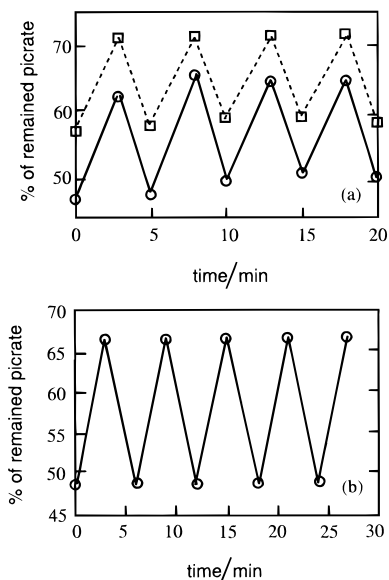
Two crown ether moieties of the open-ring isomer in the parallel conformation can cooperatively bind with a large metal ion, while in the photogenerated close-ring isomer the crown ether moieties are separated from each other and cannot capture the metal ion. Two-phase solvent extraction of alkali metal

#### Scheme 33



picrates with the open-ring isomers and their photostationary states by irradiation with 313 nm light was carried out. The decrease of the aqueous-phase absorption due to the picrates was used to estimate the extractability of the compounds.

In the case of dithienylethene with benzo-15-crown-5 ether **98a**, the solution of open-ring form extracted KPic and RbPic to the organic phase as much as 50%. Upon irradiation with 313 nm light, the extractability was dramatically decreased to 10–20%, which is similar to the extractability of a single benzo-crown model compound. The open-ring isomer



**Figure 16.** Control of the concentration of (a) KPic (—) and RbPic (· · ·) in the aqueous phase with **98** in  $\text{CH}_2\text{Cl}_2$  and **99** by alternate irradiation with  $330 \pm 70$  and  $>480$  nm light.

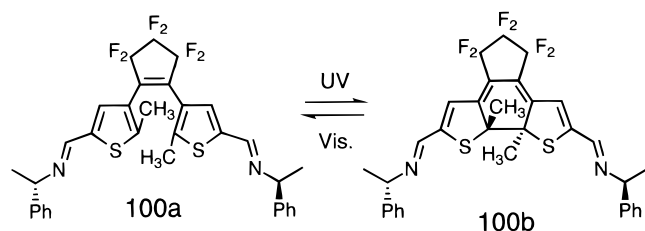
captures the large metal ions as a tweezer. When the dithienylethene with benzo-18-crown-6 ether **99a** was used, a photostimulated extractability change was observed only for CsPic.<sup>104</sup> In the case of **97a**, the extractability was very small and the photoeffect was not remarkable. Figure 16 shows the switching behavior of the metal ion capture by alternate irradiation with UV ( $330 \pm 70$  nm) and visible ( $>480$  nm) light irradiation. In all cases, good reversibility without photodestruction was observed.

Not only metal ions but also glucoses can also be reversibly captured by a diarylethene having boronic acid groups upon photoirradiation.<sup>111</sup>

#### D. Liquid Crystal Switch

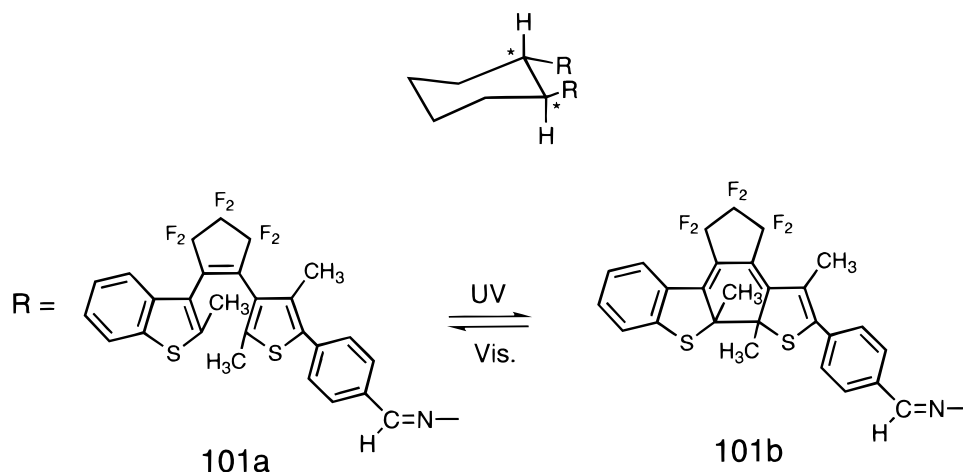
The control of optical properties of liquid crystals by photoirradiation is a major challenge in the development of molecular devices. So far, various attempts have been carried out to control the liquid-crystal alignment as well as their phases by using photochromic chromophores, almost exclusively using azobenzene derivatives.<sup>112,113</sup> It is well-known that nematic liquid crystals can be converted into chiral nematic (induced cholesteric) liquid crystals using chiral dopants.<sup>114</sup> The phase change is highly significant for display technology, because these two phases exhibit a distinct optical property change. In a few cases reversible switching between these phases has been reported by using chiral fulgides and stilbene derivatives.<sup>115–117</sup> The phase change can also be induced by using diarylethene **100** (Scheme 34) having chiral substituents.<sup>118</sup>

Scheme 34



Doping of nematic liquid-crystal materials ZLI-389 and K<sub>15</sub> with **100a** resulted in stable cholesteric

Scheme 35



phases. It was possible to induce the cholesteric phase with 0.7 wt % **100a** to ZLI-389 at 51–54 °C, and the phase was stable for many hours. When the mixture was irradiated with UV light of 300 nm for 50 s, the chiral nematic phase disappeared and a nematic phase texture was observed. Irradiation of the sample with visible light for 30 s resulted in the reappearance of the cholesteric fingerprint texture. The switching could be repeated 6 times without deterioration of the liquid-crystal phase. The result indicates that the twisting power of the closed-ring isomer is smaller than that of the open-ring isomer.

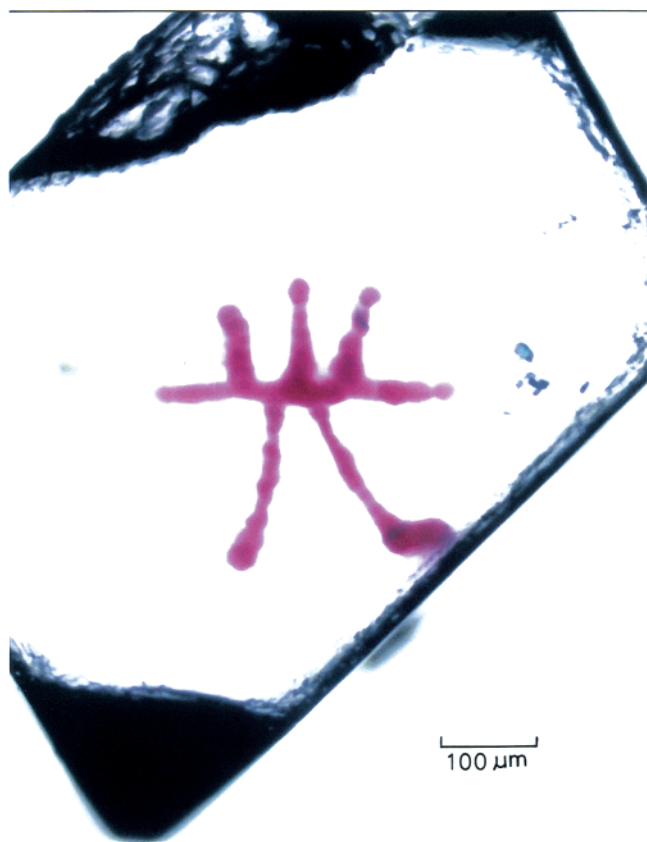
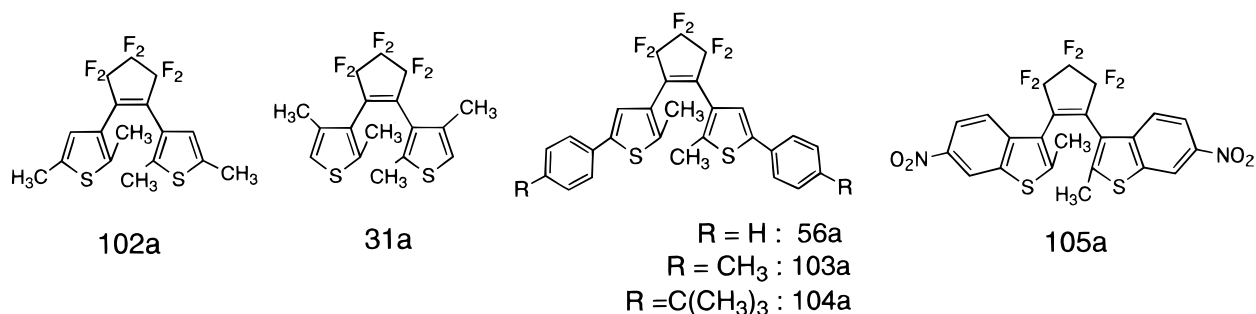
When the twisting power of the closed-ring isomer is larger than that of the open-ring isomer, it is expected that UV irradiation can induce the phase change from the nematic to chiral nematic phases. Diarylethene **101a** (Scheme 35), which has two diarylethene units in a chiral cyclohexane ring architecture,<sup>119</sup> was incorporated into K<sub>15</sub> and the phase change along with the photoisomerization was measured. In this case, photocyclization induced the nematic to chiral nematic phase change and the photocycloreversion reaction returned the phase to nematic.

#### VII. Crystalline Photochromism

Although so many photochromic compounds have been reported, compounds which show photochromic reactivity in the crystalline phases are very rare and in most cases photogenerated colored isomers are thermally unstable. When the photochromic reactions can proceed in the crystalline phases and both isomers are thermally stable, the materials potentially find various applications in photonic devices. Some of diarylperfluorocyclopentenes undergo photochromism in the crystalline phases and both isomers, the open- and the closed-ring isomers, are thermally stable.<sup>120</sup>

Compounds in Scheme 36 showed photochromic reactivity in the crystalline phases.<sup>120–125</sup> Upon irradiation with 313 nm light, a rhombus crystal of **102a** changed from colorless to red, and the red color disappeared by irradiation with visible ( $>450$  nm) light. The coloration/decuration cycles could be

## Scheme 36



**Figure 17.** Photograph of a single crystal of **102a**, on which a Chinese character “Hikari-Light” was written. (Reprinted with permission from ref 123. Copyright 1998 The Chemical Society of Japan.)

repeated more than 10 000 times without destruction of the crystal shape, and the colored form was stable even at 100 °C. Figure 17 shows a photograph of the single crystal, on which a Chinese character “Hikari-Light” is written. The red character remained stable up to the melting temperature ( $T_m = 120$  °C) and could be erased by irradiation with visible light ( $\lambda > 450$  nm).

The reactivity strongly depended on the molecular structure. When the thiophene rings have only two methyl groups, such as **102a** and **31a**, the dithienylperfluorocyclopentenes underwent photochromism in the crystals. However, 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 hexane was very similar. X-ray crystal-

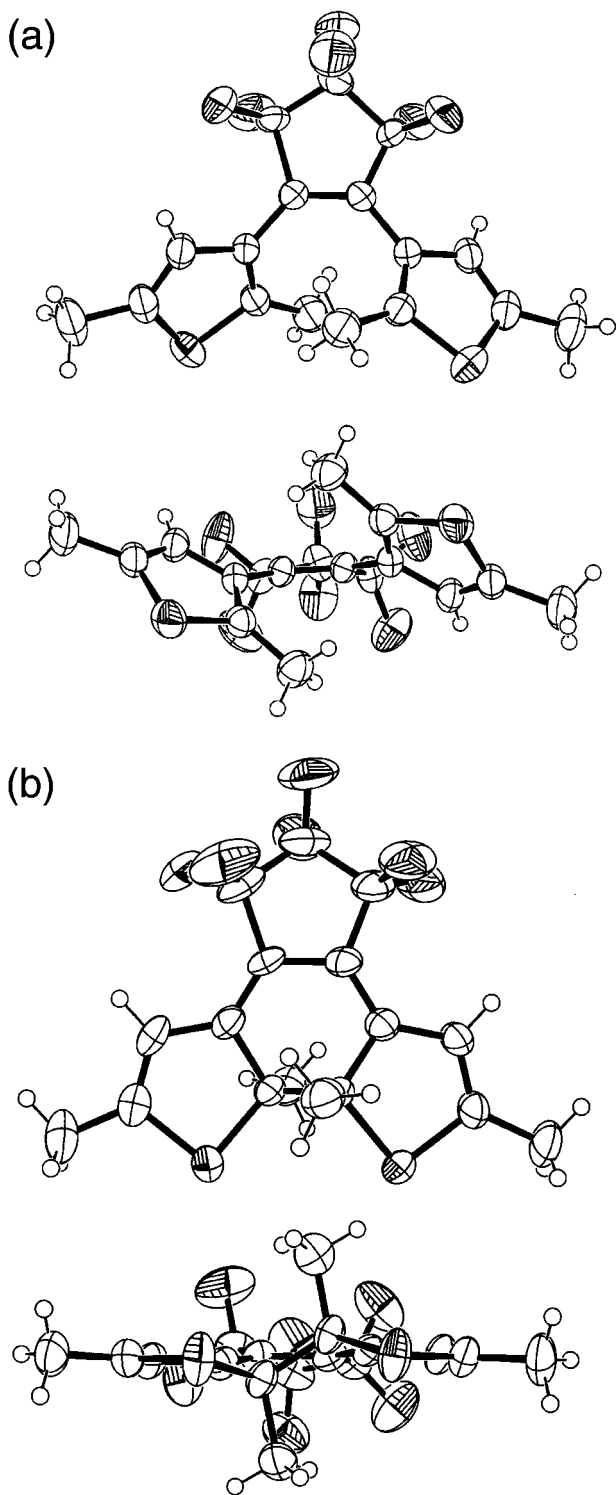
lographic analysis of the crystal structure showed that **102a** and **31a** have an antiparallel conformation while the above nonreactive dithienylethene has a parallel conformation in the crystalline phase. The molecule in the parallel conformation cannot undergo the conrotatory photocyclization reaction. The reactivity depends on the conformation in the crystal.

Figure 18a,b shows the molecular structures of the open- and closed-ring isomers of **102** determined by X-ray crystallographic analysis. As expected, structural change during the photoisomerization is rather small. Only the central reactive carbons and sulfur atoms change the positions. Other atoms including methyl groups at the reactive center remained at similar positions. Such a small movement of atoms allows the reaction to be possible in the crystal lattice. Another example of crystalline photochromic diarylethene is a copper complex with **1**.<sup>126</sup>

As already mentioned in section IV.B, the fatigue resistance is highly improved in the crystalline photochromic systems. In the photochromic crystals, all molecules are packed in a photoactive antiparallel conformation and oxygen diffusion is suppressed. The side reactions with surrounding solvents or matrices are also prohibited. Therefore, the formation of byproducts and oxidized products is minimized in crystals.<sup>125</sup> In addition, the photocyclization response time in the crystalline phase is very rapid ( $< 10$  ps).<sup>127</sup> Such robust and high-performance crystalline photochromic materials have promising potential for future photonic devices.

### VIII. Conclusions

Diarylethenes with heterocyclic aryl groups underwent thermally irreversible and fatigue-resistant photochromic reactions. When the aryl groups were furan, thiophene, selenophene, or thiazole rings, both the open- and closed-ring isomers were stable even at 80 °C. The photogenerated closed-ring isomers never returned to the open-ring isomers in the dark, while they regenerated the isomers by irradiation with visible light. The coloration/decuration cycles by alternate irradiation with UV and visible light could be repeated more than 10 000 times with adequate photochromic performance when the diarylethenes contained benzothiophene as the aryl group. Both the coloration and decoloration processes took place very rapidly in less than a few picoseconds in solution as well as in the solid states, such as in polymer films and crystals. The absorption spectrum was dependent on the types of aryl groups, the



**Figure 18.** ORTEP drawings of (a) **102a** and (b) **102b** showing 50% probability displacement ellipsoids.

substitution positions of the aryl groups to the ethene moiety, and the upper cycloalkene structures. The open-ring isomers so far synthesized had absorption maxima ranging from 230 to 460 nm and the closed-ring isomers from 425 to 830 nm. The cyclization and cycloreversion quantum yields were moderate, ranging from 0.01 to 0.86. The properties of diarylethenes have been reviewed in several papers.<sup>44,121,123,128–130</sup>

The above photochromic performance of diarylethenes satisfies the fundamental requirements for

applications to optoelectronic devices, such as optical memories and switches. For practical applications, however, several additional characteristics or technologies are required. For the optical memory media, for example, nondestructive readout capability is indispensable. Although several attempts to develop gated photochromic systems have been carried out to avoid the destructive readout as described in section IV.F, their functions are not adequate for practical use. Recently a new practical technology to avoid the destructive readout has been developed.<sup>83</sup> The method uses a reflection confocal microscope as a readout system. The wavelength of the readout laser light is longer than the absorption edge of the colored isomer. The method was successfully applied to nondestructive readout of data stored in a three-dimensional photochromic diarylethene memory. This is one of the practical approaches to photochromic memories.

Technical applications of photochromic systems to optoelectronic devices require dispersion of compounds into solid matrices. In most cases polymers are used. However, in polymers photochromic reactivity is suppressed and the quantities of compounds which can be dispersed in polymer matrices are limited. It is desired to develop bulk photochromic systems. From this point of view, crystalline and amorphous diarylethenes are of great promise in potential applications to memories and switches.

### IX. Acknowledgment

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