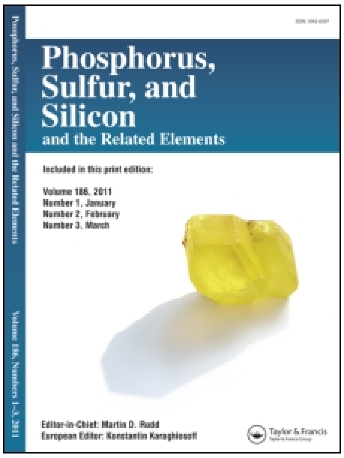

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Photochromic Dithienylethenes for Molecular Photonics

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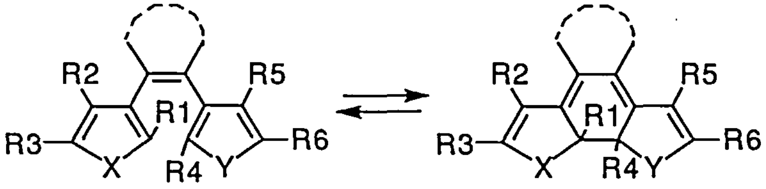
The molecular design principle and synthetic methods of thermally irreversible and fatigue resistant photochromic diarylethenes with heterocyclic rings, such as thiophene or benzothiophene rings, are described.

INTRODUCTION

A photochromic compound is characterized by its ability to undergo a reversible transformation between two different chemical forms having different absorption spectra in response to light of appropriate wavelengths. The two isomers differ in various physicochemical properties in addition to the spectral changes, such as refractive index[1,2] and dipole moment. The property changes can be utilized for photonic devices.[3-8] Although much effort has been so far made in this area, the photochromic compounds still await practical applications. The limitation is due to the lack of suitable compounds which fulfill the requirements for photonic devices. The requirements are:

1) Thermal stability of both isomers.
2) Low fatigue (can be cycled many times without loss of performance)
3) Color variation
4) Rapid response
5) High sensitivity
6) Non-destructive readout capability.

We have developed a new type of fatigue resistant and thermally irreversible photochromic compounds, diarylethenes with heterocyclic rings, such as 2-methyl-substituted thiophene or benzothiophene rings, where "a" refers to open-ring form and "b" to closed-ring form. In this review we report on our approach to gains access to photochromic compounds which fulfill the above requirements, 1), 2) and 3).

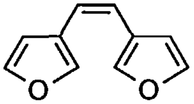


a b

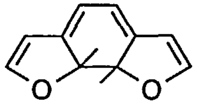
THEORETICAL STUDY

In order to come up with a guiding principle for the synthesis of photochromic diarylethenes, in which both isomers are thermally stable, we carried out a theoretical study of 1,3,5-hexatriene to cyclohexadiene type reactions.[9] Typical compounds of the hexatriene molecular framework are diarylethene derivatives having phenyl or heterocyclic rings. Semiempirical MNDO calculations were carried out for the following diarylethene derivatives.

1a 1b



2a



2b

Figure 1 and 2 show the state correlation diagrams for the reactions from 1a to 1b and from 2a to 2b in disrotatory and conrotatory modes, respectively. According to the state correlation diagrams, orbital symmetry allows the disrotatory cyclization in the ground state from 1a to 1b and from 2a to 2b. The ground state energies of the closed-ring forms are, however, much higher than those of the open-ring forms. The large energy barriers practically forbid the cyclization reactions in the ground states. No such

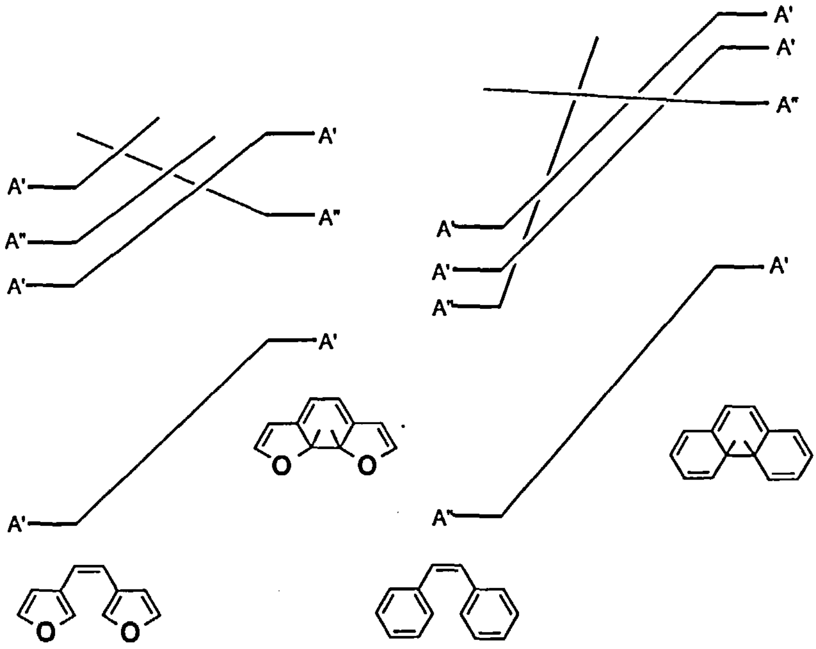


Figure 1. The state correlation diagrams for the reactions in disrotatory mode.

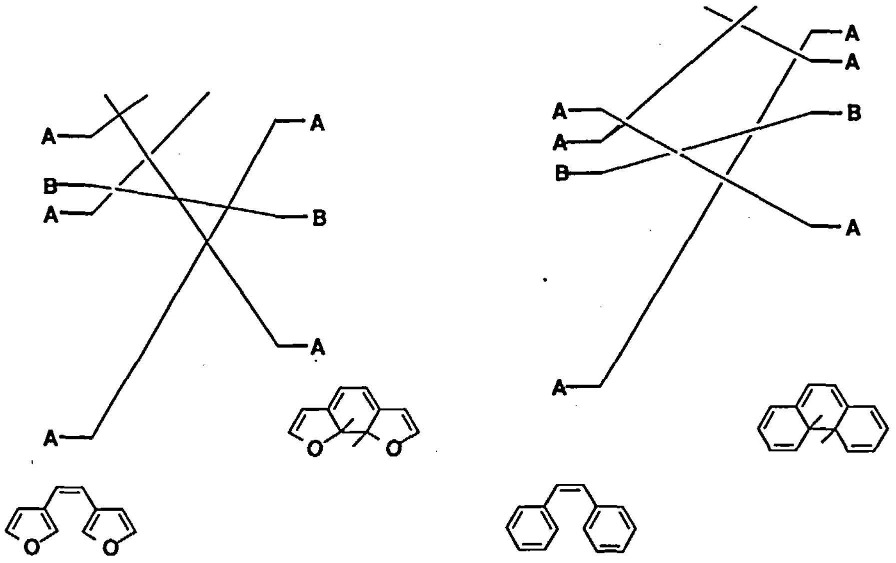


Figure 2. The state correlation diagrams for the reactions in conrotatory mode.

large energy barriers exist in the conrotatory mode reactions in the excited states from 1a to 1b and from 2a to 2b. This indicates that the cyclization of both 1a and 2a are allowed in the photochemically excited states.

First, that we should consider is the stability of the photochemically produced closed-ring forms. As seen from Figure 2, the stability depends on the energy barrier of the cycloreversion reaction in the ground state. The energy barrier correlates with the ground state energy difference between the open-ring and the closed-ring forms. The calculated values of the difference for 1,2-diphenylethene, 1,2-di(3-pyrrolyl)ethene, 1,2-di(3-furyl)ethene and 1,2-di(3-thienyl)ethene are shown in Table 1. When the energy difference is large, as in the case of 1,2-diphenylethene, the energy barrier becomes small. On the other hand, the barrier becomes large when the difference is small, as shown for 1,2-di(3-furyl)ethene. In this case, the reaction hardly occur. The ground state energy difference controls the thermal stability of the closed-ring forms.

Table 1

Relative ground state energy difference between the open-ring and the closed-ring forms

compd	disrotatory kcal / mol	conrotatory kcal / mol
1,2-diphenylethene	41.8	27.3
1,2-di(3-pyrrolyl)ethene	32.3	15.5
1,2-di(3-furyl)ethene	27.0	9.2
1,2-di(3-thienyl)ethene	12.1	-3.3

Then, the next question is what kind of molecular property causes the difference in the ground state energies. We examined the aromaticity change from the open-ring to the closed-ring forms. The difference in the energy between the following right and left side groups was calculated, as shown in Table 2.

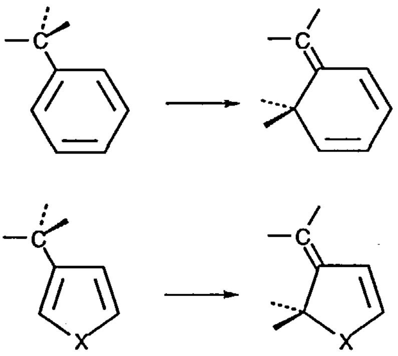


Table 2

Aromatic stabilization energy difference

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.

From the above consideration the guiding principle for thermally irreversible photochromic diarylethenes is expressed as follows: thermal stability of both isomers of diarylethenes is attained by introducing aryl groups, which have low aromatic stabilization energy, such as furan or thiophene rings.

THERMAL STABILITY

The theoretical prediction was confirmed by the synthesis of diarylethenes with various types of aryl groups as shown in Figure 3.[10-15] The stability depended on the type of aryl groups. When the aryl groups were furan, thiophene or benzothiophene rings, which have low aromatic stabilization energy, the closed ring forms were thermally stable and did not returned to the open-ring form in the dark at 80℃. On the other hand, photogenerated closed-ring forms of diarylethenes with phenyl or indole rings were thermally unstable. The photogenerated yellow color of **11b** returned to the open-ring form quickly (τ =1.5 min) in the dark.

The different behavior in the thermal stability between diarylethenes with furan or thiophene rings and phenyl or indole rings agrees well with the theoretical prediction that the thermal stability depends on the aromatic stabilization energy of the aryl groups.

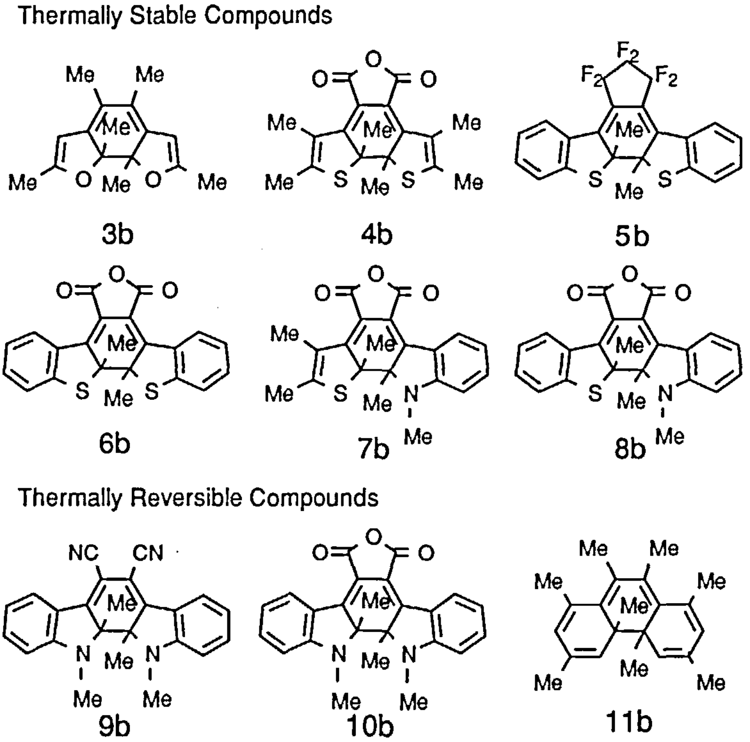
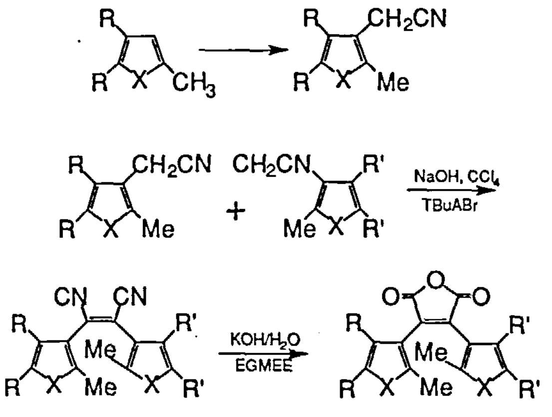


Figure 3. Thermal stability of photogenerated closed-ring forms of diarylethenes with various types of aryl groups.

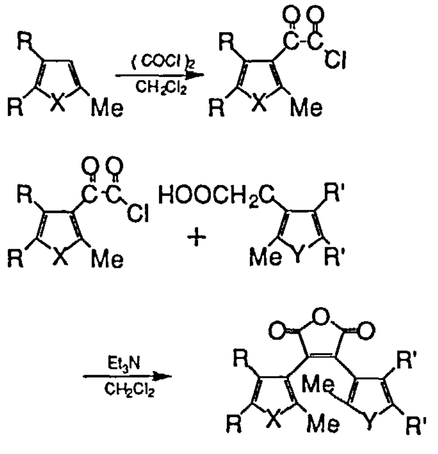
It is worthwhile noting that the closed-ring forms of 7b and 8b were found to be thermally irreversible but photochemically reversible. The result indicates that the closed-ring forms of non-symmetric diarylethenes are thermally stable when at least one of the heterocyclic rings has low aromatic stabilization energy.

SYNTHESIS

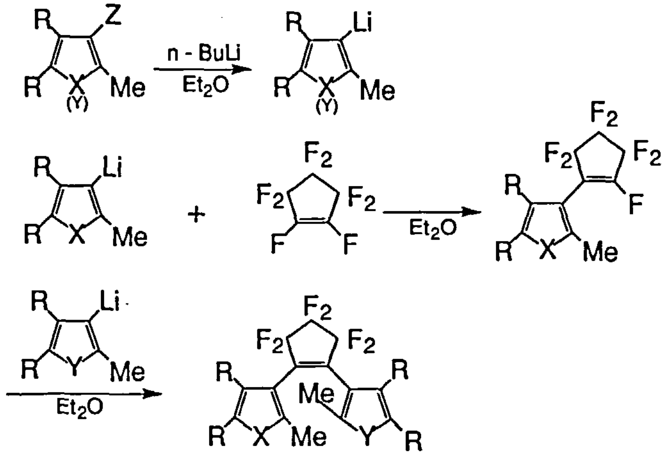
Symmetric and non-symmetric diarylethenes with various types of aryl groups can be prepared by the three methods shown in Scheme 1-3. Scheme 1 is a convenient method to prepare symmetric diarylmaleic anhydrides.[10-13] The method is hardly applied to the synthesis of non-symmetric diarylethenes.[13] Non-symmetric diarylmaleic anhydrides can be prepared by the method shown in Scheme 2. The method is especially useful for the synthesis of diarylmaleic anhydride having an indole ring. The method shown in Scheme 3 can be used for the preparation of both symmetric and non-symmetric diarylperfluorocyclopentenes.[16] The mono-and di-substituted perfluorocyclopentenes are selectively prepared by controlling the ratio of perfluorocyclopentene and organolithium compound, and the mono-substituted compounds can be used for the synthesis of non-symmetric diarylethenes[18].



Scheme 1



Scheme 2



Scheme 3

FATIGUE RESISTANT CHARACTER

Photochromic reactions are always attended by rearrangement of chemical bonds. During the bond rearrangement undesirable side reactions take place to some extent. This limits the cycles of photochromic reactions. The difficulty in obtaining fatigue resistant photochromic compounds can be easily understood by a simple calculation. We assume the following reaction scheme, in which a side reaction to produce B' is involved in the forward process.

$$B' \xleftarrow{\Phi s} A \rightleftharpoons B$$

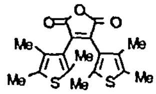
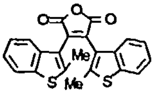
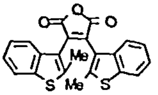
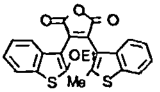
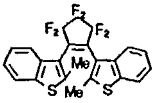
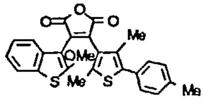
Even under the conditions that the side reaction quantum yield, Φs, is as low as 0.001 and B perfectly converts to A, 63 % of the initial concentration of A will decompose after 1,000 coloration / decoloration cycles. Thus, the quantum yield for conversion to byproducts should be less than 0.0001 in order to repeat the cycles more than 10,000 times.

Table 3 summarizes the result of repeatable cycle numbers of various diarylethenes in benzene.[10,11,15,16,20] The repeatable cycle number indicates when the absorption intensity of the colored form decreases to 80 % of the first cycle. The repeatable cycle number of the dithienylmaleic anhydride was limited to less than 480 times even in the absence of air. When the thiophene rings were replaced with benzothiophene rings, the number remarkably increased. Diarylethenes with a 2-ethoxybenzo[b]thiophene ring on one end had good fatigue resistance properties in the presence of air. Diarylperfluorocyclopentene derivatives, such as 1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene, also showed excellent fatigue resistant properties. Similar fatigue resistant properties were observed in a polystyrene matrix. The cycle number as large as 7.0×10^4 was observed for 2-(2-ethoxybenzo[b]thiophen-3-yl)-3-(2, 4, 5-trimethyl-3-thienyl)maleic anhydride in polystyrene film covered with poly (vinyl alcohol), which prevents oxygen diffusion, in the presence of singlet oxygen quenchers, such as nickel complexes.

COLOR VARIATION

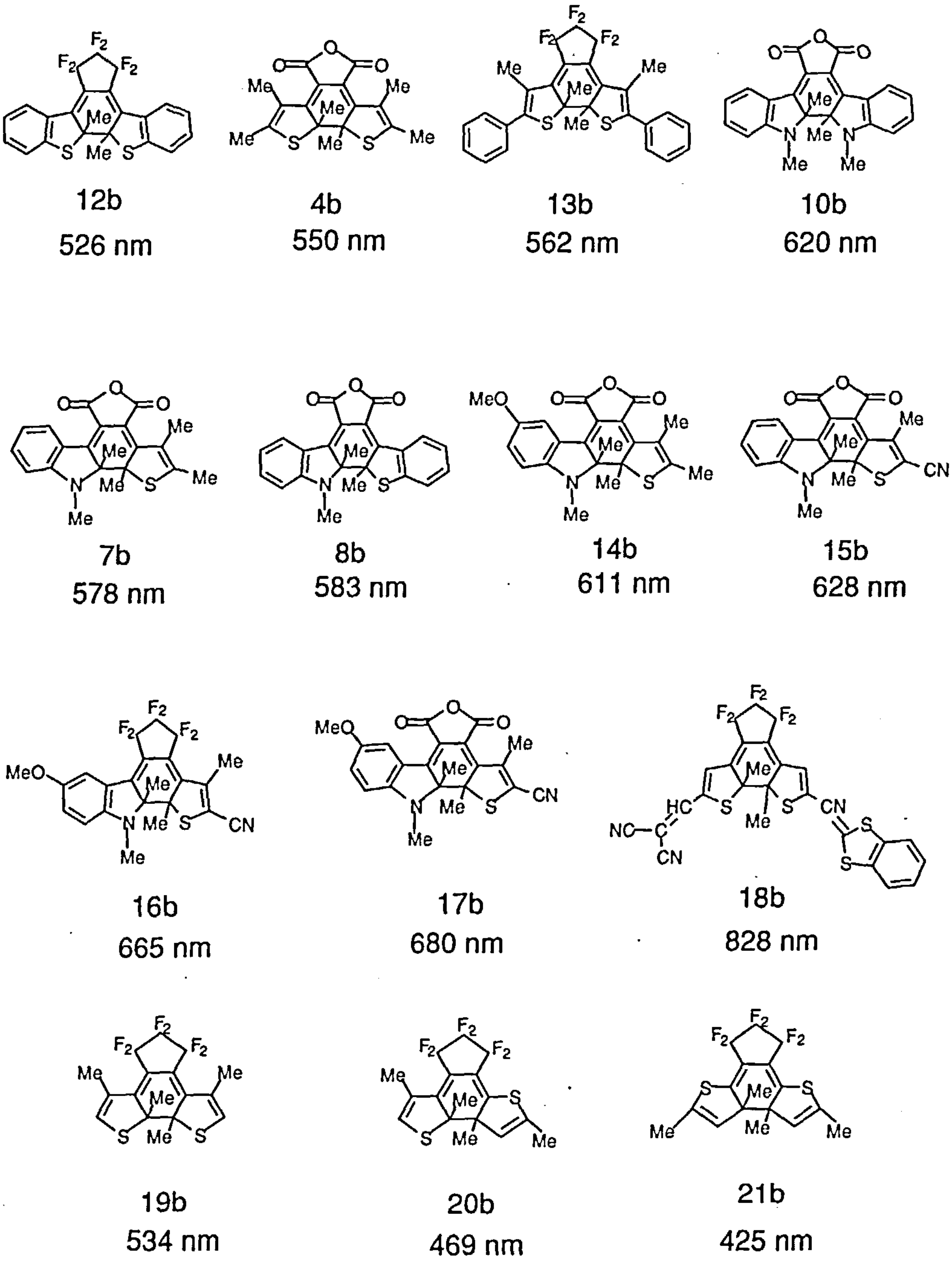
Although recently remarkable progress has been made in diode laser technologies, the wavelength of high power lasers is still longer than 650 nm. From the view point of applications to photonic devices the photochromic compounds should have the sensitivity in the region of wavelengths 650-830 nm. In order to obtain compounds which have

Table 3 Fatigue resistance property of diarylethenes in benzene

Compd	Repeatable Cycle Number	
	in air	under vacuum
	70	480
	3.7×10^3	1.0×10^4
	$>1.0 \times 10^4$	
	$> 8.0 \times 10^3$	—
	$>1.3 \times 10^4$	—
	3.0×10^4 in polystyrene	7.0×10^4 in polystyrene protected with PVA in the presence of singlet oxygen quenchers

sensitivity at longer wavelengths, symmetric diarylethenes with various heterocyclic rings such as benzothiophene or indole rings, have been synthesized. Among the compounds the closed-ring form of 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride has the longest absorption maximum at 620 nm. It was, however, thermally unstable and returned to the open-ring form in the dark.

In an attempt to get a thermally stable photochromic compounds having the absorption band at longer wavelengths we synthesized compounds having an electron donating group in the indole ring and an electron withdrawing group in the thiophene ring(Figure 4). The closed-ring forms of 2,3-diarylmaleic anhydride with a 5-methoxyindole ring on one end and a thiophene ring on the other end has the maximum at 611 nm in hexane, while the derivative with an indole ring and a 5-cyanothiophene ring absorbs at 626 nm. 2-(5-Methoxy-3-indolyl)-3-(2,4-dimethyl-5-cyano-3-thienyl)maleic anhydride, which has both electron donating and withdrawing groups in one molecule, has the absorption maximum of the closed-ring form at 680 nm. The longest absorption band of the closed-



12b
526 nm

4b
550 nm

13b
562 nm

10b
620 nm

7b
578 nm

8b
583 nm

14b
611 nm

15b
628 nm

16b
665 nm

17b
680 nm

18b
828 nm

19b
534 nm

20b
469 nm

21b
425 nm

Figure 4 Absorption maxima of closed-ring forms of diarylethenes in hexane.

ring form of diarylethenes was observed at 825 nm for compound **18b**.[18]

When we apply photochromic compounds to full color display, it is also desired to shift the absorption band to shorter wavelengths to get yellow developing compounds. We found that the substitution position of thiophene rings to the ethylene moiety alters the absorption wavelength of diarylethenes.[21] Photoirradiation with 366 nm light of a hexane solution containing 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene, **21a**, changed the color from colorless to yellow, and a new absorption was observed at 425 nm. The new visible absorption band disappeared by irradiation with light of wavelength longer than 440 nm. At a photostationary state under irradiation with 366 nm light, the ratio of the closed-ring to the open-ring forms was 77:23. The quantum yields of the cyclization and the ring-opening reactions were determined to be 0.40 and 0.58, respectively. On the other hand, the closed-ring form of 1,2-bis(2,5-dimethyl-3-thienyl)-perfluorocyclopentene, **19b**, showed the absorption band at 534 nm , and the hexane solution was red.

The blue shift observed for **21b** suggests that the π-conjugation in the closed-ring form is localized in the cyclohexadiene structure. The sp^3carbon atoms that were formed by the ring-closure reaction destroyed the π-conjugation in the benzo[2, 1-b:5,6-b']dithiophene structure. The π-conjugation delocalization of **21b** is, therefore, completely different from **19b**, in which the π-conjugation extends throughout the two thienyl moieties. Compound **20b** has the absorption at 469 nm, which is in between the bands of compounds **19b** and **21b**. The thermal stability of the closed-ring forms **19b**-**21b** was measured in heptane in the absence of air at 80℃. Optical densities of these isomers remained almost constant after 500 h. The closed-ring forms of dithienylperfluorocyclopentenes **19b**-**21b** were stable irrespective of the substitution positions of the thiophene rings.

CONCLUSION

We designed and synthesized a new type of photochromic compounds, 1,2-diarylethenes with heterocyclic rings, which are potentially useful for photonic devices. The compounds have thermal irreversible and fatigue resistance properties. In addition, we tuned up the structure to give color variation from yellow to near infrared regions.

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