

Photochromic diarylethenes for photonic devices

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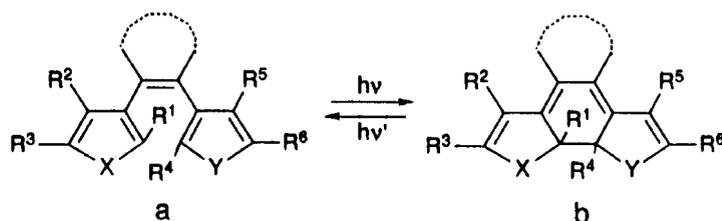
Abstract: This paper reports on a new type of photochromic compounds, diarylethenes with heterocyclic rings, for photonic devices. The diarylethenes undergo thermally irreversible and fatigue resistant photochromic reactions. The coloration / decoloration cycles can be repeated more than 7×10^4 times and both isomers are stable for more than three months at 80 °C. The response time is very fast; coloration/ decoloration processes finish in less than 10 ps. Furthermore, some of diarylethenes, such as 1,2-bis(2, 4-dimethyl-3-thienyl)perfluorocyclopentene and 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene, were found to undergo photochromic reactions in the single crystalline phase. Applications of the diarylethenes to optical memory media and photo-optical switching devices are now under way.

INTRODUCTION

Photochromism is defined as a reversible transformation in a chemical species between two forms having different absorption spectra by photoirradiation. The photochromic materials are potentially useful for various opto-electronic devices, such as optical memory, photo-optical switching and display. Optical memory using photochromic media offers advantages over magneto-optical recording with regard to speed of writing, multiplex recording capability, and low fabrication cost. At present great effort has been paid to develop erasable compact disks using photochromic diarylethenes(1). Refractive index changes in photochromic materials lead to their use in photo-optical switching devices. A self-holding Mach-Zender optical switch using thermally irreversible 1,2-bis(benzo[b]thiophen-3-yl)perfluorocyclopentene has been constructed and switching with low crosstalk and low excess loss was demonstrated(2). The photochromic switch has the advantages of a simple structure, very small size, power efficiency and remote control capability using light through the optical fiber. When we apply photochromic materials for such photonic devices, the materials have to fulfill the following requirements:

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

The more important requirements are thermal stability of both isomers, and fatigue resistant characteristics. We have developed a new type of fatigue resistant and thermally irreversible photochromic compounds, diarylethenes with heterocyclic rings, where "a" refers to open-ring form and "b" to closed-ring form hereafter.

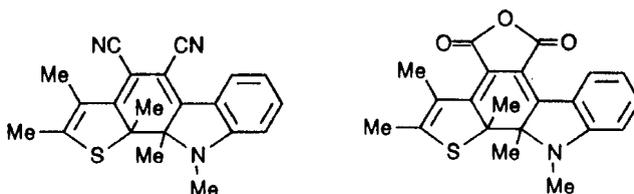


We report on our approach to gain access to photochromic compounds which fulfill the above requirements simultaneously.

THERMAL STABILITY

Theoretical consideration based on a molecular orbital theory revealed that the thermal stability of both isomers of diarylethenes is attained by introducing aryl groups, which have low aromatic stabilization energy(3). The theoretical prediction was confirmed by the synthesis of diarylethenes with various types of aryl groups(4-8). The stability of the closed-ring forms 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 return to the open-ring forms in the dark. On the other hand, photogenerated closed-ring forms of diarylethenes with phenyl or indole rings, which have rather high aromatic stabilization energy, were thermally unstable. The photogenerated yellow color of the closed-ring form of 2,3-dimesitylbutene disappeared with a half lifetime of 1.5 min at 20 °C. It returned quickly to the open-ring form. The closed-ring forms of diarylethenes with indole rings also exhibited thermally reversible reactions. 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.

It is worthwhile noting that the closed-ring forms of non-symmetric diarylethenes, as shown below, were found to be thermally stable.



The result indicates that the closed-ring forms of non-symmetric diarylethenes become thermally stable when at least one of the heterocyclic rings has low aromatic stabilization energy. In the above non-symmetric diarylethenes with an indole ring on one end and a thiophene ring on the other end, the thiophene ring plays a role to keep the thermal stability, and the indole ring to shift the absorption band to longer wavelengths.

FATIGUE RESISTANT CHARACTER

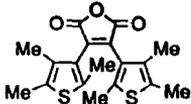
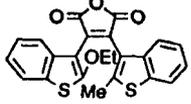
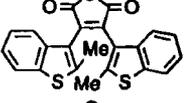
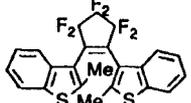
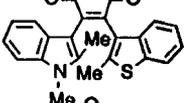
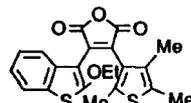
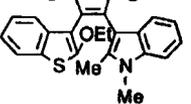
Photochromic reactions are always attended by rearrangement of chemical bonds. During the bond rearrangement undesirable side reactions take place to some extent. This limits the cycles of photochromic reactions. The difficulty in obtaining fatigue resistant photochromic compounds can be easily understood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



Even under the conditions that the side reaction quantum yield, Φ_s , 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.

With the aim of clarifying photochemically robust structures, we measured the fatigue resistance property of diarylethenes with various types of aryl groups [4, 5, 8-10]. Table 1 summarizes the result of repeatable cycle numbers in benzene. The repeatable cycle number indicates when the colored intensity decreases to 80% of the first cycle. For the symmetric diarylethenes, the repeatable cycle number was limited to less than 480 times even in the absence of air so far as the compounds have thiophene rings. When the thiophene rings were replaced with benzothiophene rings, the number remarkably increased. Diarylethenes with an 2-ethoxybenzo[b]thiophene ring on one end had good fatigue resistance properties. 2-(1,2-Dimethyl-3-indolyl)-3-(2-ethoxybenzo[b]thiophen-3-yl)maleic anhydride kept the adequate photochromic

Table 1 Fatigue resistance property of diarylethenes in benzene.

Compd	Repeatable Cycle Number		Compd	Repeatable Cycle Number	
	in air	under vacuum		in air	under vacuum
	70	480		$> 1.0 \times 10^4$	—
	3.7×10^3	1.0×10^4		$> 1.3 \times 10^4$	—
	—	$> 1.1 \times 10^4$		3.0×10^4 in polystyrene	7.0×10^4 in polystyrene protected with PVA in the presence of singlet oxygen quenchers
	$> 1.0 \times 10^4$	—			

property even after 1.0×10^4 cycles in the presence of air. Diarylperfluorocyclopentene derivatives, such as 1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene, also showed excellent fatigue resistance properties in the presence of air. Similar fatigue resistance 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.

RESPONSE TIME

How fast cyclization and ring-opening reactions are induced by photoirradiation is also an important characteristics when we apply photochromic diarylethenes to photonic devices. We measured the response times of 2,3-di(2,4,5-trimethyl-3-thienyl)maleic anhydride in hexane by using a pico-second laser photolysis apparatus(11). Figure 1 shows the rise of absorption at 560 nm after irradiation with a 355 nm laser pulse (22ps). The absorption at 560 nm is ascribed to the closed-ring form. The solid line in the figure was calculated by taking into account the pulse duration and the time constant of formation of 8 ps. The time constant well reproduces the rise profile. This indicates that the photocyclization process takes place in less than 10 ps.

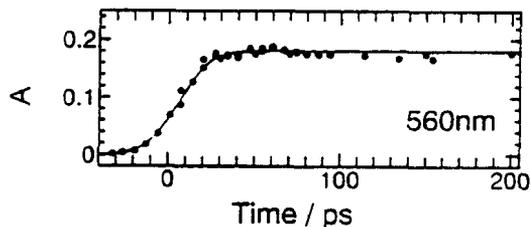


Fig. 1. Time profiles of transient absorbance of 2,3-di(2,4,5-trimethyl-3-thienyl)maleic anhydride in n-hexane after the excitation, excited with a picosecond 355 nm laser pulse.

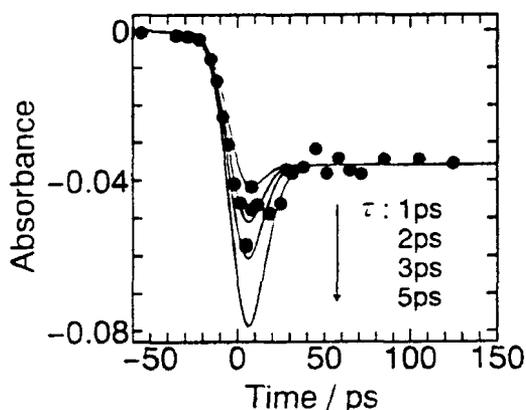
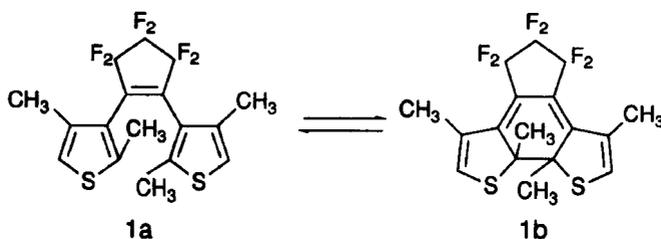


Fig. 2. Time profile of transient absorbance of the closed-ring form in n-hexane, excited with a picosecond 532 nm laser pulse and monitored at 560 nm.

The ring-opening reaction was also followed by irradiation with a 532 nm laser pulse. Immediately after the excitation, depletion of the absorbance around 560 nm and positive absorbance around 500-750 nm were observed. The positive absorbance around 700 nm is ascribable to S_1-S_n transition. The absorbance at 560 nm recovered in less than 40 ps as shown in Fig. 2. The solid lines in the figure are the calculated curves by taking into account the pulse duration and the quantum yield of the ring-opening reaction. The calculated curves with the time constants of 2-3 ps reproduce the experimental result. This indicates that the ring-opening reaction takes place with the time constant $< 2-3$ ps. It can be concluded that 2, 3-di(2, 4, 5-trimethyl-3-thienyl)maleic anhydride system undergoes the ultrafast reaction within 10 ps in both cyclization and ring-opening processes.

PHOTOCHROMISM OF SINGLE CRYSTALLINE DIARYLETHENES

If photochromic reactions proceeds in the crystalline phase, the photochromic materials can be potentially applied to many photonic devices. However, compounds which undergo photochromic reactions in the crystalline phase are rare and, in most cases, the photogenerated colored isomers are thermally unstable. They readily return to the initial colorless isomers at ambient temperature. During the course of study of substituted dithienylperfluorocyclopentenes (9) we found that compound 1 undergoes a thermally irreversible photochromic reaction in the polycrystalline state (12).



In order to judge whether the reaction takes place in the real crystalline phase or in the surface defects we examined the reaction in a single crystal. A plate form single crystal grown in a methanol solution of 1a was used. The single crystal turned red by irradiation with 313 nm light. The absorption maximum of the colored form was observed at 530 nm, which is almost similar to the closed-ring form 1b in hexane solution ($\lambda_{\text{max}} = 527$ nm). The red color remained stable up to the melting temperature ($T_m = 133$ °C) and thermal decoloration was not discerned at room temperature. The thermally stable red color was readily bleached by irradiation with 530 nm light and the coloration / decoloration cycles could be repeated more than 100 times.

The photoreactivity in the crystalline phase was further confirmed by measuring the absorption spectra under linearly polarized light. A colorless crystal was irradiated with 313 nm light and placed on the stage of a polarizing microscope. The polarizer and the analyzer were set in parallel each other. When the sample stage was turned, the red color intensity dramatically changed. Figure 3 shows the rotation angle dependence of the intensity at 530 nm. Two peaks were observed in the intensity, and the red color was strongly reduced at 0 and 180 degrees. This result clearly indicates that the photogenerated colored isomers regularly align in the crystal.

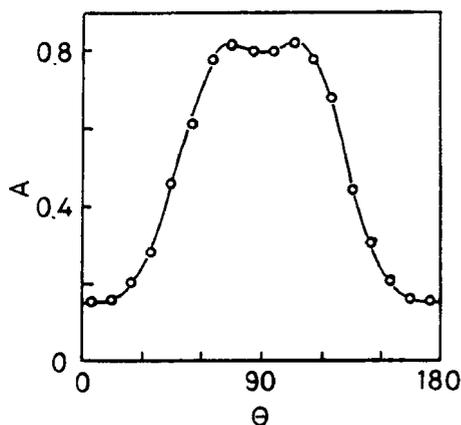


Fig. 3. Rotation angle dependence of the absorption intensity of a photoirradiated single crystal 1 at 530 nm.

During the cyclization reaction the thiophene groups are required to rotate along C-C bond between thiophene and ethylene moieties. Such a rotational motion is considered hardly to occur in crystals. X-ray crystallographic analysis indicates that adjacent molecules contact each other at the thiophene rings. Rotation of thiophene rings of a molecule is considered to reorganize the neighboring thiophene rings to some extent. Although at present the topotactic reorganization mechanism is not clear, cooperative rotation of the adjacent thiophene rings is one of possible mechanisms of the reaction.

Whether a photochromic reaction occurs or not in the crystalline phase strongly depends on the molecular structure. When hydrogens at 5 and 5' positions of the thiophene moieties were replaced with methyl groups, the reaction was no more observed. On the other hand, 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene with only one methyl group were found to undergo a photochromic reaction both in solution and in crystal. Although it is indispensable to further accumulate data on the correlation between the structure based on X ray crystallography and the reactivity in crystal for various diarylethenes to specify the structural prerequisite, the single crystalline photochromism is considered to provide a new application field of photochromic materials.

Acknowledgement

The author is grateful to the excellent co-workers K.Uchida, N.Tanio, S.Nakamura, H.Miyasaka, S.Nakayama, Y.Horikawa, M.Mohri, R.Sumiya, M.Hanazawa, F.Tatezono, T.Harada, T.Tsujioka who have contributed to the work described herein. This reserach was supported by a Grant-in-Aid for New Program "Intelligent Molecular Systems with Controlled Functionality (05N0301)" from Ministry of Education, Science and Culture.

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