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Novel Photochromic Molecules Based on 4,5-Dithienyl Thiazole with Fast Thermal Bleaching Rate

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Novel photochromic triangle terarylenes are synthesized, and their photochromic properties and thermal bleaching kinetics are investigated. Fairly high photochemical coloration reactivity is observed with photochemical quantum yield as high as 0.6 for 4,5-dithienyl thiazole derivative. Introduction of phenylethynyl groups into the molecular structure allows systematic control of thermal cycloreversion time constant over 10^5 times, and the half-lifetime shorter than 2 s is achieved at 303 K. The kinetic analysis of thermal cycloreversion reaction clearly shows significant contribution of frequency factor *A*. A novel molecular designing concept for systematic control of thermal bleaching reaction rate is presented without taking bulky functional groups on reaction center.

Introduction

Considerable interest has been focused on organic photochromic molecules from the viewpoints of fundamental organic photochemistry and also of practical applications as photoresponsive materials.[1] Spirooxazines and naphthopyrans, for example, show photoinduced coloration upon UV light irradiation and the spontaneous backward bleaching in dark, which makes them possible to use as light-modulating materials for eyewear.[2] Several such photochromic molecules showing photocoloration and thermal bleaching reactions have been reported, and some of them are currently used as the active materials in practical sunglass. The performance of these photochromic molecules for the practical light-modulating materials, such as degree of coloration response, thermal bleaching time constant, and fading temperature, has been studied and discussed in connection with the fundamental photochemical properties such as photochemical reaction mechanism,[3] quantum yield, and thermal bleaching kinetic parameters.[4] Fatigue resistivity and fast fading kinetics are currently attracting much interest for use in vehicles. Besides these photochromic molecules showing thermal fading properties, two classes of well-established hexatriene-type photochromic molecules, fulgide[5] and diarylethene,[6] have also attracted much interest recently because they show fairly high stability in both the colored and the bleached states under dark at ambient temperature. The specific thermal stability of these molecules would make them possible to be used as the active material for future photomemory medium. Another specific nature of these hexatriene type photochromic molecules is the high-performance photochromic reaction in solid states.[7−9] Some of them, indeed, show reversible photochromic reactions in polymer matrixes, organic glass matrixes, thin film, and even in single-crystalline state. Photochromic quantum yields of some diarylethenes in single-crystalline state have been reported to be almost unity.[9] Moreover, diarylethenes are known to show excellent fatigue resistivity for repetitive photochromic cycles.[10] These photochromic properties of the hexatriene-based photochromic molecules have stimulated further stud-

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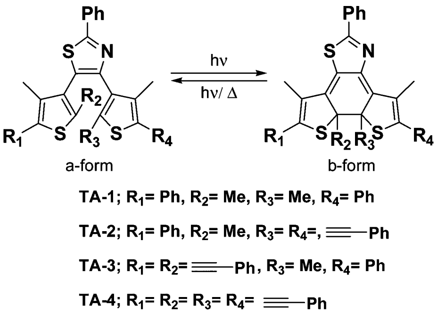
Scheme 1. Chemical Structures of TA-1, TA-2, TA-3, and TA-4



ies as active materials for future photomemory and photoswitching materials.[11] Recently, some novel classes of photochromic hexatriene molecules have been reported. One of the authors has proposed a new class of the hexatriene-type photochromic molecules with 1,2-diaryl-arylene type structure, so-called as "triangle terarylene", which can modulate the π-conjugation connection pathway with the photochromic reactions.[12]

Because of the specific photochromic performance of hexatriene-type photochromic molecules, one may expect to develop the light-modulating materials with photoinduced coloration and thermal bleaching properties on the basis of the hexatriene-type structure. One of the well-known hexatriene type molecules is *cis*-stilbene, which undergoes photocyclization to form thermally unstable ring-closed form isomer. The thermal cycloreversion reaction to *cis*-stilbene at room temperature is too fast to characterize the ring-closed form as the photoproduct.[13] Nakamura and Irie have reported that much larger aromatic stabilization on benzene unit is an origin of the thermal reactivity of ring-closed form of *cis*-stilbene. Less aromatic units such as thiophene or pyrrole introduced as the aryl units in the diarylethenes are expected to enhance the activation energy barrier of the thermal cycloreversion reaction in the ground state.[14] By controlling aromaticity, therefore, unique photochromic materials based on the hexatriene structure are expected, which show high-performance photochromic reaction even in solid state and fatigue resistivity and fast thermal fading rate constant at room temperature. Diarylethenes having bulky substituent groups at the reacting carbon atoms have been reported to show relatively high fading rate and low photobleaching properties at the elevated temperature.[15]

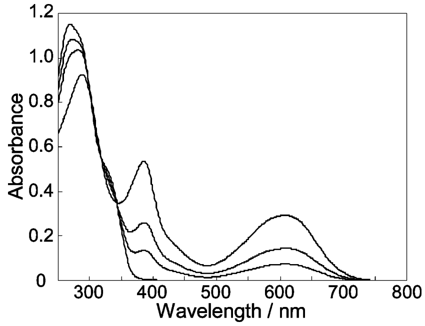


Figure 1. Absorption spectral change of **TA-1** upon UV irradiation (313 nm) in hexane (concentration = 3.3×10^{-5} M).

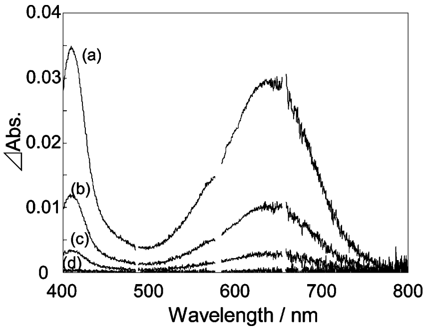


Figure 2. Differential absorption spectral change of **TA-4** after flash UV light irradiation at 293 K in toluene. Each trace corresponds to (a) 0 s, (b) 4.1 s, (c) 16 s, and (d) 28 s later following the irradiation. (Acquisition time interval was 1 ms.)

Table 1. Optical Properties and Arrhenius Parameters of Thermal Cycloreversion Reaction of TA-1, TA-2, TA-3, and TA-4

	λ_{max}/nm (ϵ/10^4 M^{-1} cm^{-1})^a	$E_a{}^d$/kJ mol^{-1}	A^d/10^{11} s^{-1}	$t_{1/2}$ (k^{-1}) at 20 °C
TA-1a	266 (3.5)^b			
TA-1b	600 (0.94)^b	92	0.16	14 days
TA-2a	333 (4.0)^c			
TA-2b	637 (−)^c	83	1.4	51 min
TA-3a	328 (3.3)^c			
TA-3b	610 (−)^c	91	18	94 min
TA-4a	329 (4.5)^c			
TA-4b	648 (−)^c	83	930	5.4 s

^{a} At room-temperature. ^{b} In hexane. ^{c} In methanol. ^{d} In toluene.

In the present study, photochromic molecules based on 4,5-dithienyl thiazole structure[16] which show large photocoloration quantum yield and rapid thermal fading kinetics at room temperature are presented. By choosing the numbers and kinds of aromatic groups, the fading kinetics can be tuned. Moreover, specific substituent effect on thermal bleaching kinetics is observed, which significantly contributes to the bleaching lifetime as short as 5 s at room temperature.

Experimental Section

Organic chemicals were purchased from Nacalai tesque, Wako, and TCI and were used as received. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a JEOL AL-300. Mass spectra

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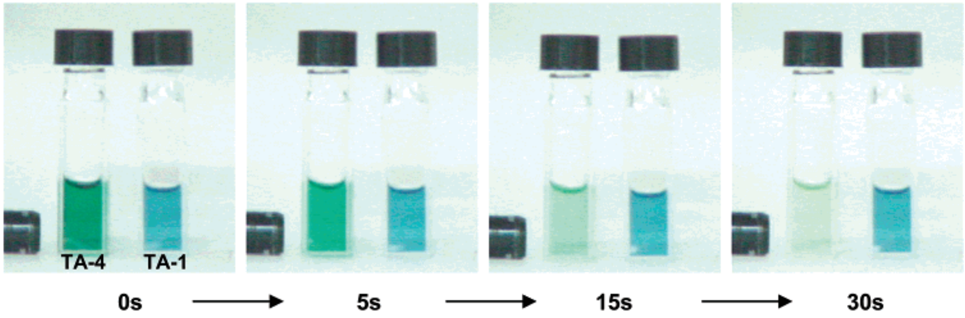

Figure 3. Comparison of photochromic coloration and spontaneous bleaching of **TA-4** and **TA-1** at room temperature (ca. 288 K).

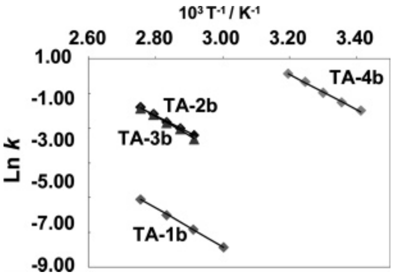

Figure 4. Arrhenius plots of the thermal cycloreversion rate constant of **TA-1**, **TA-2**, **TA-3**, and **TA-4** in toluene.

were measured with a mass spectrometer JEOL JMS-T100LC AccuTOF. Purification by high-performance liquid chromatography (HPLC) and gel permeation chromatograph (GPC) was performed with an HPLC system (JACSO PU-2080, UV-2075) and a GPC system (JASCO PU-2080, UV-2086) with appropriate columns. UV−vis absorption spectra were recorded on a JASCO V-550 spectrophotometer. Transient spectra after photoexcitation were recorded by an S2000 system (Ocean Optics).[17] An excitation pulse was generated by a short arc xenon flash lamp (SA-200E, Nisshin Electronic, Tokyo, Japan). Rate constants were estimated by fitting the absorbance decay with single-exponential curves. Absorption spectra in a polymer matrix were measured by using an Olympus BX-51 optical microscope connected with a Hamamatsu PMA-11 photodetector with an optical fiber. An ultrahigh-pressure Hg lamp (500W) and a Hg−Xe lamp (150 W) were used as light sources for steady-state measurements. The photochromic quantum yield was determined by using 1,2-bis(5-(2,4-diphenylphenyl)-2,4-dimethyl-3-thienyl)perfluorocyclopentene in hexane solution as the reference.[8e]

Results and Discussion

In the present study, four photochromic 4,5-dithienyl thiazole derivatives, **TA-1a**, **TA-2a**, **TA-3a**, and **TA-4a**, whose molecular structures are shown in Scheme 1, are prepared and their photochromic and thermal bleaching kinetics are studied. Thiazole unit is introduced as the central aromatic moiety instead of thiophene unit in “triangle terthiophene”.[12,16] Lower steric hindrance between the central aromatic group and the side thiophene units is expected to be advantageous for photocyclization reaction.[16] Improved chemical stability against oxidation is also expected for the thiazole groups. The phenylethynyl groups were introduced to modify the relative stability between the ring-open and ring-closed form isomers. The molecules shown in Scheme 1 were synthesized by conventional cross-coupling reactions of corresponding aryl bromides and aryl pinacol borate as described in the Supporting Information.

Each colorless solution of **TA-1a**, **TA-2a**, **TA-3a**, and **TA-4a** turned blue-green upon UV light irradiation, and the colored solutions were bleached by visible light irradiation or spontaneous thermal cycloreversion reaction under dark condition. Reversible absorption spectral change was observed at room temperature in all compounds, and the presence of isosbestic points supported the reversible two-component photochromic reaction schemes. The coloration and decoloration cycles can be repeated at least 20 times without any photodegradation. Figure 1 shows absorption spectral change of **TA-1a** with the photochromic reaction as a typical example, and optical properties of each compound are summarized in Table 1. The $\lambda_{\max}$ of the bleached and colored states tends to shift to longer wavelength by introducing phenyl ethynyl units. Remarkable red-shift of the absorption band of the colored state of **TA-2** in comparison with that of **TA-3** also suggests that the maximum wavelength of the colored state is predominantly affected by the expansion of the π-conjugation system in the cyclohexadiene type ring-closed form structure, in a similar manner to triangle terthiophene.[12] This is ascribed to the rerouting and switching effect of the π-conjugation expansion reported in diarylethenes with π-conjugated molecular units introduced on the carbon atoms of the reaction center,[18] which also seemed to be applicable for these terarylene derivatives.

Ring-closed form of **TA-1** was isolated from the colored solution by reversed-phase HPLC using methanol as the eluent, and its chemical structure was determined to be **TA-1b** illustrated in Scheme 1 on the basis of ^{1}H NMR spectrum. That is, characteristic signals of methyl protons of the ring-closed form isomer **TA-1b** were observed at 2.41, 2.31, 2.29, and 2.12 ppm. The ring-closed form isomer **TA-1b** was stable under dark condition at room temperature, whereas the colored isomers of **TA-2b**, **3b**, and **4b** spontaneously turned back to the original bleached state. Therefore, it was difficult to isolate those colored isomers from their colored solutions. The photochemical quantum yields of the ring-cyclization reaction from **TA-1a** to **TA-1b** and of the reverse reaction were evaluated to be 0.6 and 0.07, respectively. The former value is considerably large and no less than those of well-established diarylethenes so far reported.[6] **TA-1a** also

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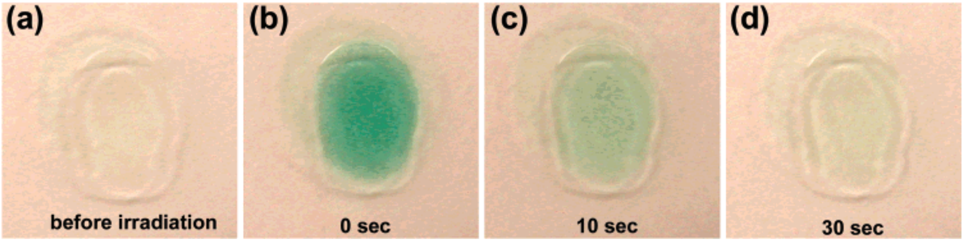

Figure 5. Photochromic coloration and spontaneous bleaching of **TA-4** dispersed in PMMA film at room temperature (ca. 288 K).

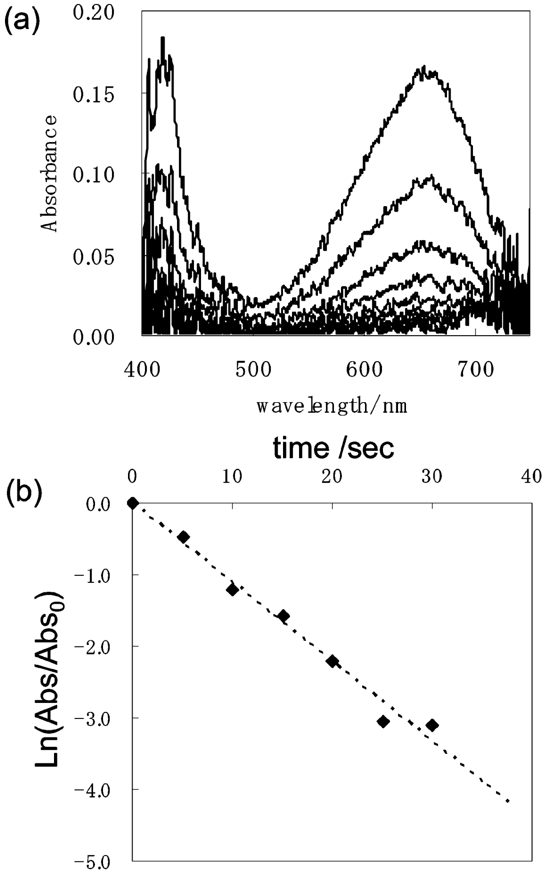

Figure 6. (a) Absorption spectral change in the visible region of **TA-4** with thermal cycloreversion in a PMMA film. (b) Decay line of peak absorbance by thermal cycloreversion reaction of **TA-4** in a PMMA film.

showed photochromic coloration and bleaching even in polycrystalline powder state, which suggests photochromic reactivity even in crystalline state. The lower photochemical quantum yield of the photochromic cycloreversion reaction than that of the cyclization reaction allows high contrast coloration under the illumination of ambient light. The similar effect would be also expected for other 4,5-dithienyl thiazole derivatives **TA-2**, **-3**, and **-4** since the introduction of arylethynyl units into the reacting carbon atoms did not affect much the ring-cyclization reaction.[18b] The UV irradiated colored solutions of **TA-2** and **TA-3** showed additional NMR signals of three methyl groups at 2.54, 2.17, and 2.16 ppm and at 2.46, 2.27, and 2.18 ppm, respectively, which were attributed to the ring-closed form isomers **TA-2b** and **TA-3b**, respectively. The colored state of **TA-4** was so unstable at room temperature that NMR study was conducted at 249 K. In the original **TA-4a** solution, two methyl groups exhibited doubly split NMR signals with the ratio of about 1.1 (2.45 ppm):1.8 (2.11 ppm):1.9 (2.05 ppm):1.2 (1.88 ppm) at 249 K. At 273 K, the split signals merged into two peaks at 2.25 and 2.00 ppm, which indicates thermal tautomerization in the ring-open form isomer **TA-4a**. From the merging temperature of the signals, $\Delta G^{\ddagger}$ of the conformational tautomerization was estimated to be ca. 5×10^1 kJ mol^{-1} by using the Eyring equation. Similar splitting in NMR peaks has already been reported for photochromic diarylethenes and was assigned to the rotational isomerization around the single bonds between the aryl units and the central ethene unit.[19] In the colored state of **TA-4**, additional NMR peaks were observed at 2.59 and 2.32 ppm at 249 K, which can be attributed to **TA-4b**.

We then investigated the thermal cycloreversion kinetics of **TA-1**, **-2**, **-3**, and **-4** at various temperatures in toluene. The absorption spectrum of colored state was measured at elevated temperature, and the bleaching of visible absorption band was detected. The flash lamp-induced photochromic coloration and rapid thermal bleaching can be repeated for more than 100 times with no marked degradation. Figure 2 shows differential absorption spectra of **TA-4**, which was acquired at certain time intervals after flash UV light irradiation. The rapid decrease of absorption band at 648 nm indicates thermal bleaching from **TA-4b** to **TA-4a** and the absorbance decay followed the single-exponential kinetics. The first-order cycloreversion reaction rate constant k was evaluated to be 0.14 s^{-1} at 293 K. The rapid bleaching of the colored solution of **TA-4** at room temperature (ca. 288 K) is demonstrated in Figure 3. **TA-1** maintained its color at 30 s after the UV light irradiation, while **TA-4** was almost bleached at that time. Figure 4 shows the temperature dependence of the first-order thermal cycloreversion reaction rate constants k for each photochromic compound. The activation energy (E_a) and frequency factor (A) are estimated from the linear regression lines and are summarized in Table 1. The present E_a values are considerably smaller than those of diarylethenes.[15,20] The molecules have three aromatic units in the ring-open form isomers, and those aromatic units collapse simultaneously on the photocyclization reaction, which makes the ring-closed form unstable and is partly responsible for the faster cycloreversion kinetics. On the other hand, the frequency factors of the thermal cycloreversion reaction were progressively enhanced by the increase of the number of phenylethynyl groups introduced. In particular, the frequency factor of **TA-4b** is considerably larger than those of diarylethenes,[15,20] which is also responsible to the rapid bleaching of colored state of **TA-4** in combination with

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the small activation energy. The present results suggest that introduction of rigid phenylethynyl groups onto the reacting carbon atoms of the cyclohexadiene structure would enhance the frequency factor and reaction rate constant of the thermal cycloreversion reaction. The half-lifetimes at 293 K of each ring-closed isomer extrapolated from the temperature dependence are also summarized in Table 1. Interestingly, the half-lifetime $t_{1/2}$ of **TA-4** became 5 orders of magnitude shorter than that of **TA-1** by the introduction of four phenylethynyl groups at 2,5-positions of both side thienyl groups. This value is short enough for the practical application to light-modulating sunglass.

The UV light-induced coloration and spontaneous bleaching of **TA-4** were also observed in a polymer matrix. As shown in Figure 5, poly(methylmethacrylate) (PMMA, Mw = ca. 1×10^5) film contained **TA-4** colored with UV light irradiation and was bleached thermally in 10 s at room temperature. Absorption spectral change and the decay line of absorbance peak of **TA-4** are shown in Figure 6. The tone of color in PMMA is almost the same as that of in solution, while the absorption maximum slightly shitted to longer wavelength. The thermal fading rate follows first-order kinetics even in solid film. The value of k was estimated to be 0.11 s^{-1}, which is almost equal to that observed in solution. The spontaneous fading of spirooxazine has been reported not to obey a single-exponential kinetics.[21] The existence of plural structural isomers of colored photomerocyanines or a nonuniform distribution of the free volume in a polymer seems to be responsible for the complicated and relatively slow fading kinetics. On the other hand, unity in the photoproduct and the smaller free volume necessary for isomerization are expected in the case of hexatriene-based terarylenes.

Conclusion

We have synthesized novel terarylene derivatives on the basis of 4,5-dithienyl thiazole with high coloration reactivity. Time constant of thermal cycloreversion of terarylene derivatives could be modulated over 10^5 times by introducing phenylethynyl groups. In particular, four phenylethynyl-containing **TA-4** shows efficient coloration under ambient sunlight and rapid bleaching under dark condition, suggesting possibility of light-modulating function with thermal bleaching time shorter than 10 s at 293 K and even shorter than 1 s at 313 K even in polymer matrix.

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Supporting Information Available: Detailed experimental section including description of the preparation and characterization of compounds **TA-1, -2**, **-3**, and **-4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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