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Strategy for Molecular Design of Photochromic Diarylethenes Having Thermal Functionality

Daichi Kitagawa^[a] and Seiya Kobatake*^[a]



Abstract: Thermal reactivities of photochromic diarylethene closed-ring isomers can be controlled by introduction of substituents at the reactive positions. Diarylethenes having bulky alkyl groups undergo thermal cycloreversion reactions. When bulky alkoxy groups are introduced, the diarylethenes have both thermal cycloreversion reactivities and low photocycloreversion quantum yields. Such photochromic compounds can be applied to thermally reusable photoresponsive-image recordings. The thermal cycloreversion reactivity of the closed-ring isomers can be evaluated using specific steric substituent constants and be correlated with the parameters. By introduction of trimethylsilyl or methoxymethyl groups at the reactive positions, the diarylethene closed-ring isomers undergo thermal irreversible reactions to produce byproducts at high temperature. These diarylethenes may be useful for secret image recordings. Furthermore, thiophene-S,S-dioxidized diarylethenes having secondary alkyl groups at the reactive positions undergo thermal byproduct formation reactions in addition to the photostability of the colored closed-ring isomers. Such materials may be used for light-starting thermosensors. The thermal byproduct formation reactivity can be evaluated by the specific substituent constants and theoretical calculations of quantum chemistry. These results supply the strategy for the molecular design of the photochromic diarylethenes having thermal functionality.

1. Introduction

Materials that can reversibly switch their states have attracted much attention because of various possibilities of global applications. Photochromism is described to as a reversible transformation of molecules between two isomers having different absorption bands.^[1] Photochromic reactions accompany the changes in not only colors but also geometric structures and physicochemical properties such as conductivity, dielectric constant, refractive index, and fluorescence. Therefore, photochromic compounds have attracted much attention because of their optoelectronic device applications.

Photochromic compounds can be classified into two types: T- and P-types. T-type photochromic compounds undergo thermal reversible photochromism. The photogenerated colored isomer returns to the initial colorless isomer by not only photoreaction but also thermal reaction. Azobenzene, spiropyran, spirooxazine, naphthopyran, and hexaarylbiimidazole are known as the representative T-type photochromic compounds. T-type photochromic compounds can be used for photomodulated materials such as ophthalmic lenses.^[2] On the other hand, the photogenerated colored isomer of P-type photochromic compounds is thermally stable. The colored isomer returns to the initial colorless isomer by only photoreaction. The representative

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 E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp P-type photochromic compounds are diarylethene, furylfulgide, and so on. P-type photochromic compounds are expected for application in optical memories,^[3] photooptical switches,^[4] displays,^[5] nonlinear optics,^[6] and photoresponsive actuators.^[7]

Diarylethene derivatives undergo the photoreversible isomerizations between the colorless open-ring isomer and the colored closed-ring isomer upon alternating irradiation with ultraviolet (UV) and visible light.^[8] Although most of diarylethene derivatives are classified into P-type photochromic compounds, the thermal stability of the colored closed-ring isomer can be modified according to the substituent. The effect of thermal stability of the closed-ring isomer can be modulated by the following three factors: (i) aromatic stabilization energy of the aryl groups,^[10] (ii) electron-withdrawing substituents at the aryl groups,^[11] and (iii) steric hindrance of the substituents at the reactive positions.^[12]







Theoretical calculation also revealed that the thermal stability of the colored closed-ring isomer depends on the energy difference (ΔH) between the open-ring isomer and the closed-ring isomer in the ground state, as shown in Figure 2.^[9a,13] The larger ΔH results in an increase in the thermal cycloreversion. The free energy barrier of the thermal cycloreversion reaction is correlated with the geometrical and vibrational characters at the transition state, such as the distance between the two reactive carbon atoms, the out-of plane angles of the methyl groups at the reactive carbon atoms, and the imaginary vibrational frequency.^[14] In recent studies, the novel materials using the thermal reaction of the closed-ring isomer of diarylethenes have attracted much attention because their function can be remotely induced by photoirradiation. Kawai et al. have reported the photoacid generator using photochromic terarylene that is an analogue of diarylethenes.^[15] The photogenerated closed-ring isomer of the terarylene is thermally unstable, which results in the elimination of a methanesulfonic acid. Thus, the strategy for molecular design of the thermally functional photochromic diarylethenes is quite important.



Figure 2. Potential energy surfaces of the ground state (S_{0}) and the excited state (S_{1}) of diarylethene molecules.

Herein, we report on recent developments in the diarylethene derivatives with thermal functionality. We succeeded in controlling the thermal functionality of the colored closed-ring isomer by introduction of various substituents at the reactive positions, as shown in Scheme 1. The molecular design for

Table 1. Optical properties and photoreactivities of diarylethenes in n-hexane

reusable imaging, secret imaging, and light-starting thermosensor using diarylethene framework is described.



Scheme 1. Diarylethene derivatives.

No and a the area	Open-ring isomer		en-ring isomer Closed-ring isomer Quantum yields		um yields	D-(
larylethene	λ_{\max} / nm	ε / M ⁻¹ cm ⁻¹	λ_{\max} / nm	ε / M ⁻¹ cm ⁻¹	$\pmb{\varPhi}_{o ightarrow c}$	${\pmb \phi}_{{\sf c} o {\sf o}}$	Ref.
1	280	35600	575	15600	0.59	0.013	16
2	286	40000	600	17000	0.52	0.0081	17
3	288	34100	603	14500	0.52	0.015	9b
4	286	37200	615	14700	0.50	0.025	18
5	290	34900	600	14800	0.50	0.026	12
6	292	34700	584	13600	0.51	0.022	18
7	290	36200	602	14000	0.54	0.046	18
8	296	37600	602	12600	0.48	0.074	18
9	309	33000	625	15000	0.44	1.7 × 10⁻⁵	19a,b
10	310	33000	625	13000	0.48	2.5 × 10 ^{−4}	19b
11	311	38700	627	13500	0.41	2.2 × 10 ⁻⁴	19d
12	310	36800	628	14500	0.22	2.2 × 10 ⁻⁴	19d
13	312	32000	635	13000	0.46	6.6 × 10 ⁻⁴	19b
14	313	34000	635	13000	0.43	6.4 × 10 ⁻⁴	19b
15	306	33000	656	10000	0.48	0.031	19c
16	280	_	615	_	_	_	20
17	280	40000	580	16300	0.53	0.0055	21
18 ^{a)}	350	51600	640	29800	0.47	0.00014	22
19 ^{a)}	350	43800	655	22600	0.47	0.0024	22

Diarylethene	<i>k /</i> s ⁻¹ at 100 °C	<i>t</i> _{1/2} / h at 100 °C	$E_{\rm a}$ / kJ mol ⁻¹	A / s ⁻¹	Ref.
1	3.5 × 10⁻ ⁷	550	139	1.0 × 10 ¹³	16
2	4.8×10^{-6}	40	128	4.0 × 10 ¹²	17
3	6.7 × 10 ^{−6}	29	125	2.1 × 10 ¹²	9b
4	1.0 × 10 ⁻⁴	1.9	120	6.5 × 10 ¹²	18
5	5.8 × 10 ⁻⁴	0.33	118	1.9 × 10 ¹³	12
6	7.3 × 10 ⁻⁴	0.26	113	4.9 × 10 ¹²	18
7	1.9 × 10⁻³	0.10	109	3.8 × 10 ¹²	18
8	9.9 × 10 ⁻³	0.019	95	2.1 × 10 ¹¹	18
9	1.4 × 10 ⁻⁶	140	137	2.1 × 10 ¹³	19b
10	4.8×10^{-6}	40	129	5.5 × 10 ¹²	19b
11	5.8 × 10 ⁻⁶	33	130	7.7 × 10 ¹²	19d
12	8.4 × 10 ⁻⁶	23	128	5.6 × 10 ¹²	19d
13	3.3 × 10 ⁻⁵	5.8	123	5.5 × 10 ¹²	19b
14	7.0 × 10 ⁻⁵	2.8	120	4.4 × 10 ¹²	19b
15	8.2 × 10 ⁻²	0.0024	92	5.7 × 10 ¹¹	19c
19	8.9 × 10 ⁻⁴	0.21	112	4.4 × 10 ¹²	22

Table 2. Kinetic parameters in thermal cycloreversion reactivities of diarylethene closed-ring isomers in toluene or decalin

2. Effect of bulky substituents at the reactive positions

The photogenerated colored closed-ring isomer of the representative diarylethene derivative (1) is stable for more than 1900 years at 30 °C.^[16] In contrast, when the bulky substituents were introduced at the reactive positions, the thermal cycloreversion reaction can be observed. Diarylethene derivatives with alkyl groups at the reactive positions, such as ethyl (2), propyl (3), isobutyl (4), isopropyl (5), cyclohexyl (6), secbutyl (7), and 4-heptyl (8) groups undergo the thermal cycloreversion reaction at high temperature in addition to the photochromic reaction. The optical properties of diarylethenes 1-8 are summarized in Table 1. Kinetic parameters for the thermal cycloreversion of the closed-ring isomers of 1-8 are summarized in Table 2. The half-life time of the closed-ring isomer decreases as increasing the bulkiness of the substituent. For example, the half-life time of the colored closed-ring isomer of the diarylethene having isopropyl groups at the reactive positions (5) is 0.33 h at 100 °C, while the methyl-substituted derivative (1) is stable even at 100 °C. This indicates that introduction of bulky substituents at 2- and 2'-positions of the thiophene ring can control the thermal cycloreversion reaction.

When alkoxy substituents were introduced at the reactive positions, the photocycloreversion quantum yield decreases significantly.^[19a] If a bulky alkoxy substituent is introduced at the reactive positions, diarylethene has the thermal cycloreversion

reactivity and the photostability of the closed-ring isomer. Such photochromic compounds are applicable for thermally reusable photoresponsive image recordings. Diarylethene derivatives with various types of alkoxy substituents at the reactive positions, such as ethoxy (10), isobutoxy (11), neopentyloxy (12), isopropoxy (13), cyclohexyloxy (14), and t-butoxy (15) groups were prepared and their photochromic properties and thermal stability of the coloredclosed-ring isomer were investigated.^[19] The optical properties and kinetic parameters for the thermal cycloreversion of diarylethenes 10-15 are also summarized in Tables 1 and 2. Diarylethenes 10-14 have good photocyclization quantum yields $(\Phi_{o\rightarrow c} = \sim 0.4)$ and low photocycloreversion quantum yields $(\Phi_{c\rightarrow o})$ = $\sim 10^{-4}$). Furthermore, diarylethenes **10–14** undergo thermal cycloreversion reaction at high temperature above 100 °C. The half-life time of the thermal cycloreversion reaction of their closedring isomers decreases with the bulkiness of the substituent. Especially, diarylethene 15 exhibits very fast decoloration. The half-life time of the thermal cycloreversion reaction for 15 is 8 s at 100 °C.

Figure 3 shows photocoloration and thermal and photochemical decoloration using diarylethenes **14** and **1**. Before photoirradiation, both samples are colorless. Upon irradiation with UV light, diarylethenes **14** and **1** turned blue. Upon irradiation with visible light, only the color of **1** disappeared, while the blue color of **14** remained the original color. In contrast, by heating at 160 °C in dark for 5 min, the blue color of **14** disappeared, while the color of **1** remained. Diarylethene **14** with the cyclohexyoxy group at the reactive positions has two different characteristics compared with diarylethene **1**. One is the photostability of the closed-ring isomer

by introducing alkoxy group at the reactive positions. The other is the acceleration of thermal cycloreversion reaction by introducing the bulky cyclohexyl group. Diarylethene **14** could accomplish the introduction of such a multi-functionality. The substituents at the reactive positions play an important role in the photocycloreversion and thermal cycloreversion reactions.



Figure 3. Photocoloration and thermal and photochemical decoloration of **14** (left side on the paper) and **1** (right side) in the polymer film. The colored sample was irradiated with visible light (> 520 nm) for 10 min. On the other hand, the colored sample was kept at 160 °C in the dark for 5 min.

Another strategy to decrease the photocycloreversion quantum yields of diarylethenes is to introduce long π -conjugation to diarylethenes.^[23,24] Diarylethenes 18 and 19 were synthesized.^[22] The diarylethene bearing methyl group (18) underwent the photocyclization reaction at 100% conversion to the closed-ring isomer upon irradiation with 350 nm light. The photocycloreversion quantum yield of 18 was determined to be 1.4×10^{-4} . The small quantum yield is ascribed to the introduction of the long π -conjugation. The photocyclization quantum yield of the diarylethene with isopropyl group (19) was similar to those of 5 and 18. The π -conjugation length and the introduction of isopropyl groups scarcely affected the photocyclization guantum vields. On the other hand, the photocycloreversion quantum vield was determined to be 0.0024 for 19, which is smaller than that of 5 by a factor of 11. Diarylethene 19 underwent thermal cycloreversion reaction at high temperature. The half-life time of the thermal cycloreversion reaction for 19 is 5 s at 160 °C. The fast thermal bleaching at the temperature may be used for thermally reusable photoresponsive-image recordings.

3. Correlation between the thermal cycloreversion reactivity and substituent constant

As mentioned above, the bulkiness of the substituent at the reactive carbons in photochromic diarylethenes plays an important role in the thermal cycloreversion reactivity of the photogenerated closed-ring isomers. Herein, we have dealt with the steric substituent constants to evaluate the relationship between the steric hindrance of the alkyl substituent R and the thermal cycloreversion reactivity.^[9b] We employed three steric substituent constants, $E_{\rm s}({\rm R})$, $E_{\rm s}^{\rm c}({\rm R})$, and $\nu({\rm R})$. $E_{\rm s}({\rm R})$ is known as Taft's steric substituent constant.^[25,26] It concerns the rate of hydrolysis of RCOOCH₂CH₃. The hydrolysis is affected by hyperconjugation of the α -hydrogens of R in ester. The hyperconjugation effect can be removed according to the method proposed by Hancock et al.,^[27] which is defined as $E_{\rm s}^{\rm c}({\rm R})$ in the following equation:

$$E_{\rm s}^{\rm c}({\rm R}) = E_{\rm s}({\rm R}) + 0.306(N-3) \tag{1}$$

where *N* is the number of hydrogen atoms of the α -carbon of substituent R. ν (R) also corresponds to the steric-effect substituent constant determined from van der Waals radii for the substituent as defined by Charton.^[28] The values of each substituent constant are summarized in Table 3.

Table 3.	Steric substituent constants,	<i>E</i> _s (R),	$E_{s}^{c}(R)$,	<i>v</i> (R),	and
E _s °(CH ₂ R	() ^{a)}				

=3 (2)				
R	<i>E</i> _s (R)	$E_{s}^{c}(R)$	<i>v</i> (R)	Esc(CH ₂ R)
CH ₃	0	0	0.52	-0.38
CH ₂ CH ₃	-0.07	-0.38	0.56	-0.67
$CH_2CH_2CH_3$	-0.36	-0.67	0.68	-0.70
CH ₂ CH(CH ₃) ₂	-0.93	-1.24	0.98	-0.82
$CH_2C(CH_3)_3$	-1.74	-2.05	1.34	-0.65
CH(CH ₃) ₂	-0.47	-1.08	0.76	-1.24
cyclo-C ₆ H ₁₁	-0.79	-1.40	0.87	_
CH(CH ₃)C ₂ H ₅	-1.13	-1.74	1.02	_
CH(C ₃ H ₇) ₂	-2.11	-2.72	1.54	_
C(CH ₃) ₃	-1.54	-2.46	1.24	-2.05

a) The $E_{\rm s}(R)$ values were cited from ref. 26. The $E_{\rm s}^{\circ}(R)$ and $E_{\rm s}^{\circ}(CH_2R)$ values were calculated from eq. (1). The $\nu(R)$ values were cited from ref. 28.

Figures 4a-4c show the relationship between each substituent constant and the rate constant of the thermal cycloreversion for diarylethenes 1-8. Although the $E_s(R)$ and $\nu(R)$ values show no good correlation with the rate constant, the $E_s^{\rm c}(R)$ value correlates well with the rate constant. These results indicate that the thermal cycloreversion reactivity is affected by only the steric hindrance of the substituents at the reactive positions and not affected by the hyperconjugation of α -hydrogens in substituent R. The activation energy (Ea) is also an important factor to determine the thermal cycloreversion reactivity. Figures 4d-4f show the relationship between each substituent constant and the E_a of the thermal cycloreversion reaction. The $E_s(R)$ and $\nu(R)$ values show no good correlation with the E_a value. In contrast, the $E_s^{c}(R)$ value had a good correlation. Thus, the thermal cycloreversion reactivity of diarylethene having alkyl groups at the reactive positions can be estimated using the substituent constant $E_{s}^{c}(R)$.

Here, we performed the universal correlation for diarylethenes with alkyl and alkoxy groups (1-15) by introduction of $E_{s}^{c}(CH_{2}R')$ for alkoxy group (OR'), where $CH_{2}R'$ corresponds to the substituent with CH₂ instead of oxygen in substituent OR'. For example, when the substituent is methoxy group, the substituent constant for ethyl group was applied. Figure 5 shows the relationship between $E_{s}^{c}(R)$ and the rate constant and activation energy of the thermal cycloreversion for diarylethenes 1-15. There is a very good correlation between the thermal cycloreversion reactivity and the steric substituent constant $E_{s}^{c}(R)$. These results indicate that the oxygen atoms in alkoxy groups were found to function as a spacer without the electronwithdrawing inductive effect and the electron-donor effect in conjugation. These results also supply very useful strategy for the molecular design of diarylethenes with desired thermal stability.



Figure 4. Relationship between $\log(k)$ at 100 °C (a-c) and the activation energy of the thermal cycloreversion (d-f) and the steric substituent constants, $E_s(R)$ (a,d), $E_s^{c}(R)$ (b,c), and $\nu(R)$ (c,f).





Figure 5. Relationship between log(*k*) at 100 °C (a) and the activation energy of the thermal cycloreversion (b) and the steric substituent constant, $E_s^{\circ}(R)$. The $E_s^{\circ}(R)$ value for diarylethene having alkoxy group (OR') was calculated as $E_s^{\circ}(CH_2R')$ using CH₂ instead of oxygen in OR'.

4. Thermally irreversible reaction of the closed-ring isomer

In the course of study on the thermal stability of the colored closed-ring isomer, we found the thermally irreversible reaction of the closed-ring isomer. If the colored state immediately and irreversibly changes to a colorless state by heating and the colorless state is stable under both UV and visible light, such photochromic compounds can be used for secret display materials and light-starting thermosensors. Diarylethene having trimethylsilyl (TMS) group at the reactive positions (16) exhibits photoreversible photochromism in a polymer film, as well as in solution.^[20] Furthermore, the colored state changes to colorless immediately upon heating at 100 °C. The colorless state was stable under both UV and visible light. It was revealed by HPLC analysis that there are two types of thermal bleaching byproducts. The molecular structures of the byproducts were confirmed by the X-ray crystallographic analysis. The proposed mechanism to generate the byproducts is shown in Scheme 2. One of the TMS groups in 16-BP1 is no longer present, and the cleavage of the C-S bond is confirmed. In the case of 16-BP2, both TMS groups are no longer present. In both cases, the elimination of TMS group can be observed. Furthermore, secret image recordings using the irreversible thermo-bleaching function were demonstrated as shown in Figure 6. The switching between the secret state and the image patterning state can be repeated more than 100 cycles by alternating irradiation with UV and visible light.

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Scheme 2. Proposed byproduct formation reactions of diarylethene 16.



Figure 6. Secret image recordings using a photomask by UV irradiation and heating at 100 °C. Diarylethene **16** is present on the paper surface. Reproduced from Ref. 20 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

The closed-ring isomer of a photochromic diarylethene having methoxymethyl group at the reactive positions (17) also undergoes both the thermal cycloreversion reaction and thermally

irreversible reaction at 120 °C.^[21] When the colored closed-ring isomer was heated in toluene for 70 h at 120 °C, the blue color was largely bleached by the thermal reactions. After irradiation with visible light to bleach the remaining blue color, the color of the solution turned to pale yellow, which is different from those of the open-ring isomer and the closed-ring isomer. From ¹H NMR, MS, and X-ray crystallographic analysis, the structure of the thermal byproduct (**17-BP**) was determined as shown in Figure 7. The elimination of a methoxymethyl group and the cleavage of the C–S bond were confirmed. This result is very similar to that of the TMS derivative (**16**).



Figure 7. Molecular structure of byproduct **17-BP**. Adapted from Ref. 21 with permission from The Chemical Society of Japan.



Scheme 3. Byproduct formation of diarylethene 17.

Table 4.	Optical properties	and photoreactivi	ties of thiophene-S,S-	-dioxidized diar	ylethenes in <i>n</i> -hexane
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Diamdathana	Open-ring isomer		Closed-ring isomer		Quantum yields		Def
Diarylethene	λ_{\max} / nm	ε / M ⁻¹ cm ⁻¹	λ_{\max} / nm	ε / M ⁻¹ cm ⁻¹	${\pmb \phi}_{{o} o {c}}$	$\pmb{\Phi}_{c ightarrow o}$	Ref.
20	286	25000	542	19000	0.62	2.7 × 10 ⁻⁴	18
21	284	29200	556	20600	0.49	2.1 × 10 ⁻⁴	18,30
22	285	31500	571	19600	0.41	7.7 × 10 ⁻⁴	18
23	282	24100	550	17300	0.36	2.8 × 10 ⁻⁵	18,30
24	284	26000	554	17000	0.30	2.0 × 10 ⁻⁵	18
25	282	29700	555	16800	0.34	2.4 × 10 ⁻⁴	18
26	284	26200	548	16400	0.32	2.4 × 10 ⁻⁴	18
27	286	29500	580	_	_	—	18,30
28	272	19400	536	15100	0.26	3.1 × 10 ⁻⁴	18
29	286	31000	580	_	—	—	18

5. Light-starting irreversible thermosensor

When diarylethenes have a photostability of the closed-ring isomers in addition to the formation of colorless byproducts, a light-starting irreversible thermosensor as illustrated in Figure 8 can be created by combining the following conditions: (i) fast coloration upon irradiation with UV light, (ii) a photostability of the colored state, (iii) thermal bleaching at an appropriate temperature, and (iv) a photostability of the thermal bleaching state. The light-starting irreversible thermosensor can be used as a sensor which can detect a rise in heat at low temperature below room temperature. Such a thermosensor can be used as Time-Temperature Indicators (TTI) to indicate exposure to excessive temperature on food, pharmaceutical, and medical products,^[29] and has an advantage that it can be stored at room temperature before use.



Figure 8. Concept in light-starting irreversible thermosensors.

We synthesized thiophene-S,S-dioxidized diarylethenes with secondary alkyl substituent at the reactive positions (20-29) and revealed that they can be used as the light-starting irreversible thermosensor.^[18,30] The optical properties of diarylethenes 20-29 are summarized in Table 4. The photocycloreversion quantum yields of the thiophene-S,Sdioxidized diarylethenes were determined to be 10^{-4} – 10^{-5} , which is extraordinarily smaller than those of non-oxidized thiophene derivatives by a factor of 10^2-10^3 ; while, the photocyclization quantum yields keep moderate values as high as 0.3-0.5. Furthermore, the colored closed-ring isomers of thiophene-S.Sdioxidized diarylethenes with secondary alkyl substituent at the reactive positions undergo thermally irreversible reaction to the colorless state as shown in Scheme 4. Kinetic parameters for the thermal byproduct formation of diarylethenes 20-29 are also summarized in Table 5. The thermal bleaching reaction of the closed-ring isomer depends on the bulkiness of the substituents at the reactive positions. The relationship between the rate of thermal bleaching reaction and the substituents can be discussed using the steric substituent constant $E_{s}^{c}(R)$. Figure 9 shows the relationship between the rate constant or the activation energy (E_a or E_a') of the thermal bleaching reaction and the $E_s^{c}(R)$ values of the substituents at the reactive carbons. The plots showed good correlations for $E_s^{c}(R)$ vs. log(k) at 100 °C and $E_s^{c}(R)$ vs. the activation energy. In the case of the non-oxidized diarylethenes, the closed-ring isomers undergo the thermal cycloreversion reaction. In contrast, in the case of the oxidized diarylethenes, the closed-ring isomers undergo the thermal byproduct formation reaction. Although the bleaching reactions for the non-oxidized diarylethenes and the oxidized diarylethenes are different from each other, the activation energy can be correlated.



Scheme 4. Photochromic reaction and byproduct formation of diarylethene 23.

Table 5.	Arrhenius parameters for	thermal byproduct formation
of the clo	osed-ring isomers.	

Dia	rylethene	<i>k</i> /s ^{−1} at 100 °C	<i>t</i> ₁/₂/h at 100 °C	<i>E</i> a′ ∕kJ mol⁻¹	<i>A</i> /s ⁻¹
2	23	1.2 × 10 ^{−3}	0.17	121	9.7 × 10 ¹³
	24	1.8 × 10 ^{−3}	0.11	113	9.6 × 10 ¹²
	25	1.5 × 10 ^{−2}	0.013	109	2.6 × 10 ¹³
	26	1.2 × 10 ^{−2}	0.015	109	2.5 × 10 ¹³
	27	3.6 × 10 ⁻¹	0.00054	101	5.3 × 10 ¹³
	28	1.0 × 10 ⁻²	0.019	113	6.6 × 10 ¹³
	29	2.8	0.000069	88	5.8 × 10 ¹²



Figure 9. Relationship between steric substituent constants $E_s^{c}(R)$ and the logarithm of *k* at 100 °C (a) and the activation energy (E_a or E_a') (b) for the thermal bleaching reaction of the non-oxidized diarylethenes (•) and the oxidized diarylethenes (o), respectively. Adapted from Ref. 18 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Moreover, the thermal bleaching reaction was accelerated by the introduction of methyl groups at the 4-position of thiophene rings. Thermal reaction of diarylethene 28 easily proceeded even at 10 °C. The rate of the thermal reaction of 28 was 7.8 times faster than that of 23 at 100 °C. Furthermore, we performed to correlate the thermal byproduct formation reactivity with the energy difference ($\Delta H'$) in the ground state between the closedring isomer and the total energy of the byproduct and SO₂ using theoretical calculation. Theoretical calculations were performed with density functional theory (DFT) at the B3LYP/6-31G(d) level. The energy differences for diarylethenes 20, 23-29 are summarized in Table 6. Figure 10 shows the energy diagram of **O**, **C**, and **BP**. The total energy of **BP** and SO₂ becomes much stable than the energy of C. Figure 11 shows the relationship between the thermal byproduct formation reactivity and the $\Delta H'$ value. The plots showed good correlations with r-factors of 0.984 and 0.955 for $\Delta H'$ vs. log(k) at 100 °C and $\Delta H'$ vs. E_a' , respectively. When the bulky substituents are introduced at the reactive positions, the $\Delta H'$ becomes large. Moreover, when the $\Delta H'$ value is large, the E_a' value becomes small. These results revealed that the thermal byproduct formation reactivity can be estimated by theoretical calculation.

Table 6. Energy gap ($\Delta H'$) calculated between the dioxidized diarylethene closed-ring isomer (**C**) and the byproduct (**BP**) and the activation energy (E_a ') for the thermal byproduct formation.

Diarylethene	$\Delta H'$ /kJ mol ⁻¹	<i>E</i> _a ′/kJ mol ^{−1}
20	163.08	-
23	214.56	121
24	220.26	113
25	228.09	109
26	229.67	109
27	239.95	101
28	226.21	113
29	244.43	88

a) $\Delta H' = \text{Energy}(\mathbf{C}) - (\text{Energy}(\mathbf{BP}) + \text{Energy}(SO_2)).$

b) *E*_a: Activation energy of the byproduct formation determined experimentally.



Figure 10. Schematic energy diagram of the oxidized diarylethene system in the ground state. Adapted from Ref. 18 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.



Figure 11. Relationship between $\Delta H'$ and the logarithm of *k* (a) and the activation energy (b) for the thermal byproduct formation of the oxidized diarylethenes. Adapted from Ref. 18 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Conclusion

Recent developments for the photochromic diarylethenes having thermal functionality by introduction of various substituents at the reactive positions have been described. The thermal

cycloreversion reactivity of the closed-ring isomer can be controlled by introduction of the bulky alkyl or alkoxy substituents at the reactive positions. Especially, when the alkoxy groups were introduced at the reactive positions, a diarylethene with a thermal cycloreversion reactivity and a low photocycloreversion quantum yield can be prepared. Such photochromic compounds are expected for application in thermally reusable imaging devices. Moreover, the closed-ring isomers of diarylethenes having TMS or methoxymethyl groups at the reactive positions exhibit thermally irreversible reaction to colorless compounds at high temperature. These photochromic compounds can be applied to secret image recordings. Furthermore, the thiophene-S,Sdioxidized diarylethenes having secondary alkyl groups at the reactive positions exhibit thermal byproduct formation reaction. The thermal byproduct formation reactivity can be modified by introduction of the bulky secondary alkyl groups at the reactive positions and the 4-position of thiophene rings. Such compounds can be used as a light-starting irreversible thermosensor. In addition, when five-membered heterocyclic rings, such as thiophene and thiazole, are used as the ethene bridges, the closed-ring isomers become thermally unstable.^[31] The thermal stability depends on the type of bridges. The modification of the ethene bridge may be useful for control of the photoreactivity and

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thermal reactivity in addition to the substituents at the reactive positions. Thus, the control of the thermal stability of the closedring isomer is quite important for development of the novel materials with thermally functionable diarylethenes.

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Entry for the Table of Contents

PERSONAL ACCOUNT



Thermal cycloreversion and byproduct formation reactivities of photochromic diarylethene closed-ring isomers can be controlled by introduction of substituents at the reactive positions. The reactivities can be correlated by steric substituent constants. These results supply the strategy for the molecular design of the photochromic diarylethenes having thermal functionality.

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Strategy for Molecular Design of Photochromic Diarylethenes Having Thermal Functionality