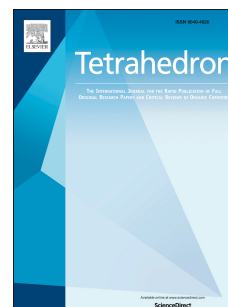


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Graphical Abstract

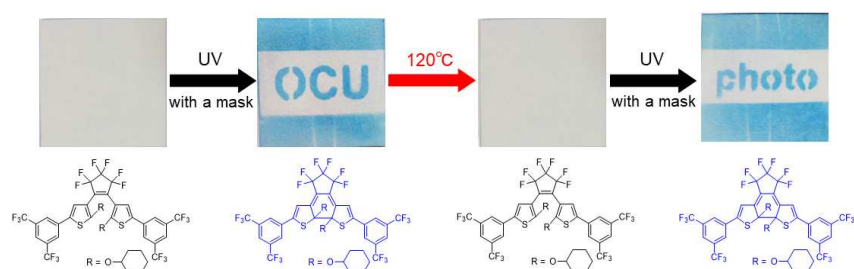
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Molecular design for a write-by-light/erase-by-heat recording system using photochromic diarylethenes with thermal cycloreversion

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ABSTRACT

We designed and synthesized photochromic diarylethenes for a write-by-light/erase-by-heat recording system. The introduction of polar substituents at both sides of the diarylethene maintained the photocyclization and photocycloreversion reactivities, but significantly changed the thermal cycloreversion reactivity. The introduction of electron-withdrawing substituents accelerated the thermal reaction and the introduction of electron-donating substituents suppressed the thermal reaction. The rate constants of the thermal reaction were well correlated with Brown-Okamoto's substituent constant σ^+ that is a modified value of Hammett's substituent constant σ . The large rate constants are ascribed to the lower activation energy for the thermal reaction. These results provide new knowledge for the molecular design of diarylethenes for a write-by-light/erase-by-heat recording system.

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1. Introduction

Materials that can reversibly switch their color have attracted much attention because of the various possibilities of application for rewritable media and switching devices. Photochromism is defined as a photoreversible transformation between two isomers having different absorption bands [1]. Photochromic compounds can be switched between two states upon photoirradiation. There are two types in the photochromic systems: T- and P-types. T-type photochromic compounds undergo thermal back reactions of the photogenerated isomers. Azobenzene [2], spiropyran [3,4], spirooxazine [4], naphthopyran [5], and hexaarylbiimidazole [6] are known as the representative T-type photochromic compounds. T-type photochromic compounds can be used for photomodulated materials such as ophthalmic lenses [7]. In contrast, P-type photochromic compounds are thermally stable for both isomers. The photogenerated isomer returns to the initial isomer only by photoreaction. The representative P-type photochromic compounds are diarylethene [8], furylfulgide [9], and phenoxynaphthacenequinones [10]. Among them, diarylethenes have the most excellent properties such as fatigue resistance, high sensitivity, and rapid response, and are expected to be applicable in optical memories [11], photooptical switches [12], displays [13], nonlinear optics [14], and photoresponsive actuators [15].

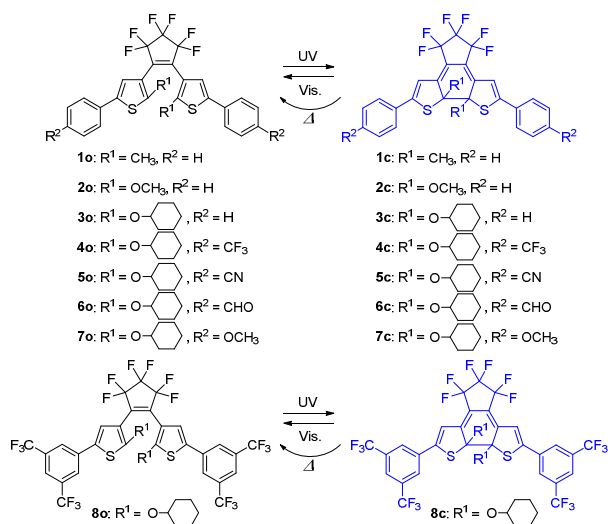
The photochemical and thermal properties of diarylethenes can be modified by changing the substituent. For example, when

the substituent (R^1) at the reacting positions of a typical diarylethene derivative changes from methyl (**1o**) to methoxy groups (**2o**), the photocycloreversion quantum yields extraordinarily decrease by a factor of 1000, whereas the cyclization quantum yields are almost constant [16]. On the other hand, the introduction of the bulky substituents at the reacting positions leads to accelerating the thermal cycloreversion reaction [17]. As a result, a diarylethene derivative with the cyclohexyloxy group at the reacting positions has specific photochromic properties [18]. Thus, 1,2-bis(2-cyclohexyloxy-5-phenyl-3-thienyl)perfluorocyclopentene (**3o**) undergoes the photocyclization reaction with a moderate quantum yield of 0.43. In contrast, the photocycloreversion reaction is prohibited as can be seen from the extraordinarily low quantum yield of 6.4×10^{-4} . However, the thermal cycloreversion reaction takes place with a half-life time of 45 s at 160 °C, whereas the colored isomer is significantly stable at room temperature. These properties are an advantage for application to a write-by-light/erase-by-heat recording system. It is desirable to design diarylethene molecules whose closed-ring isomers exhibit the thermal cycloreversion reaction at temperatures much lower than 160 °C but exist enough stable at room temperature.

An introduction of electron-withdrawing substituents on both sides in the π -conjugation of diarylethene leads to the fast thermal cycloreversion reaction [19]. Here, trifluoromethyl, cyano, and formyl groups have been introduced as the electron-

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withdrawing substituent at both sides of diarylethene. For comparison, methoxy groups have been introduced as the electron-donating substituent and trifluoromethyl groups at two *m*-positions have also been introduced. Thermal cycloreversion reactivities of the closed-ring isomers were correlated using Hammett's polarity parameters to reveal the effect of inductive and resonance of the substituents to the thermal cycloreversion reactions.



Scheme 1. Molecular structure of diarylethenes used in this work.

2. Results and discussion

2.1. Photochromism

Diarylethenes **4**–**8** prepared in this work undergo photocyclization reactions as well as diarylethenes **1**–**3** upon irradiation with ultraviolet (UV) light. Fig. 1 shows absorption spectral changes of **4**–**8** in *n*-hexane or dichloromethane. The open-ring isomers **4**–**8** are colorless and have absorption maximum wavelength (λ_{max}) at the range from 310 to 369 nm. Upon irradiation with 313 nm light, a new absorption band derived from the closed-ring isomers appeared in the visible region and the solution color turned to blue. The λ_{max} of **4**–**8** appeared at 635, 640, 664, 673, 645, and 638 nm, respectively. The photogenerated closed-ring isomers were stable at room temperature and they were possible to be isolated by HPLC. Upon irradiation with visible light, the closed-ring isomers returned to the open-ring isomers very slowly. The photocyclization and photocycloreversion quantum yields ($\Phi_{\text{o} \rightarrow \text{c}}$ and $\Phi_{\text{c} \rightarrow \text{o}}$) of **4**–**8** were examined to quantitatively discuss the photochemical reactivity of the diarylethenes. Table 1 shows

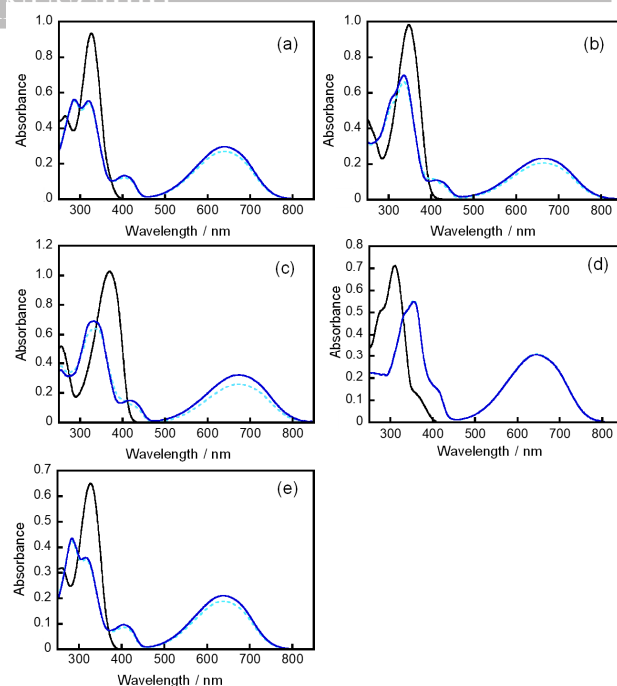


Fig. 1. Absorption spectral change of (a) **4** (2.19×10^{-5} M in *n*-hexane), (b) **5** (1.63×10^{-5} M in dichloromethane), (c) **6** (1.84×10^{-5} M in dichloromethane), (d) **7** (1.71×10^{-5} M in *n*-hexane), and (e) **8** (1.66×10^{-5} M in *n*-hexane) by photoirradiation: open-ring isomer (black solid line), solution in the photostationary state under irradiation with 313 nm light (blue dashed line), and closed-ring isomer (blue solid line).

λ_{max} , molar absorption coefficient, and photocyclization and photocycloreversion quantum yields. The $\Phi_{\text{o} \rightarrow \text{c}}$ for **4**–**8** were determined to be 0.38, 0.45, 0.46, 0.33, and 0.35, respectively. There is hardly any change in $\Phi_{\text{o} \rightarrow \text{c}}$ compared to that of **3** ($\Phi_{\text{o} \rightarrow \text{c}} = 0.43$) [18], which indicates that high photocyclization reactivity was maintained. Moreover, the $\Phi_{\text{c} \rightarrow \text{o}}$ values for **4**–**8** were determined to be 4.6×10^{-4} , 1.5×10^{-4} , 8.6×10^{-5} , 1.5×10^{-4} , and 5.9×10^{-4} , respectively. The $\Phi_{\text{c} \rightarrow \text{o}}$ hardly changed in comparison with that of **3** ($\Phi_{\text{c} \rightarrow \text{o}} = 6.4 \times 10^{-4}$) [18], which means that high photostability was also maintained. Thus, it was found that the $\Phi_{\text{o} \rightarrow \text{c}}$ and $\Phi_{\text{c} \rightarrow \text{o}}$ were hardly affected even when substituents were introduced into the terminal phenyl groups of the diarylethene having the cyclohexyloxy group at the reactive positions. Thus, diarylethenes **4**–**8** have the good photocoloration reactivity and the high photostability in the colored state enough for use as the write-by-light/erase-by-heat recording system.

2.2. Thermal cycloreversion reactivity

The thermal reactivity of **4**–**8** in toluene was investigated.

Table 1
Optical properties in *n*-hexane.

Diarylethene	Open-ring isomer		Closed-ring isomer		$\Phi_{\text{o} \rightarrow \text{c}}$	$\Phi_{\text{c} \rightarrow \text{o}}$	Ref.
	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$			
1	280	35600	575	15600	0.59	0.0083	20,21
2	309	33000	625	15000	0.44	1.7×10^{-5}	16,18
3	313	34000	635	13000	0.43	6.4×10^{-4}	18
4	326	42700	640	13500	0.38	4.6×10^{-4}	This work
5 ^{a)}	347	59700	664	14200	0.45	1.5×10^{-4}	This work
6 ^{a)}	369	56000	673	17500	0.46	0.86×10^{-4}	This work
7	310	41500	645	17900	0.33	1.5×10^{-4}	This work
8	327	39300	638	12700	0.35	5.9×10^{-4}	This work

a) In dichloromethane.

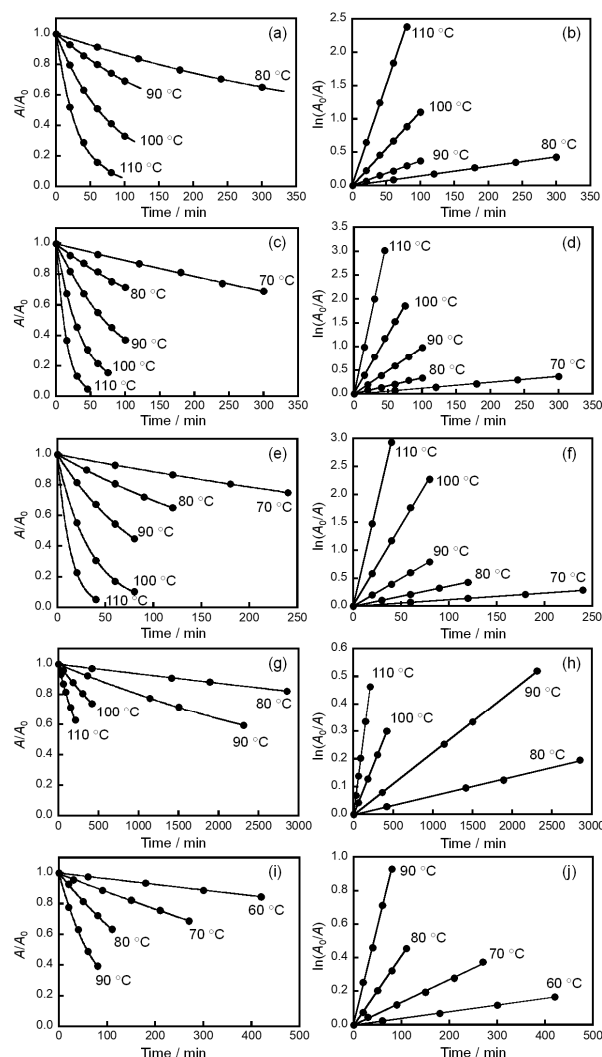


Fig. 2. Thermal bleaching behavior of (a) **4c**, (c) **5c**, (e) **6c**, (g) **7c**, and (i) **8c** in toluene. Absorbance (A) was monitored at the maximum wavelength of the closed-ring isomer. The first-order plots for the decay curves of **4c**, **5c**, **6c**, **7c**, and **8c** are shown in (b), (d), (f), (h), and (j), respectively.

The closed-ring isomers **4c–8c** underwent thermal bleaching reactions from blue to colorless. The absorption spectra after the thermal bleaching reaction remained almost the same in the shape and intensity compared with the absorption spectra of the open-ring isomers. This indicates that the thermal bleaching is ascribed to the cycloreversion reaction from the closed-ring isomer to the open-ring isomer. Fig. 2 shows decay curves of the absorption peaks of **4c–8c** in toluene. The absorbance of the

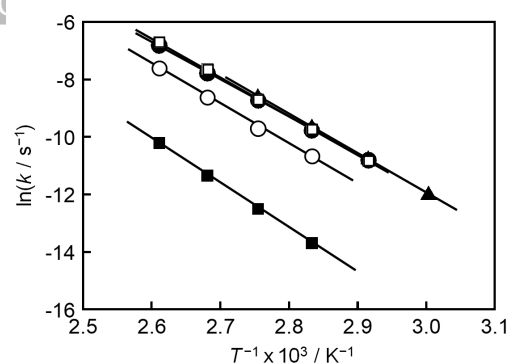


Fig. 3. Temperature dependence of the rate constant for the thermal bleaching reaction of **4c** (○), **5c** (●), **6c** (□), **7c** (■), and **8c** (▲) in toluene.

closed-ring isomers at $\lambda_{\max}$ decreased slowly above 60 °C. The decay curves followed the first-order kinetics plots, as also shown in Fig. 2. The rate constants (k) for the thermal cycloreversion reactions of **4c–8c** were determined from the slope of the first-order kinetic plot

Fig. 3 shows the temperature dependence of k for the thermal bleaching reaction of **4c–8c**. The kinetic parameters (activation energy (E_a) and pre-exponential factor (A)) of the thermal bleaching reaction were calculated from the slope and the intercept of the linear relationship and are summarized in Table 2. The E_a values for **4–8** were determined to be 114, 109, 113, 131, and 113 kJ mol^{−1}, respectively. The E_a values for the diarylethene derivatives introduced electron-withdrawing substituents (**4**, **5**, **6**, and **8**) are smaller than that of **3** (E_a = 120 kJ mol^{−1}), while the E_a value for diarylethene introduced electron-donating substituent (**7**) is higher. This result indicates that the introduction of the electron-withdrawing substituents leads to a decrease in E_a , which is a preferable condition for the acceleration of the thermal bleaching reactivity. On the other hand, the A values for **4–8** were determined to be 2.2×10^{12} , 8.8×10^{11} , 3.0×10^{12} , 2.4×10^{13} , and 4.2×10^{12} s^{−1}, respectively. The A values for diarylethenes introduced electron-withdrawing substituents (**4**, **5**, **6**, and **8**) are also smaller than that of **3** (A = 4.4×10^{12} s^{−1}), while the A value for diarylethene electron-donating substituent (**7**) is higher. This result indicates that the introduction of the electron-withdrawing substituents also leads to a decrease in A , which is an unpreferable condition for the acceleration of the thermal bleaching reactivity. To compare the thermal bleaching reactivity, the k values for **3–8** at 120 °C were calculated to be 5.0×10^{-4} , 1.6×10^{-3} , 2.9×10^{-3} , 2.9×10^{-3} , 9.4×10^{-5} , and 4.1×10^{-3} s^{−1}, respectively, using the kinetic parameters. The introduction of electron-withdrawing substituents accelerated the

Table 2
Thermal bleaching properties of **1c–8c** in toluene.

Diarylethene	k/s^{-1} at 120 °C	$E_a/kJ\ mol^{-1}$	A/s^{-1}	$t_{1/2}/min$ at 120 °C	$t_{1/2}/month$ at 25 °C	Reference
1c ^{a)}	4.4×10^{-6}	139	1.3×10^{13}	2600	46000	20
2c	1.3×10^{-5}	137	2.1×10^{13}	880	13000	16,18
3c	5.0×10^{-4}	120	4.4×10^{12}	23	67	18
4c	1.6×10^{-3}	114	2.2×10^{12}	7.4	12	This work
5c	2.9×10^{-3}	109	8.8×10^{11}	4.0	4.0	This work
6c	2.9×10^{-3}	113	3.0×10^{12}	4.0	5.9	This work
7c	9.4×10^{-5}	131	2.4×10^{13}	120	1050	This work
8c	4.1×10^{-3}	113	4.2×10^{12}	2.8	4.2	This work

a) In 3-methylpentane.

Table 3

The polarity parameters of the substituents and the kinetic parameters for the thermal cycloreversion reaction

Substituent R^2	σ	σ^+	$\log(k/k_H)$ at 120 °C	$E_a/kJ\ mol^{-1}$	$\log(A/s^{-1})$
H	0	0	0	120	12.6
<i>p</i> -CF ₃	0.54	0.61	0.505	114	12.3
<i>p</i> -CN	0.66	0.66	0.763	109	11.9
<i>p</i> -CHO	0.42	0.73	0.763	113	12.5
<i>p</i> -OCH ₃	-0.27	-0.78	-0.726	131	13.4
<i>m,m</i> -(CF ₃) ₂	2×0.43	2×0.52	0.914	113	12.6

reaction and the introduction of electron-donating substituents suppressed the reaction. This result clearly indicates that the thermal cycloreversion reactivity is largely influenced by the E_a value than the A value.

When these materials are applied as a rewritable paper, the stability of the colored state at room temperature is important. The half-life time ($t_{1/2}$) of the thermal cycloreversion reaction at room temperature (25 °C) was at least 4 months for the diarylethenes synthesized in this work. These results indicate that these diarylethenes have sufficient stability for common use as a write-by-light/erase-by-heat recording system.

2.3. Relationship between the substituent and the thermal cycloreversion reactivity

The thermal cycloreversion reaction is expected to be influenced by both the inductive effect and resonance effect of the substituent R^2 because the substituent affects the electron density in the π -conjugated system of the diarylethene closed-ring isomer. To elucidate the relationship between the introduced substituents and the thermal properties, Hammett's substituent constant (σ) [22] and Brown-Okamoto's substituent constant (σ^+) [22,23] were employed. The σ^+ values correspond to $r = 1$ in the Yukawa-Tsuno equation [24]. The σ and σ^+ values include not only the inductive effect but also the resonance effect. The contribution of the resonance effect for the σ^+ value is larger than that of the σ value. Table 3 shows σ and σ^+ together with the kinetic parameters for the thermal cycloreversion reactions. The difference between σ and σ^+ is the difference between the content

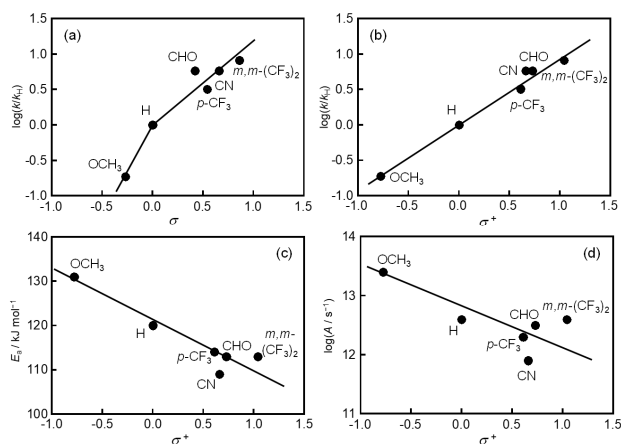


Fig. 4. The relationship between (a) traditional Hammett's parameter (σ) or (b) Brown-Okamoto's parameter (σ^+) and $\log(k/k_H)$ at 120 °C. (c) and (d) show the relationship between σ^+ and E_a (c) and $\log(A)$ (d).

of the inductive effect and the resonance effect, and the σ^+ values proposed by Brown-Okamoto have been widely adopted in the electrophilic reaction. Furthermore, using the equation proposed by Yukawa-Tsuno, the electronic effect of the substituents can be separated into a contribution of the inductive and resonance effects.

Hammett's plot was performed as shown in Fig. 4a. The natural logarithm of the rate constant of the substituted diarylethenes relative to the unsubstituted diarylethene ($\log(k/k_H)$) at 120 °C was plotted for the σ value. Although the electron-withdrawing substituents exhibited a linear relation to the σ value, the electron-donating substituent was out of the relation. Thus, the σ value was replaced into the σ^+ value. The relationship using the σ^+ value showed a linear relationship for both the electron-withdrawing and the electron-donating substituent. It means that the thermal cycloreversion reaction is affected by not only the inductive effect but also the resonance effect. However, the resonance effect of the methoxy group negatively affected the reaction. Thus, the large resonance effect of the methoxy group is considered to contribute to the stabilization of the energy level of the closed-ring isomer, resulting in the small reactivity. The normal logarithm of the pre-exponential factor ($\log(A)$) and the E_a values were plotted versus σ^+ . All of the values are linearly related to the substituent constant. As the substituent constant value increases, the E_a and $\log(A)$ values decrease, while the $\log(k/k_H)$ increases. This result also indicates that the magnitude of the electron-withdrawing property of the substituent has a large influence on the E_a as mentioned above, resulting in an increase of the rate constant. The relationship between the substituent constant and the rate constant would provide a guideline for molecular design to synthesize molecules exhibiting a desired thermal bleaching reactivity.

2.4. Application

For a write-by-light/erase-by-heat recording system, we investigated the thermal bleaching reactivity in the filter paper.

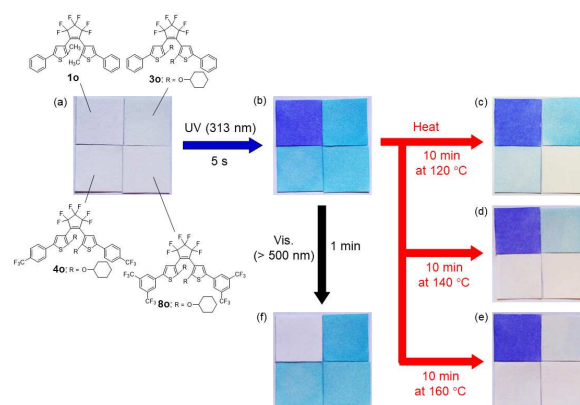


Fig. 5. Photocoloration and thermal and photochemical bleaching of **1** (upper left), **3** (upper right), **4** (bottom left), and **8** (bottom right) in the filter paper. (a) Before UV irradiation and (b) after UV irradiation. When the colored sample was kept for 10 min at 120 °C, 140 °C, and 160 °C in the dark, it changed to sample (c), (d), and (e), respectively. The blue color of **3c**, **4c**, and **8c** disappeared at an appropriate temperature, while the blue color of **1c** remained the original color. When the colored sample was irradiated with visible light (> 500 nm) for 1 min, it changed to (f). The blue color of **1c** disappeared, while the color of **3c**, **4c**, and **8c** remained.

Fig. 5 shows the color changes of **1**, **3**, **4**, and **8** by light and heat in the filter paper. To disperse the diarylethene at the molecular level in the filter paper, the diarylethene was mixed with poly(methyl methacrylate) (PMMA). The sample was prepared by dipping the toluene solution containing diarylethene and PMMA to the filter paper and drying. The colorless open-ring isomers (Fig. 5a) turned blue upon UV irradiation due to the generation of the closed-ring isomers (Fig. 5b). Then, the samples were kept at 120 °C in the dark. After 10 min, the blue color of **8c** disappeared, while the blue color of **1c**, **3c**, and **4c** remained (Fig. 5c). When the samples were kept for 10 min at 140 °C in the dark, the blue color of **4c** and **8c** disappeared, while the blue color of **1c** and **3c** remained (Fig. 5d). Moreover, when the samples were kept for 10 min at 160 °C in the dark, the blue color of **3c**, **4c**, and **8c** disappeared, while the blue color of **1c** remained (Figure 5e). On the other hand, when the colored sample (Fig. 5b) was irradiated with visible light (> 500 nm) for 1 min, the blue color of **1c** disappeared, while the color of **3c**, **4c**, and **8c** remained (Fig. 5f). Thus, diarylethenes **4** and **8** that we synthesized in this work showed high photostability and thermal cycloreversion reactivity even in solid medium. We succeeded in tuning the thermal cycloreversion reactivity by introducing various substituents into the terminal phenyl groups.

3. Conclusion

We have synthesized diarylethenes for a write-by-light/erase-by-heat recording system. The introduction of polar substituents at both sides of the diarylethene significantly changed the thermal cycloreversion reactivity. The introduction of electron-withdrawing substituents accelerated the reaction and the introduction of electron-donating substituents suppressed the reaction. The rate constants, k , were well correlated with Brown-Okamoto's substituent constant σ^+ that is a modified value of Hammett's substituent constant σ . The increase in the k value is ascribed to lower E_a . These results provide new knowledge for molecular design of diarylethenes for a write-by-light/erase-by-heat recording system.

4. Experimental section

4.1. General

Solvents used were of spectroscopic grade and purified by distillation before use. ^1H NMR (300 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained on a Bruker FT-ICR/SolariX mass spectrometer. The photoirradiation was carried out using a 200 W mercury-xenon lamp (MORITEX MUV-202) as the light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin-Yvon H10 UV). Absorption spectra were measured using a JASCO V-560 absorption spectrometer. HPLC was carried out using a HITACHI L-7150 pump/L-2400 detector/D-2500 Integrator and a Kanto Chemical Mightysil Si 60 column.

4.2. Materials

Diarylethenes **4a–8a** were synthesized in a method similar to that described in the literature [10]. The details are described in the electronic supplementary information.

4.3. Thermal bleaching reaction

The thermal bleaching reaction of diarylethene closed-ring isomers was carried out in toluene as follows. The diarylethene open-ring isomer was put in an optical quartz cell degassed and sealed under vacuum. The solution in the cell was irradiated with 313 nm light to give the closed-ring isomer. The cell was placed in a constant temperature chamber (ESPEC ST-110) during the thermal bleaching reaction. The reaction yields were periodically determined by absorption spectroscopic measurements.

4.4. Preparation of photochromic papers and thermal cycloreversion reaction in the papers

PMMA was dissolved in toluene to prepare a 10 wt% solution. Diarylethene (ca. 1 wt% relative to the polymer) was added to the polymer solution. The mixed solution was poured into a petri dish, and a filter paper was dipped into the dish. The paper was pulled out using tweezers and dried with a dryer. The filter paper was cut into squares. The paper was irradiated with 313 nm light. The colored filter paper after the photoirradiation was heated in a constant temperature chamber (ESPEC ST-110) during the thermal cycloreversion reaction. The same papers were used repeatedly.

5. Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.****.**.***.

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Highlights

We designed photochromic diarylethenes for a write-by-light/erase-by-heat recording system.

Diarylethenes having polar substituents at both sides were newly synthesized.

Photocyclization and photocycloreversion quantum yields remained constant even in the introduction of the polar substituents.

Thermal cycloreversion reactivities were significantly accelerated by introduction of the electron-withdrawing substituents.

We demonstrated a write-by-light/erase-by-heat recording system in the filter paper with the ability to erase even at 120 °C.